



Decoupled water splitting for hydrogen generation

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ABSTRACT

Green hydrogen (H_2) has the potential to displace fossil fuels because it has a high energy density, and its consumption yields solely water (H_2O). Water electrolysis generates green H_2 , but it is expensive to operate. In conventional water splitting (CWS), hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are closely correlated, producing H_2 and oxygen (O_2) concurrently. Decoupled water splitting (DWS) may geographically and temporally isolate HER from OER. The costly membrane may no longer be necessary. Since 2013, utilizing an auxiliary electrode or redox mediator to separate the rate, time frame, or location of H_2 and O_2 generation during water splitting has been extensively studied. This review provides a comprehensive overview of the latest developments in decoupled water splitting, which offers various benefits over conventional water splitting, including improved safety, higher purity, reduced membrane degradation, and greater design flexibility. The development history, electrolyzer configuration design, improved decoupled water splitting techniques, as well as challenges and future perspectives, are extensively reviewed. We also discuss H_2 generation mechanisms of different DWS technologies, i.e., electron-coupled proton buffers, proton-independent electron reservoirs, electrochemical-thermally activated chemical (E-TAC) water splitting, pseudocapacitors by using soluble molecular redox mediators, insoluble solid-state redox mediators, and hybrid water splitting by integrating oxidative biomass valorization in acidic, alkaline, and neutral environments. Overall, DWS offers promising applications for long-term, renewable energy-driven, viable hydrogen generation from water. Future hydrogen generation from renewable sources may be improved with the help of DWS due to its greater versatility and consistency.

KEYWORDS

decoupled water splitting (DWS), water electrolysis, redox mediators, HER/OER, hybrid water splitting, green hydrogen

1 Introduction

Hydrogen (H_2) is one of the best clean and green energy sources due to its high energy density ($140 \text{ MJ}\cdot\text{kg}^{-1}$) and ecologically benign application [1]. Approximately, the globe produces 96% (~ 84 million tonnes in 2024) of hydrogen from fossil fuels and 4% from water electrolysis (energy efficiency of 55%–80%) [2]. H_2 produced by reforming fossil fuels is neither well-advised nor eco-friendly [3–6]. Ammonia (NH_3) made by the Haber–Bosch process is a crucial precursor of fertilizer in agriculture, and hydrogen plays a vital part in its synthesis and is an essential feedstock in the petroleum industry for numerous chemical transformations [7]. As a rough estimation, in 2024, about 18 million tonnes of H_2 were produced from renewable energy resources [8]. Water is the primary, accessible source of hydrogen.

Renewable energy sources, such as hydro, solar, wind, and tidal, can power water splitting to create green H_2 gas [4, 5, 9, 10]. The utilization of hydrogen generates water as a product. Therefore, the whole process can be recycled again, water into hydrogen, and then hydrogen into the water using water electrolysis and fuel cells. If this scheme has become widespread and demanding, it is suggested that it be made proficient and, hence, mandatory to explore advanced electrolytic water-splitting devices and electrolyzer designs [11–15].

Innovation in electrocatalysts, as well as electrolyzer designs, is pivotal in water electrolysis [16]. In 1789, Troostwijk proposed the simplest configured water-splitting electrolyzer for the first time [17–19]. In conventional water splitting (CWS), H_2 and O_2 are generated simultaneously inside the electrochemical (EC) cell. Electrochemical water splitting involves two key half-reactions:

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hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [20–22]. HER and OER are correlated processes in conventional water electrolysis (CWE), where the HER occurs at the cathode, producing two moles of H_2 , while the OER takes place at the anode, generating one mole of oxygen (O_2) simultaneously [14, 17, 23, 24]. This coupled reaction in conventional water electrolysis leads to the mixing of H_2/O_2 (gas crossover), producing explosive reactive oxygen species (ROS), regardless of whether a “gas inviolable” proton-exchange membrane (PEM) is deployed, which causes PEM failure and minimizes overall performance [24]. When applying constant sources of current, it operates under both acidic and alkaline environments, providing current densities for H_2 and O_2 production on the order of $1\text{ A}\cdot\text{cm}^{-2}$ for acidic environment electrolysis and $0.2\text{--}0.5\text{ A}\cdot\text{cm}^{-2}$ for alkaline environment electrolysis [25]. To overcome these issues, a new strategy should be developed for decoupled water electrolysis (DWE) (Fig. 1).

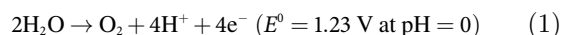
Recently, a new approach was developed, which decouples hydrogen and oxygen in separate time and space temporarily. This model was first developed by Symes and Cronin in 2013 [21, 25, 26]. H_2 and O_2 are created separately in cells. This electrolysis is completed in two steps using mediators, either soluble (molecular redox mediators (RMs)) or insoluble (solid-state redox mediators), using an electron-coupled proton buffer (ECPB) strategy. In the first step, water oxidation at the anode leads to a reversible reduction of the mediator, not a direct reduction of the cathode that generates oxygen. In the second step, the oxidation of the reversibly reduced mediator leads to the reduction of the cathode, which produces hydrogen. This two-step process happened in a different cell compartment and was not directly linked to each other. It separates and produces H_2 and O_2 from each other at different times and spaces in an electrochemical cell. This has triggered significant interest from researchers worldwide in hydrogen generation, leading to the field of decoupled water splitting (DWS) growing fast. Further studies were done by Symes and Wallace in 2018, together with Liu and coworkers [27, 28].

Presently, noble metals, such as Pd, Pt, Ru, and Ir and their alloys, are common electrocatalysts; nevertheless, their high cost and scarcity limit commercial output [26, 29–34]. The

development of noble-metal-free electrocatalysts with enhanced HER and OER performance has received considerable attention and effort [35–37]. Water electrolysis can be done in acidic, basic, or neutral environments [38, 39]. To split water electrochemically, a thermodynamic potential in parallel of 1.23 V is required, with an associated energy input of $237.1\text{ kJ}\cdot\text{mol}^{-1}$ under standard circumstances [5]. The updated overview of sustainable energy production and utilization from decoupled water splitting, as illustrated in Fig. 2, emphasizes the role of renewable energy sources like solar, wind, and hydropower in driving vital electrocatalytic reactions. These reactions involve key molecules, such as carbon dioxide (CO_2), nitrogen (N_2), and water (H_2O), which are converted into crucial energy carriers like hydrocarbons ($C_xH_yO_z$), NH_3 , and H_2 . These products serve as different storage forms of energy, such as hydrogen for use in fuel cells, or are converted into valuable chemicals and materials that are further used as fertilizers, including those derived from biomass. A fuel cell is also used to generate electricity by using hydrogen gas. Furthermore, hydrogen gas showcases its flexibility in supplying energy to various sectors, including residential power, transportation, communication, and even space exploration. The overall depiction highlights how renewable energy sources, coupled with advanced decoupled catalytic technologies, play a central role in transitioning toward a sustainable and circular energy economy. By integrating these technologies, society can efficiently produce, store, and utilize energy while minimizing environmental impact. This approach contributes to long-term energy sustainability by ensuring that renewable resources are harnessed effectively to meet the growing energy demand across multiple industries. Figure 2 shows the schematic procedure for the production of H_2 and its applications through electrochemical water splitting using renewable energy inputs. We can also get value-added products by replacing OER with hybrid water-splitting mechanisms.

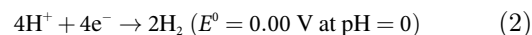
In acidic solutions [17, 40]:

At anode: OER

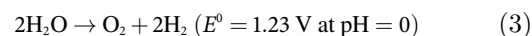


where the standard thermodynamic potential (E^0) is referenced to the standard hydrogen electrode (SHE).

At cathode: HER

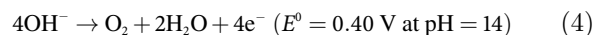


Overall reaction

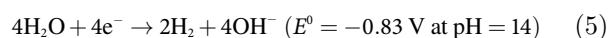


In alkaline solutions [27, 29]:

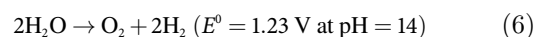
At anode: OER



At cathode: HER



Overall reaction



Electrocatalytic water splitting occurs in acidic or alkaline solutions, as shown by the half-cell reactions of HER/OER and their related thermodynamic potentials (vs. SHE), as shown in

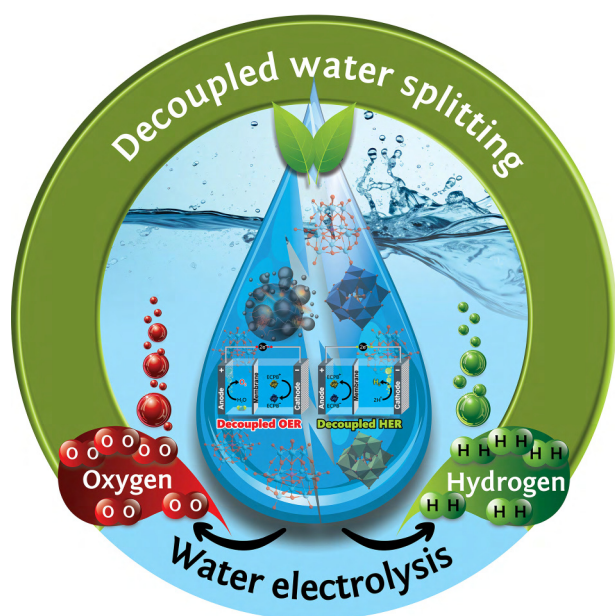


Figure 1 Decoupled water splitting with separate O_2 and H_2 evolution for safer, low-cost, and efficient electrolysis.

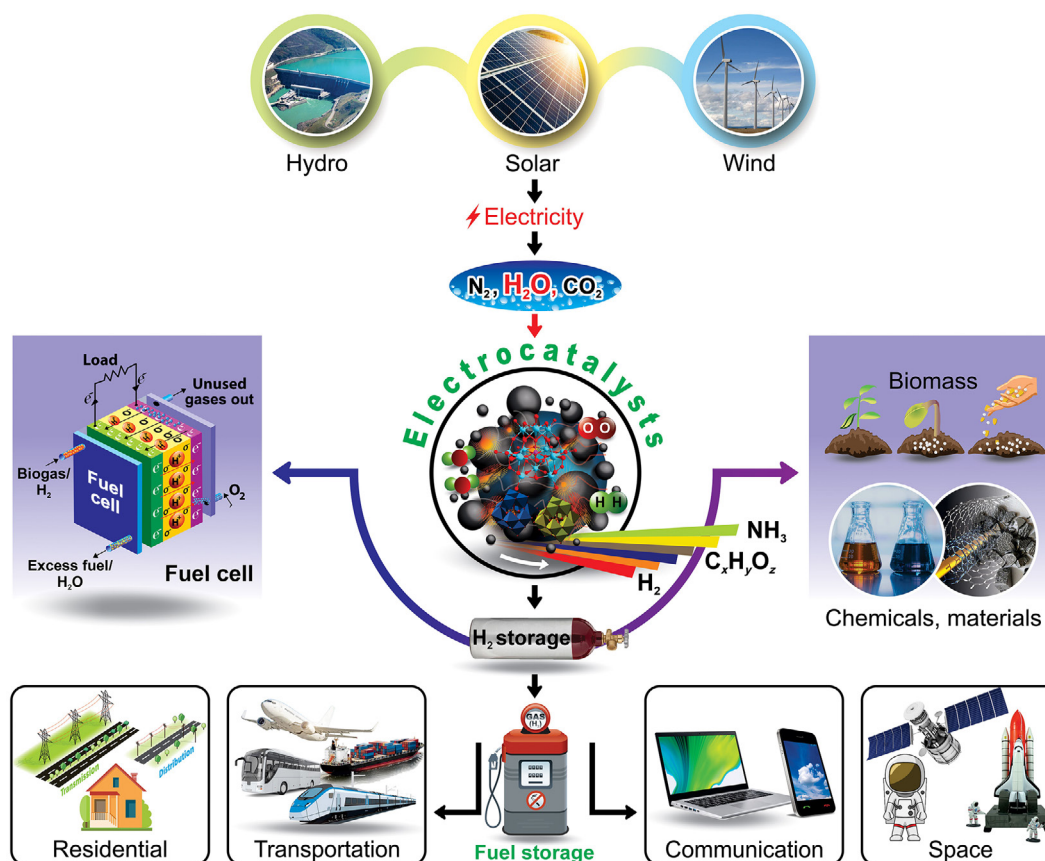


Figure 2 Schematic depiction of electrocatalytic water splitting utilizing renewable energy inputs to generate hydrogen and value-added products.

(Eqs. (3) and (6)). Pt is a typical electrocatalyst for HER, while $\text{RuO}_2/\text{IrO}_2$ are used for OER, both of which are verified experimentally [27]. However, their broad applications are constrained by prohibitively high costs. Carbon-based materials and transition metal-based catalysts, including Co, Fe, Ni, and Mn, as well as their composites, are advantageous in this regard [29, 41–44]. Transition metal compounds present a compelling alternative, offering enhanced electrocatalytic efficiency and robust electrochemical stability. To optimize HER performance, different systematically investigated strategies to augment active sites through morphological modifications, including various doping techniques, crystallization control, structural engineering, and the integration of carbon nanomaterials, were applied. Despite these advancements, the economic viability of water splitting for large-scale applications remains a formidable challenge [45–53].

The primary objective of water oxidation is to facilitate the extraction of electrons and their subsequent transport to the cathode for hydrogen generation. The growing application of electrocatalysts like NiFe and NiMo-based materials in both OER and HER underscores their high catalytic efficiency, further substantiated by extensive utilization in electrolyzer-level studies, particularly in hydrogen production from alkaline water electrolysis (AWE) [54, 55]. Although harnessing renewable energy sources, such as wind, thermal, solar, tidal, and self-powered methods for water electrolysis, is theoretically feasible, these technologies remain in the early stages of development. Challenges, such as strong catalyst adhesion and suboptimal gas transport pathways, can also adversely impact catalytic performance. It is well established that the binding strength of intermediates plays a crucial role in determining catalytic performance for both HER and OER. Therefore, developing

electrocatalysts that achieve optimal binding strength with intermediates is vital for enhancing electrocatalytic efficiency. HER occurs more rapidly under acidic conditions, while OER is favored in alkaline environments [56, 57]. During the electrochemical DWS, high gas pressure builds up in both HER and OER chambers, and the relative pressure differential can compromise membrane stability and longevity. Furthermore, in practical electrolysis scenarios, elevated current densities (exceeding $2 \text{ A}\cdot\text{cm}^{-2}$) increase pore diameter and the number of active pores within the membrane, enhancing gas permeation [58]. Three primary technologies are utilized for water splitting: AWE, which was first introduced by Troostwijk and Diemann in 1789 [27]; acidic proton exchange membrane water electrolysis (PEMWE), employing solid polysulfonated membranes, such as Nafion; and solid oxide electrolysis (SOE). AWE is widely implemented globally due to its low cost. It utilizes a 20 wt.%–30 wt.% KOH or NaOH solution as the electrolyte, Ni-based catalysts as working electrodes (WE), and asbestos as the diaphragm or separator [59–61]. In contrast, PEMWE, conceptualized by Grubb in the 1960s [60, 62, 63], addresses many limitations associated with AWE. PEMWE benefits from high proton conductivity, low gas permeability, and a thin membrane design, resulting in compactness, high current density (above $2000 \text{ mA}\cdot\text{cm}^{-2}$), enhanced efficiency, rapid response, a small footprint, and high hydrogen purity. Consequently, a growing interest is focused on developing highly active, stable, and cost-effective bifunctional electrocatalysts that can effectively drive both HER and OER for efficient overall water splitting.

From an energy perspective of view, the energy barrier for the anodic OER is significantly higher than that for HER, primarily due to the multiple proton-coupled electron transfer steps

involved in OER. This disparity plays a crucial role in determining the overall efficiency of hydrogen production through water splitting. In response to the challenges associated with traditional water electrolysis, researchers have proposed many decoupling strategies, i.e., ECPB, proton-independent electron reservoirs (ERs), electrochemical-thermally activated chemical (E-TAC) water splitting, electrocatalysts, and a pseudocapacitor mechanism by using soluble molecular redox mediators, insoluble solid-state redox mediators, and hybrid water splitting (HWS), which aims to substitute the OER with alternative oxidation reactions that are both thermodynamically more favourable and economically attractive. Conventional water electrolysis requires substantial electrical energy to facilitate the electrolytic reaction, primarily due to the kinetically unfavourable nature of the anodic OER. This necessitates a considerable voltage input for OER. If electricity is sourced from non-renewable energy resources, such as fossil fuels, it increases carbon emissions and causes environmental degradation. Moreover, conventional electrochemical water splitting involves significant infrastructure requirements, including equipment construction, electricity supply, and processing of generated oxygen, all of which demand substantial capital and resources, thereby elevating the cost of hydrogen production. Additionally, the energy conversion efficiency of traditional water electrolysis for hydrogen production is relatively low, typically around 70%–80% [64]. This inefficiency results in considerable energy losses during the hydrogen production process. Furthermore, while hydrogen possesses a high energy density, it has an extremely low volumetric density and high combustibility, presenting technical challenges for its storage and transportation that necessitate specialized equipment and measures [62, 65]. These factors collectively highlight the need for more efficient and sustainable hydrogen production methods.

A promising approach to overcome the obstacles associated with electrolytic hydrogen production is substituting the OER

with thermodynamically favorable organic oxidation reactions [66–69]. Notably, the electrooxidation of renewable alcohols has demonstrated an impressive 67% energy savings compared to conventional water electrolysis, yielding equivalent hydrogen outputs [70]. These oxidation reactions frequently involve sacrificial agents, which can be employed to remediate environmental pollutants, such as urea and hydrazine (Hz) substances, commonly utilized in industrial applications that pose significant ecological hazards. Such reactions can effectively remove toxic contaminants from industrial wastewater without necessitating additional oxidants or complex separation techniques while substantially reducing the voltage required for hydrogen production via water electrolysis. Figure 3 depicts the evolution of water-splitting technology, illustrating the shift from traditional, conventional water splitting systems to current decoupled water splitting. Water electrolysis was first introduced in 1789, followed by the commercialization of alkaline water electrolyzers in 1888, and General Electric Co. was developed to overcome drawbacks of PEM electrolyzers in 1966 [60, 71–73]. Decoupled water splitting was initially developed in 2013–2014, employing soluble molecular redox mediators, such as $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and hydroquinone sulfonate. Solid-state redox mediators, such as $\text{Ni}(\text{OH})_2$ and FeO_x , were introduced between 2016 and 2017, making significant progress. Bifunctional catalysts were prioritized during 2018–2019, followed by hybrid water splitting methods using materials, such as WO_3 and MnO_2 , from 2020–2021. Recent research has focused on renewable-assisted water electrolysis (2022–2023) and pseudocapacitive strategies (2024), with materials like H_2MoO_3 and TiO_2 nanoparticles being studied, respectively. Additional research in 2024 aims to advance DWS and increase its commercial viability by utilizing new catalysts and renewable technologies. This timeline depicts the important milestones in water-splitting technology, from early discovery to hybrid and renewable-integrated techniques.

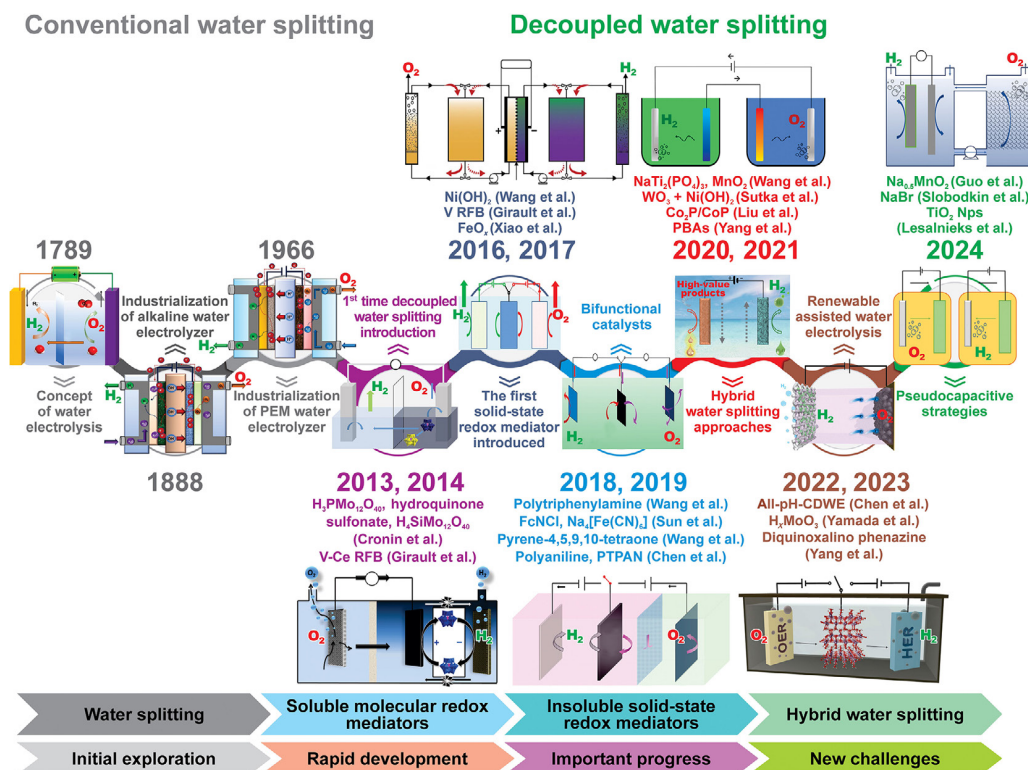


Figure 3 Development history of conventional and decoupled water splitting.

In this review, we comprehensively discuss recent progress on DWS strategies like decoupling of HER/OER using ECPBs, proton-independent ERs, electrochemical-thermally activated chemical (E-TAC) water splitting, and pseudocapacitor by using molecular redox mediators, solid-state redox mediators, and hybrid water splitting by integrating oxidative biomass valorization in acidic, alkaline, and in neutral environments. Different reaction strategies, i.e., electrochemical-electrochemical, electrochemical-chemical, electrochemical-thermochemical, and electrochemical-photoelectrochemical (PEC) cycles, are discussed for hydrogen production in separate space and time with maximum output through non-conventional decoupled water splitting by intermittent renewable energy inputs. Finally, future applications and the remaining challenges, including technical limitations and potential solutions, are also discussed.

2 The working mechanism of decoupled water splitting

HER and OER follow different reaction mechanisms in decoupled water splitting in acidic or alkaline environments, as discussed below.

2.1 Reaction mechanism of HER

HER mechanism in acidic media consists of three basic steps to complete the reaction. The first step is called the Volmer step (adsorption); in this step, protons (H^+) are adsorbed on the surface of the catalyst (in acid solutions) or dissociation of H_2O molecule (in alkaline solutions); this step is pH-dependent because it requires an additional amount of energy to proceed the reaction rate in alkaline solutions further. After adsorption, the Volmer step can continue either through the Volmer-Tafel mechanism or the Volmer-Heyrovsky mechanism. Tafel step (desorption) is the second stage, wherein the two adsorbed hydrogen atoms on the catalyst surface recombine and liberate hydrogen gas at the cathode (Volmer-Tafel mechanism). The third step is called the Heyrovsky step (reduction); in this step, adsorbed hydrogen atoms directly combine with hydrogen ion (H^+) by electron transfer from the cathode surface (Volmer-Heyrovsky mechanism) (Fig. 4). HER catalyst activity relies on Gibbs free energy (ΔG) in acidic media. The Gibbs free energy of adsorbed hydrogen is more favorable when it is equal to zero ($\Delta G = 0$) [60, 74]. If hydrogen ion adsorption on the catalyst surface is poor, the reaction will not proceed ($\Delta G > 0$), and the Volmer step will be limited. When hydrogen ions are strongly attracted to the catalyst surface, the

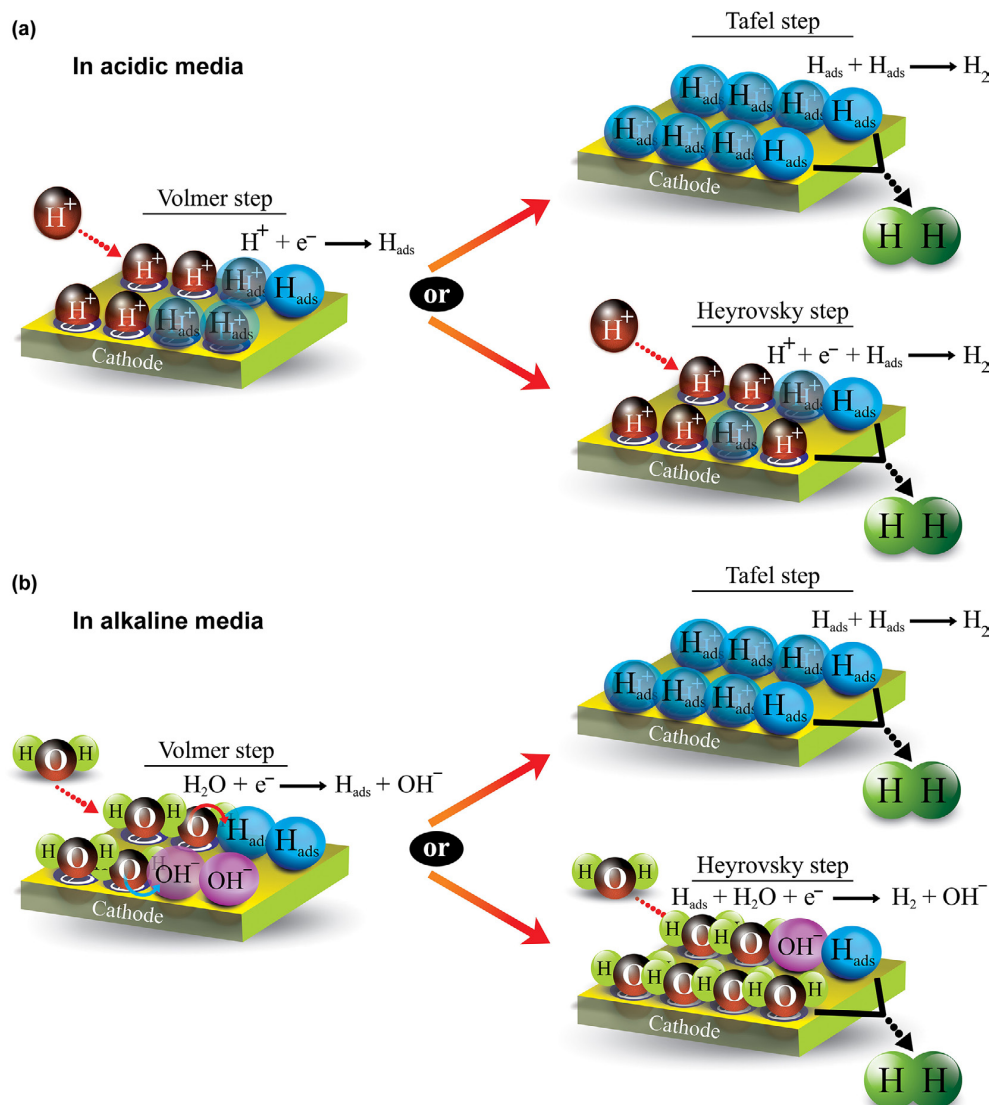


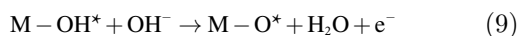
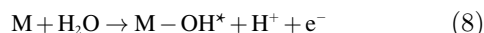
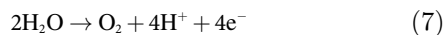
Figure 4 HER mechanisms (a) in acidic and (b) in alkaline media.

reaction proceeds ($\Delta G < 0$) desorption step, either Volmer–Tafel or Volmer–Heyrovsky, will limit the reaction rate. So, in both cases, catalyst activity will be affected. An ideal catalyst has ΔG of 0 on a volcano plot [75, 76]. To investigate the rate-determining step (RDS), the Tafel slope is the most relevant metric. It is a unit of measurement for the magnitude of the potential rise at the cathode. Small Tafel slopes are preferable for actual applications because of the fast H_2 generation rate at an adequate increase of overpotential (η) [51]. Table 1 shows all steps involved during decoupled water splitting in either acidic or alkaline electrolyte solutions with Tafel slope.

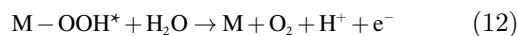
2.2 Reaction mechanism of OER

The OER plays a vital role in water splitting, where water is oxidized to form oxygen and hydrogen ions (H^+) in acidic electrolytes or hydroxide ions (OH^-) in alkaline electrolytes. Unlike the HER at the cathode, OER is more complex, as it requires the transfer of four electrons. This makes OER kinetically challenging, particularly in acidic electrolytes where breaking the strong HO–H bond in water is necessary to initiate the reaction. In contrast, in neutral or alkaline electrolytes, the availability of free OH^- ions facilitates the conversion to HO^* intermediates without the need for water dissociation, resulting in relatively faster reaction kinetics. OER is a complex process involving multiple proton and electron transfers. The mechanisms vary between alkaline and acidic media due to the distinct properties of the electrolytes present in each environment (Eqs. (7)–(18)) [75].

In acidic media

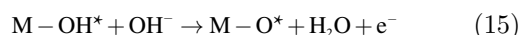
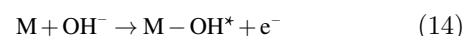
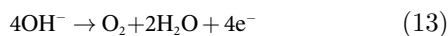


or

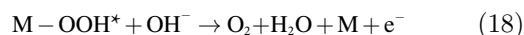
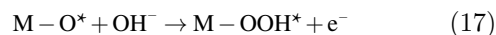
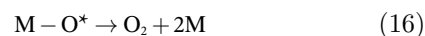


where M refers to the catalytic metal active site.

In alkaline media



or



The oxygen evolution mechanism has been widely studied over the years, and various pathways have been proposed for different electrocatalysts (Table 2) [78–88]. These pathways reveal that most proposed OER pathways share a common initial step: forming the HO^* intermediate. This occurs via the adsorption of H_2O or hydroxide ions (OH^-) onto the catalyst surface, depending on the electrolyte. For instance, H_2O is adsorbed in acidic conditions and splits into HO^* , while free OH^- ions directly convert to HO^* in alkaline conditions. Two prominent categories of OER pathways exist: the adsorbate evolution mechanism (AEM) and the lattice oxygen-mediated mechanism (LOM) [74, 89]. In the AEM pathway, which occurs in both acidic and alkaline media, three key intermediates are formed on the catalyst surface: HO^* , O^* , and HOO^* . In both acidic and alkaline AEM pathways, oxygen can be formed through either the coupling of O^* intermediates or the decomposition of HOO^* species, derived from the interaction of O^* with H_2O or OH^- , depending on the medium. While the exact pathway may vary based on the catalyst and the electrolyte, these mechanisms share the involvement of the three adsorbed intermediates (HO^* , O^* , and HOO^*), which play critical roles in determining the overall kinetics and efficiency of the OER process. The LOM, in contrast, involves the direct participation of lattice oxygen from the catalyst structure in oxygen evolution, bypassing some of the adsorbed intermediates of the AEM. Although less common, this mechanism is still an essential consideration in advanced catalyst design, as it may offer alternative pathways to optimize OER performance.

In summary, understanding these OER mechanisms is crucial for developing efficient catalysts, particularly for applications involving water splitting and renewable energy storage, as they determine the overall oxygen production rate and efficiency in both acidic and alkaline conditions. The performance of OER and HER electrocatalysts largely depends on the binding strength of reaction intermediates. Optimizing the interaction between the catalyst surface and these intermediates is crucial to enhancing catalytic activity and efficiency. Developing catalysts with optimal

Table 1 Reaction mechanisms of HER in acidic and alkaline solutions [53, 77]

Steps	Acidic electrolyte	Alkaline electrolyte	Tafel slope
Volmer	$H^+(aq) + e^- \rightarrow H_{ads}^a$	$H_2O + e^- \rightarrow H_{ads} + OH^-$	$b = \frac{2.3RT}{\alpha F} = 120 \text{ mV} \cdot \text{dec}^{-1b}$
Tafel-step	$H_{ads} + H_{ads} \rightarrow H_2(g)$	$H_{ads} + H_{ads} \rightarrow H_2(g)$	$b = \frac{2.3RT}{2F} = 30 \text{ mV} \cdot \text{dec}^{-1}$
Heyrovsky-step	$H_{ads} + H^+(aq) + e^- \rightarrow H_2(g)$	$H_{ads} + H_2O + e^- \rightarrow H_2(g) + OH^-$	$b = \frac{2.3RT}{(1+\alpha)F} = 40 \text{ mV} \cdot \text{dec}^{-1}$
Overall	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	$H_2O + e^- \rightarrow H_2(g) + OH^-(aq)$	

^a H_{ads} refers to adsorbed hydrogen. ^b b , R , T , α , and F refer to Tafel slope, gas constant, absolute temperature, charge-transfer coefficient, and Faraday constant.

Table 2 Reaction mechanism of OER in acid and alkaline media with different pathways. * represents an active site [90, 91]

Acidic electrolyte		Alkaline electrolyte	
Electrochemical oxide path		Electrochemical oxide path	
(1)	$* + \text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$	(1)	$* + \text{OH}^- \rightarrow \text{HO}^* + \text{e}^-$
(2)	$\text{HO}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$	(2)	$\text{HO}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + \text{e}^-$
(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$	(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$
Oxide path		Oxide path	
(1)	$* + \text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$	(1)	$* + \text{OH}^- \rightarrow \text{HO}^* + \text{e}^-$
(2)	$2\text{HO}^* \rightarrow \text{O}^* + * + \text{H}_2\text{O}$	(2)	$2\text{HO}^* \rightarrow \text{O}^* + * + \text{H}_2\text{O}$
(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$	(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$
Krasil'shchikov path		Krasil'shchikov path	
(1)	$* + \text{H}_2\text{O} \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$	(1)	$* + \text{OH}^- \rightarrow \text{HO}^* + \text{e}^-$
(2)	$\text{HO}^* \rightarrow \text{O}^* + \text{H}^+$	(2)	$\text{HO}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O}$
(3)	$\text{O}^* \rightarrow \text{O}^* + \text{e}^-$	(3)	$\text{O}^* \rightarrow \text{O}^* + \text{e}^-$
(4)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$	(4)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$
Wade and Hackerman's path (WHP)		Yeager's path	
(1)	$2^* + 2\text{H}_2\text{O} \rightarrow \text{O}^* + \text{H}_2\text{O}^* + 2\text{H}^+ + 2\text{e}^-$	(1)	$* + \text{OH}^- \rightarrow \text{HO}^* + \text{e}^-$
(2)	$\text{O}^* + 2\text{HO}^* \rightarrow 2^* + \text{H}_2\text{O}^* + \text{O}_2 + 2\text{e}^-$	(2)	$\text{HO}^* \rightarrow \text{HO}^{+1*} + \text{e}^-$
		(3)	$2\text{HO}^{+1*} + 2\text{OH}^- \rightarrow 2^* + 2\text{H}_2\text{O} + \text{O}_2$
Adsorbate evolution mechanism		Adsorbate evolution mechanism	
(1)	$\text{H}_2\text{O} + * \rightarrow \text{HO}^* + \text{H}^+ + \text{e}^-$	(1)	$\text{OH}^- + * \rightarrow \text{HO}^* + \text{e}^-$
(2)	$\text{HO}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$	(2)	$\text{HO}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + \text{e}^-$
(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$	(3)	$2\text{O}^* \rightarrow 2^* + \text{O}_2$
(4)	or $\text{O}^* + \text{H}_2\text{O} \rightarrow \text{HOO}^* + \text{H}^+ + \text{e}^-$	(4)	or $\text{O}^* + \text{OH}^- \rightarrow \text{HOO}^* + \text{e}^-$
(5)	$\text{HOO}^* \rightarrow * + \text{O}_2 + \text{H}^+ + \text{e}^-$	(5)	$\text{HOO}^* + \text{OH}^- \rightarrow * + \text{O}_2 + \text{H}_2\text{O} + \text{e}^-$

binding strength can significantly impact the overall electrocatalytic performance, as it reduces overpotential and increases reaction rates.

2.3 Reaction mechanism and recent approaches for decoupled water splitting

In conventional water splitting, two electrodes are dipped in electrolyte (acidic, alkaline, or neutral) solutions within a single-cell glass chamber (Fig. 5(a)). When an external voltage is applied, the cathode creates hydrogen through the HER. At the same time, the anode produces oxygen through the OER. Constant production of hydrogen and oxygen within the cell through the crossover, and generates H_2/O_2 gas mixing. Gases produced at slower rates mix, yield explosive reactive oxygen species. Moreover, such a type of mixing reduces the amount of hydrogen collected at the cathode. There are some drawbacks in conventional water splitting: (1) the rate of H_2 production coupled with the rate of O_2 production, which is the limitation for overall water splitting; (2) the diffusion of gases cannot be avoided so that either a membrane or diaphragm is applied; and (3) reactive oxygen species impair the electrolyzer and reduce the cell's overall performance. Considering these issues, it is time to develop new strategies for decoupling hydrogen from oxygen during water splitting using renewable energy inputs (Fig. 5(b)). Anodic OER reaction can be replaced with different oxidation reactions like urea oxidation reaction (UOR), alcohol oxidation reaction (AOR), polysulfide oxidation reaction (SOR), and hydrazine oxidation reaction (HzOR) to get hydrogen at the cathode; a low voltage input is needed to initiate the anodic reaction (Fig. 5(c)). Currently, many reviews on conventional and decoupled water

splitting were reported in this regard [23, 26, 27, 29, 47, 53, 71, 73, 74, 78, 79, 83, 92–138], but a thorough and in-depth summary of the decoupled water splitting is still needed.

2.4 In-situ characterization techniques for decoupled water splitting

Understanding the mechanisms underlying DWS remains a central challenge for developing efficient and stable electrocatalysts. *Ex-situ* approaches often fail to capture transient intermediates and dynamic transformations at the electrode/electrolyte interface, limiting mechanistic insights. By contrast, *in-situ* and *operando* techniques enable real-time monitoring of intermediate species, catalyst oxidation states, and active-site evolution, offering a more detailed view of catalytic processes [139]. These approaches can be broadly divided into four categories (Fig. 6) [140, 141]. The first is microscopy-based *in-situ* techniques, which allow direct visualization of catalyst morphology and structural evolution during electrochemical reactions. Representative examples include *in-situ* optical microscopy (OM), *in-situ* scanning electron microscopy (SEM), *in-situ* transmission electron microscopy (TEM), *in-situ* scanning TEM (STEM), *in-situ* atomic force microscopy (AFM), *in-situ* scanning electrochemical cell microscopy (SECCM), *in-situ* liquid-phase TEM (LP-TEM), and *in-situ* scanning probe microscopy (SPM). The second category is *in-situ* X-ray spectroscopy techniques, which are powerful for probing structural and electronic changes under working conditions. Common methods include *in-situ* X-ray diffraction (XRD), *in-situ* X-ray photoelectron spectroscopy (XPS), and *in-situ* X-ray absorption spectroscopy (XAS). The third is *in-situ* vibrational spectroscopy,

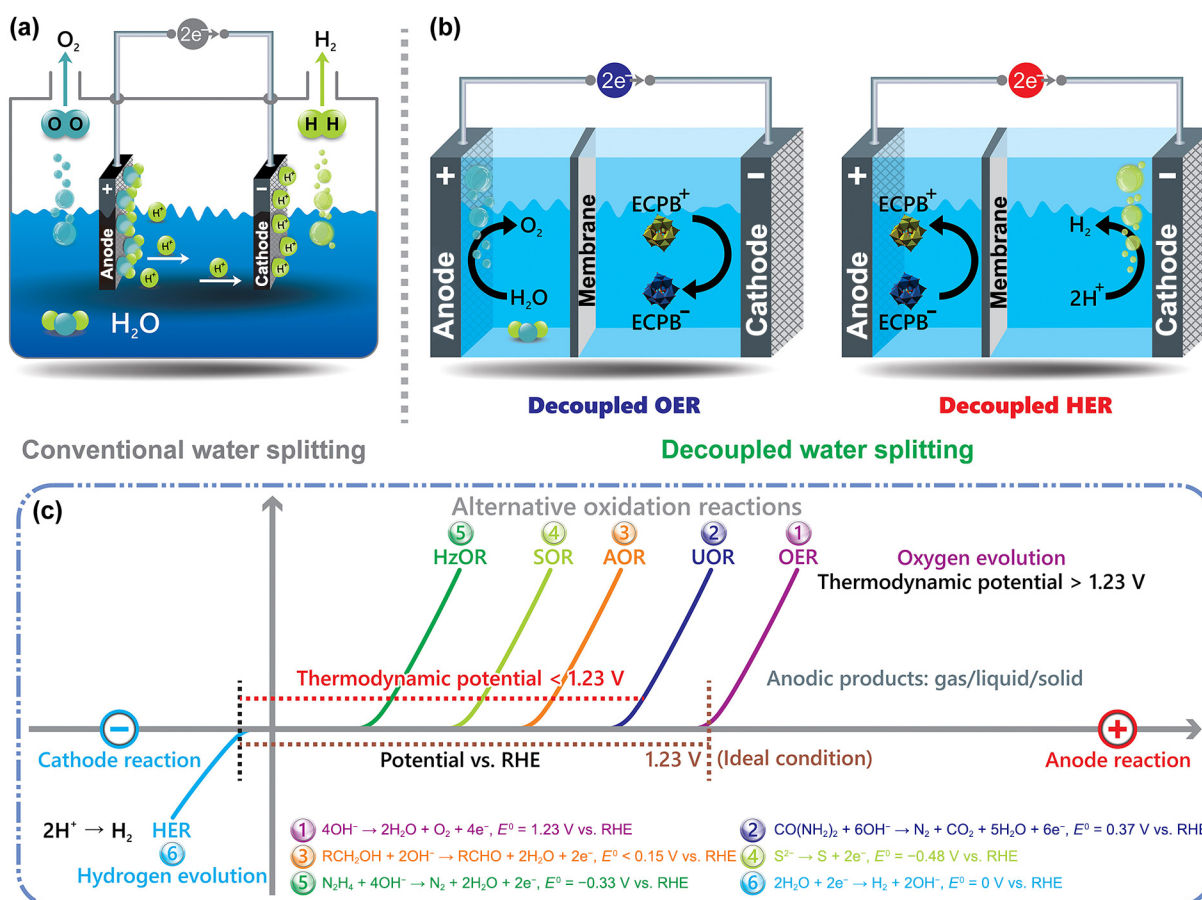


Figure 5 (a) Conventional water splitting. (b) Decoupled water splitting. (c) Anodic alternative oxidation reactions, which can be replaced with OER to produce hydrogen at the cathode.

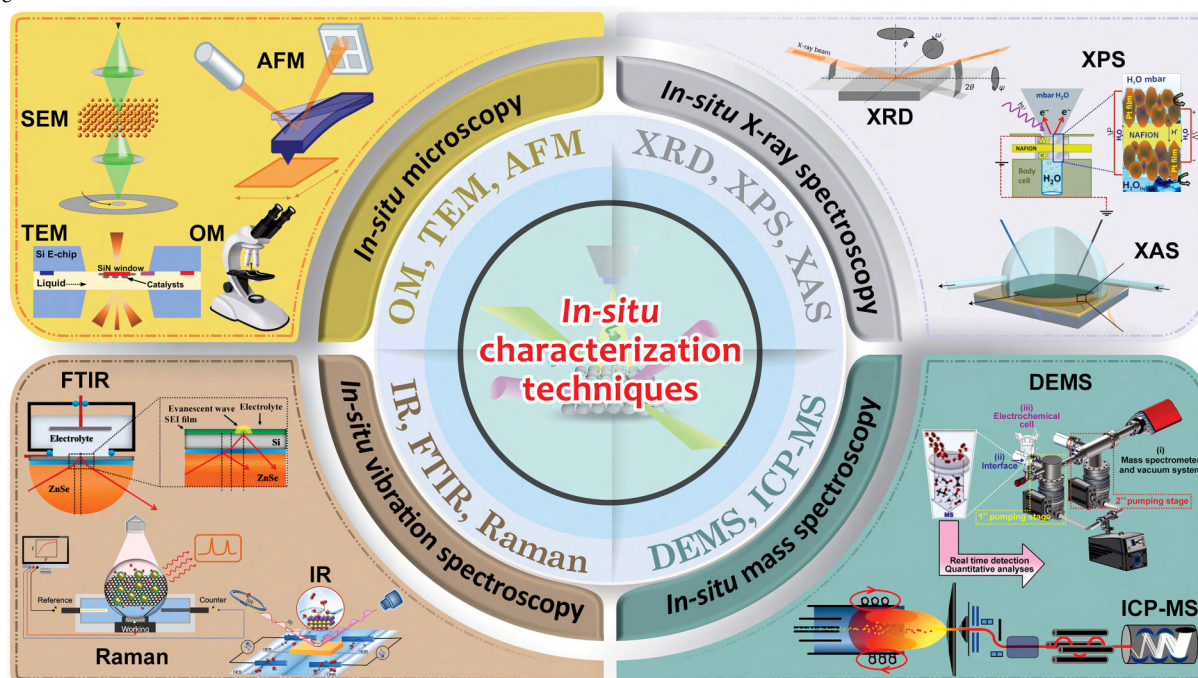


Figure 6 Schematic illustration of *in-situ* characterization techniques for decoupled water splitting. Reproduced with permission from Ref. [143], © The Royal Society of Chemistry 2024. *In-situ* microscopy. Reproduced with permission from Ref. [144], © American Physical Society 2011. Reproduced with permission from Ref. [145], © The Author(s), 2023. *In-situ* X-ray spectroscopy. Reproduced with permission from Ref. [146], © Harrington, G. F. et al., under exclusive licence to Springer Science Business Media, LLC, part of Springer Nature 2021. Reproduced with permission from Ref. [147], © The Author(s), 2018. Reproduced with permission from Ref. [148], © Springer Nature Limited 2017. *In-situ* vibrational spectroscopy. Reproduced with permission from Ref. [149], © American Chemical Society 2017. Reproduced with permission from Ref. [150], © American Chemical Society 2023. Reproduced with permission from Ref. [151], © Elsevier Ltd. 2020. *In-situ* mass spectrometry. Reproduced with permission from Ref. [152], © Wiley-VCH GmbH 2022. Reproduced with permission from Ref. [153], © The Author(s), 2022.

which provides insights into adsorbed intermediates and surface chemical bonding, with widely used methods, such as *in-situ* infrared (IR) spectroscopy, *in-situ* Fourier-transform IR spectroscopy (FTIR), and *in-situ* Raman spectroscopy. The fourth category is *in-situ* mass spectrometry (MS), which enables sensitive detection and quantification of products and intermediates, with notable techniques, including *in-situ* differential electrochemical MS (DEMS) and *in-situ* inductively coupled plasma MS (ICP-MS). Collectively, these complementary *in-situ* techniques allow real-time monitoring of morphological, structural, compositional, and electrochemical changes, thereby providing critical insights into catalytic behavior under realistic operating conditions [142].

In-situ microscopy is essential for probing electrochemical processes. OM enables direct observation of reactions using visible light, offering simplicity and low cost, but its sub-micron resolution limits nanoscale and atomic-level studies. It is widely used in electrocatalysis to monitor electrode morphology, color changes, and dendrite growth on lithium, sodium, magnesium, and zinc anodes, allowing real-time tracking of reaction inhomogeneities [139]. For instance, Dastafkan et al. [154] developed an *operando* strategy that combines single-frequency impedance spectroscopy with *in-situ* optical microscopy to investigate gas bubble evolution on $\text{Ni}(\text{OH})_2/\text{N-NiC}/\text{nickel foam}$ (NF). At optimized frequencies, dynamic resistance variations were directly linked to bubble growth, detachment, and surface coverage, while electrode wettability and architecture strongly influenced the fluctuation amplitude. Coupling with optical microscopy further connected resistance changes to bubble size and release rate. Applied to superaerophobic, anisotropic $\text{Ni}(\text{OH})_2/\text{N-NiC}$, this method enabled real-time monitoring of ultrafast hydrogen and oxygen bubble dynamics in non-transparent electrolyzers, offering valuable guidance for designing advanced gas-repelling electrodes (Fig. 7(a)).

In-situ electron microscopy, including SEM, TEM, STEM, AFM, SECCM, LP-TEM, and SPM, provides higher resolution and dynamic structural insights. *In-situ* SEM, with nanometer-scale resolution and simple sample preparation, tracks microstructural changes under external stimuli, such as temperature, stress, or electric current. *In-situ* TEM achieves sub-nanometer or atomic resolution for internal structures but requires thin samples and sophisticated instrumentation. *In-situ* advanced TEM approaches, such as environmental TEM (ETEM) and specialized sample holders, allow real-time observation of material transformations under controlled gas, liquid, or high-temperature conditions, enabling studies of nanoparticle nucleation, growth, coalescence, phase transitions, defect formation, and molecular processes. Fu et al. [145] reported that *in-situ* formation of amorphous surface layers is crucial for enhancing alkaline HER performance in layered catalysts. By employing *in-situ* liquid electrochemical TEM, they directly visualized edge amorphization in Ru-NiPS_3 nanosheets (NSs), which stabilizes Ru dopants and prevents the loss of functional groups. Their combined experimental and theoretical studies revealed that the amorphous layer, enriched with bridging S_2^{2-} species, optimizes the adsorption of reaction intermediates and facilitates water dissociation, thereby significantly improving HER kinetics. This work highlights the importance of reconstructed amorphous layers and offers a practical strategy for improving the catalytic efficiency of transition metal-based layered materials (Fig. 7(b)).

In-situ SPM, including scanning tunneling microscopy (STM)

and AFM, maps atomic-scale surface structures via tunneling currents or cantilever deflection. Electrochemical variants EC-STM, EC-AFM, scanning electrochemical microscopy (SECM), and SECCM permit *in-situ* monitoring of electrode surface dynamics, adsorption of intermediates, and localized electrochemical activity, providing key insights for catalyst design and water-splitting optimization. SECCM further allows high-resolution, site-specific voltammetry and galvanostatic measurements in liquid-phase electrocatalysis. LP-TEM incorporates electrochemical cells to visualize real-time structural evolution in solution, directly linking morphology and performance. LP-TEM has elucidated atomic-level transformations in catalysts. Despite challenges such as electron-beam effects, a limited field of view, and constraints in atomic-scale imaging, LP-TEM remains a powerful tool for tracking dynamic electrocatalyst behaviors and elucidating reaction mechanisms in water splitting [155].

In-situ X-ray spectroscopy is a powerful non-invasive approach for electrocatalysis, providing real-time insights into structural and electronic changes in catalysts under working conditions. Key techniques include *in-situ* XRD, XPS, and XAS. XRD is widely applied to track structural evolution and phase transitions of materials, such as metals, ceramics, and polymers. By operating in reflection or transmission modes, XRD reveals reaction-driven structural changes within electrodes, offering mechanistic insights and guiding catalyst design, although challenges in cell configuration and data interpretation remain [156]. Fan et al. [157] showed that S-doped Co_3O_4 on carbon cloth ($\text{S-Co}_3\text{O}_4/\text{CC}$) undergoes *in-situ* reconstruction during HER, forming active metallic Co and S-Co^+ sites. *In-situ* studies revealed the sequential formation of $\text{Co}(\text{OH})_2$ at 0 mV, metallic Co at -200 mV, and complete reduction at -250 mV, which enhances H^+ adsorption and water dissociation. Extending this strategy, S, Fe-codoped $\text{Ni}(\text{OH})_2$ achieved $1.0 \text{ A}\cdot\text{cm}^{-2}$ at 1.72 V, providing a practical approach to identify active sites and design efficient electrocatalysts (Fig. 7(c)).

XPS provides surface-sensitive information on elemental composition, chemical states, and charge-transfer pathways by probing photoelectron emission, enabling a detailed understanding of oxidation, corrosion, and electronic structure in water-splitting systems. Du et al. [158] showed that constructing a $\text{RuO}_2/\text{CoO}_x$ interface stabilizes RuO_2 beyond its Pourbaix limit while maintaining high OER activity. The CoO_x substrate preferentially oxidizes, transferring electrons to RuO_2 , and interfacial Ru/Co dual-atom sites synergistically adsorb oxygen intermediates to promote the reaction. *In-situ* XPS confirmed the persistence of Ru^{3+} species at high potentials, highlighting the interface's key role in stabilizing RuO_2 (Fig. 7(d)). XAS complements these approaches by characterizing local atomic environments and dynamic evolution under operating conditions. Its two components, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), provide complementary insights: XANES determines oxidation states while EXAFS quantifies coordination numbers, bond lengths, and structural disorder [159]. Soft XAS (sXAS, < 5 keV) further enhances sensitivity to surface states, transition-metal oxidation, and light elements, such as oxygen, though it typically requires ultrahigh vacuum conditions, limiting its broader application. Hung et al. [160] used *operando* high-energy resolution fluorescence detected (HERFD)-XAS to show that oxygen interacts with Co 3d orbitals while nearby Fe ions stabilize Co in higher oxidation states, enhancing OER activity. Orbital

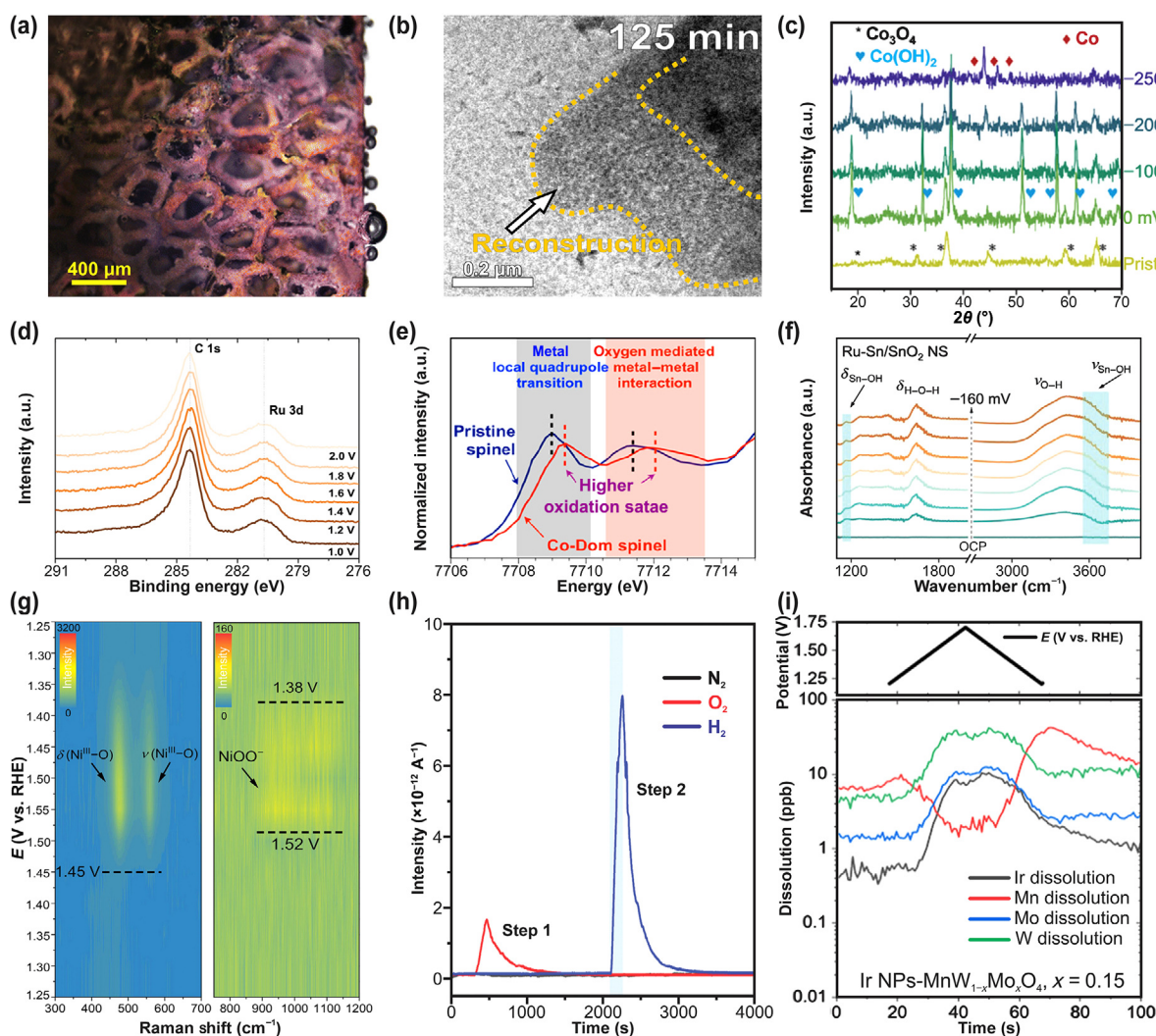


Figure 7 *In-situ* microscopy. (a) Optical microscopy image of gas bubble formation on $\text{Ni}(\text{OH})_2/\text{N-NiC}/\text{NF}$ at 0.245 V vs. RHE. Reproduced with permission from Ref. [154], © The Author(s), 2023. (b) *In-situ* liquid TEM of Ru-NiPS₃ NSs after chronopotentiometry test. Reproduced with permission from Ref. [145], © The Author(s), 2023. *In-situ* X-ray spectroscopy. (c) *In-situ* XRD of S-Co₃O₄/CC-HER. Reproduced with permission from Ref. [157], © Wiley-VCH GmbH 2024. (d) *In-situ* XPS of RuO₂/CoO_x catalyst. Ru 3d spectra at 1.0–2.0 V vs. RHE and corresponding Ru³⁺ and Ru⁴⁺ content ratios. Reproduced with permission from Ref. [158], © The Author(s), 2022. (e) High-energy resolution fluorescence detection XAS of Co K-edge for pristine and cobalt-dominated spinel oxide (Co-Dom spinel). Reproduced with permission from Ref. [160], © American Chemical Society 2018. *In-situ* vibration spectroscopy; (f) *In-situ* IR spectra of Ru-Sn/SnO₂ NS at different potentials during alkaline HER. Reproduced with permission from Ref. [162], © Wiley-VCH GmbH 2024. (g) Potential-dependent *in-situ* Raman spectra of Ni(OH)₂/C-120 catalyst in 0.1 M KOH during cycling. Ni-O vibration (left panel) of the NiOOH active phase between 400–600 cm⁻¹ and NiOO⁻ active species (right panel) between 900–1050 cm⁻¹. Reproduced with permission from Ref. [163], © The Author(s), 2024. *In-situ* mass spectroscopy. (h) *In-situ* DEMS analysis of the electrolytic cell at 250 mA confirmed the high-purity production of H₂ and O₂ during DWS. Reproduced with permission from Ref. [166], © Wiley-VCH GmbH 2025. (i) *In-situ* ICP-MS dissolution profiles of Ir, Mn, Mo, and W during a triangular potential sweep for Ir nanoparticles supported on MnW_{1-x}Mo_xO₄ ($x = 0, 0.05$, and 0.15). Reproduced with permission from Ref. [167], © American Chemical Society 2025.

hybridization between Co 3d and O 2p orbitals facilitates the formation of reactive intermediates, independent of structural changes. This approach highlights the role of local orbital interactions at the catalyst surface in promoting efficient water oxidation (Fig. 7(e)). Together, these *in-situ* X-ray techniques enable a comprehensive understanding of structural dynamics, surface chemistry, and electronic states, thereby offering critical guidance for the design and optimization of efficient and stable water-splitting catalysts.

In-situ vibrational spectroscopy, including IR, FTIR, and Raman spectroscopy, probes molecular vibrations and chemical bonds to reveal structural features and transient intermediates at the molecular level. IR spectroscopy is based on the detection of dipole moment changes during molecular vibrations and rotations, with near, mid, and far-infrared regions tailored to

different materials and applications. FTIR, which employs continuous-wavelength IR light, records molecular absorption patterns by comparing transmitted and absorbed signals, with background interference eliminated through subtraction of a reference spectrum [161]. When coupled with electrochemical cells, *in-situ* FTIR provides real-time monitoring of reactions at gas-liquid-solid interfaces, yielding information on reactants, intermediates, products, and electrode surface bonding. It can operate in transmission mode or in reflection mode, the latter divided into external reflection and internal reflection configurations, such as Kretschmann and Otto geometries. Yan et al. [162] employed *in-situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) to probe the catalytic mechanism of Ru-Sn/SnO₂ nanosheets during alkaline HER. The spectra reveal enhanced water adsorption,

evidenced by more intense O–H stretching ($3200\text{--}3600\text{ cm}^{-1}$) and bending ($= 1621\text{ cm}^{-1}$) modes compared with Ru and Ru–Sn nanosheets. A distinct band at 1144 cm^{-1} corresponding to Sn–OH vibrations confirmed the preferential *OH adsorption at Ru–Sn dual sites. Furthermore, the emergence and progressive growth of a terminal Sn–OH band near 3700 cm^{-1} highlighted the hydroxyl spillover effect on SnO_2 , which facilitated rapid *OH transfer and maintained active site availability. These spectral observations directly support the proposed cooperative mechanism that underpins the superior activity and durability of the catalyst (Fig. 7(f)).

Raman spectroscopy, in contrast, relies on inelastic scattering of monochromatic light due to changes in molecular polarizability, offering complementary information to IR techniques. *In-situ* Raman enables detection of frequency, intensity, and polarization changes in scattered light under applied electrode potentials, thereby uncovering molecular structures, adsorption states, and catalytic intermediates [151]. Advanced methods, such as confocal Raman microscopy, polarized Raman, resonance Raman, and surface-enhanced Raman spectroscopy (SERS), extend sensitivity and selectivity, particularly for surface-confined species. Wei et al. [163] investigated the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox chemistry during OER using *in-situ* electrochemical Raman spectroscopy. Below 1.38 V, no clear signal was observed, but upon $\text{Ni}(\text{OH})_2$ oxidation, distinct bands emerged at 474 and 555 cm^{-1} , corresponding to $\delta(\text{Ni}^{3+}\text{--O})$ bending and $\nu(\text{Ni}^{3+}\text{--O})$ stretching modes of NiOOH . At potentials above 1.42 V, a broad band at $850\text{--}1200\text{ cm}^{-1}$ was assigned to the O–O vibration of NiOO^- species, regarded as the active precursor for O_2 release. Importantly, NiOO^- formed at lower potentials than the onset of anodic OER (1.56 V), indicating that O_2 liberation, rather than O–O coupling was the rate-determining step. The attenuation of the NiOO^- signal during potential reversal correlated well with cathodic O_2 evolution detected by DEMS, confirming its role as the reactive intermediate. In contrast, $\text{Ni}(\text{OH})_2/\text{C-120}$ and Fe-doped $\text{Ni}(\text{OH})_2$ catalysts exhibited delayed or suppressed NiOO^- formation, consistent with the absence of cathodically evolved O_2 . This established NiOO^- as the key species governing the anodic–cathodic sequential OER (ACS-OER) pathway (Fig. 7(g)). The versatility of Raman allows applications across electrocatalysis, batteries, temperature-variable reactions, and gas-phase studies. Specialized setups, including variable-temperature Raman for high-temperature processes (e.g., crystal growth, metallurgical reactions, and geological transformations) and through-atmosphere cells for controlled gas environments, expand its applicability to dynamic systems.

In electrochemical studies, *in-situ* Raman is often integrated with a three-electrode configuration, where the working electrode contains active materials and the counter electrode is relatively inert. The setup typically incorporates gas venting and dual circuits to measure the WE potential against a reference electrode (RE) while enabling current flow through the auxiliary electrode (AE). This configuration accommodates powders, films, flakes, and bulk electrodes, and has been widely used to investigate electrocatalytic oxidation of methanol, ethanol, and formic acid, as well as reduction of carbon dioxide, nitrogen, oxygen, and nitrate/nitrite. Importantly, Raman spectroscopy provides mechanistic insights into the electrode–electrolyte interface during water electrolysis. Analysis of O–H stretching vibrations ($3000\text{--}3800\text{ cm}^{-1}$) reveals hydrogen-bonding networks and interfacial water structures, allowing real-time tracking of adsorption, dissociation, and recombination processes of water

molecules. Together, *in-situ* IR, FTIR, and Raman spectroscopy deliver a molecular-level understanding of electrocatalytic reaction pathways, interfacial mechanisms, and catalyst dynamics, offering essential guidance for the design of advanced water-splitting systems [140].

Advanced *in-situ* mass spectrometry enables precise detection of material components, particularly gaseous and volatile species, across a wide analytical range from hydrogen to complex organics. It offers picogram-level detection limits, high sensitivity, broad linearity, and minimal sample consumption. Isotope labeling further facilitates pathway studies, making these techniques indispensable for electrocatalysis research. The two main approaches commonly applied are *in-situ* DEMS and *in-situ* ICP-MS [140, 164]. *In-situ* DEMS is a core method for studying electrochemical reactions, allowing real-time tracking and quantitative analysis of gaseous and volatile products. By integrating electrochemical workstations with high-resolution mass spectrometers, DEMS captures characteristic signals of short-lived intermediates and traces product origins through isotope labeling, providing molecular-level insights into reaction pathways. Unlike traditional methods combining steady-state polarization and chromatography, which only yield total current information, DEMS resolves stepwise reaction dynamics under varying potentials. Electrochemical cells are coupled directly to the mass spectrometer to ensure rapid transmission of reaction products while maintaining interface stability. With millisecond-level detection, DEMS identifies key intermediates and rate-determining steps, supporting catalyst design and water electrolysis optimization [165]. Huang et al. [166] introduced a dibenzo[b,i]phenazine-5,7,12,14-tetrone (DPT)-based pseudocapacitive electrode for decoupled acidic water electrolysis, enabling reversible storage of six proton–electron pairs with high capacity and fast kinetics. The DPT electrode maintained excellent performance even at ultrahigh mass loading, combining battery-like capacity with pseudocapacitive rate capability. Using this electrode as a solid-state electron-coupled proton buffer, they achieved decoupled H_2 and O_2 generation with a current density up to $800\text{ mA}\cdot\text{cm}^{-2}$. The gas purity was confirmed by *in-situ* DEMS: Only O_2 was detected during the oxidation step, while exclusive H_2 evolution occurred during the subsequent reduction step. This process delivered nearly quantitative Faradaic efficiency ($\text{FE} = \sim 98.70\%$) with a $\text{H}_2:\text{O}_2$ ratio of 2:1, validating the high selectivity and stability of the decoupled system (Fig. 7(h)). *In-situ* ICP-MS extends these capabilities to solution-phase metal ions, combining electrochemical workstations with inductively coupled plasma mass spectrometry. In this technique, high-temperature ionization converts metal atoms into ions, which are separated and detected based on their mass-to-charge ratio [167]. *In-situ* ICP-MS overcomes the limitations of offline analyses, offering high sensitivity, element specificity, and wide linear range. With internal calibration, it enables real-time monitoring of metal dissolution, migration, and redeposition under dynamic reaction conditions, providing molecular-level insights into catalyst stability [168, 169]. Kim et al. [167] investigated the stability and activity of Ir-based OER catalysts using a rational design strategy that leverages catalyst-support interactions. Mo doping was found to enhance the formation of high-valent Ir species, improving intrinsic activity, but at the cost of reduced electrical conductivity, highlighting the need for balanced interface engineering. Using *in-situ* identical location-STEM (IL-STEM) and ICP-MS, the authors monitored dissolution behavior of Ir, Mo, W, and Mn during

OER. Ir, Mo, and W exhibited potential-dependent dissolution, peaking at the highest anodic potentials, indicating a reaction-driven oxidative dissolution process. In contrast, Mn showed a distinct profile: Dissolution was greatest at low potentials and decreased above ~ 1.5 V, consistent with its redox thermodynamics and Pourbaix diagram. During the cathodic sweep, Mn^{4+} species were reduced back to soluble Mn^{2+} , producing a reversible dissolution signal. These findings underscore the importance of both catalyst and support stability and demonstrate that interface and element-specific behaviors must be considered to optimize OER performance (Fig. 7(i)). Together, *in-situ* DEMS and ICP-MS provide complementary capabilities for monitoring both gaseous and solution-phase species, offering detailed mechanistic and stability insights that are essential for the rational design and optimization of electrocatalysts in water-splitting and related electrochemical processes.

3 Soluble molecular redox mediators

Soluble molecular redox mediators are redox-active compounds that can dissolve in water. They are broadly classified into two categories: inorganic and organic molecular redox mediators, both of which are explored and discussed in the following.

3.1 Inorganic molecular redox mediators

In this scheme (Fig. 8(a)), water soluble molecular redox mediators are used for decoupling water spatially at different times and spaces. This technique requires two steps. In the first phase, a

reducing molecular redox mediator catalyzes OER at the anode. In the second phase, HER occurs at the cathode by re-oxidizing a reduced molecular redox mediator, which provides electrons to produce hydrogen. On the contrary, if the molecular redox mediator is in a lower valence state in the first step, it oxidizes. It is coupled with HER by releasing hydrogen at the cathode, followed by the second step reduction of oxidized molecular redox mediator by OER, releasing oxygen at the anode. For the sake of simplicity, both HER/OER are decoupled, producing hydrogen and oxygen at different spaces and times. Both gases are independent of their counterparts. The hydrogen production rate is faster than oxygen without mixing H_2/O_2 . The pH of electrolyte solution is also buffered by these molecular redox mediators, known as ECPB. To achieve successful molecular redox mediator-based decoupling, promising electrochemical properties should be considered by selecting a suitable candidate, including (1) high solubility in water, (2) rapid switching oxidation/reduction rates with inert electrode, (3) good stability during redox cycles, and (4) inexpensive configuration and ease of synthesis. Decoupled water splitting in acidic electrolytes using a variety of soluble molecular redox mediators, such as phosphomolybdic acid (PMA), silicotungstic acid (STA), and quinone derivatives, was initially reported in 2013 by the group led by Symes and Cronin.

For the first time, a soluble molecular redox mediator, phosphomolybdic acid ($\text{H}_3\text{O}^+[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$) was used in a strongly acidic electrolyte having a pH of 0.3 by Symes and Cronin [28, 170]. In the first step, reduction of ($\text{H}_3\text{O}^+[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$) occurs with two-electron reduced species in aqueous solutions,

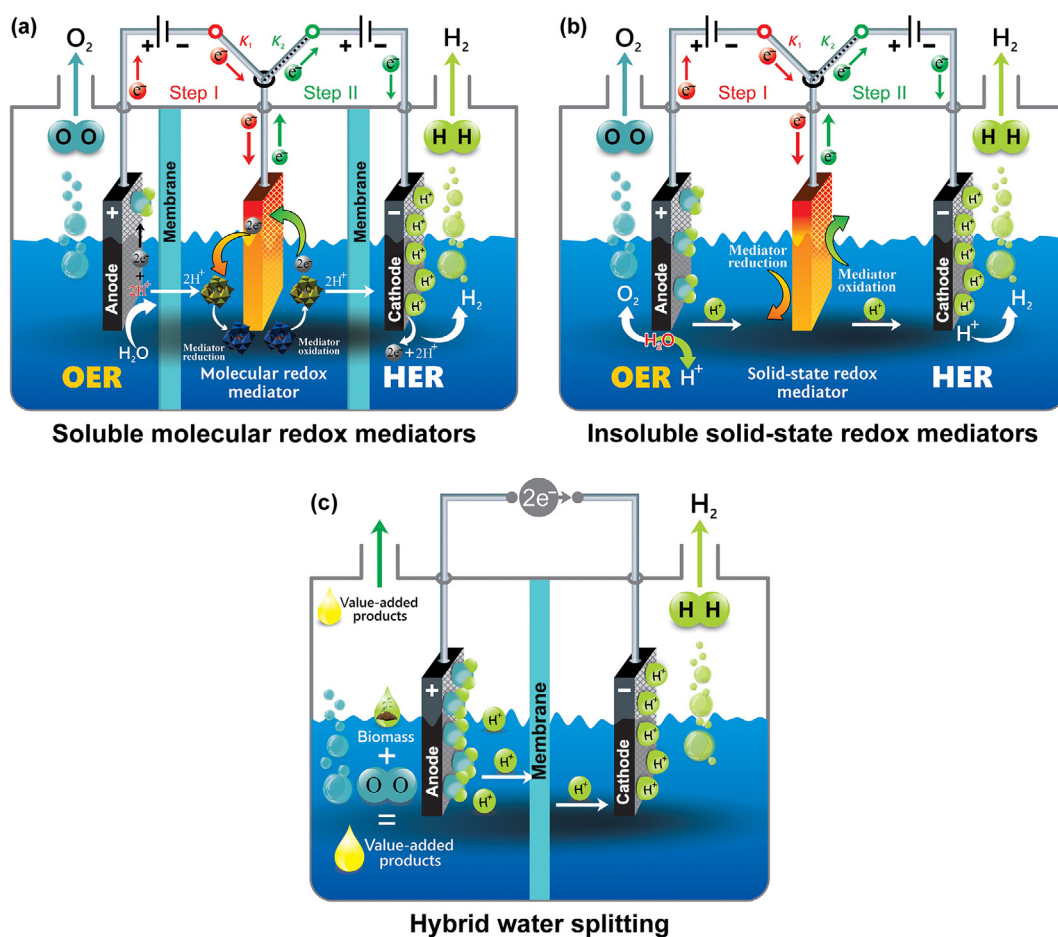


Figure 8 Schematic illustrations of decoupled water splitting. (a) Soluble molecular redox mediators based decoupled water splitting. (b) Insoluble solid-state redox mediators based decoupled water splitting. (c) Hybrid water splitting.

followed by the formation of $(\text{H}_3\text{O}^+)[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$. In the second step, re-oxidation of reduced ECPB species $(\text{H}_3\text{O}^+)[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$ resulting in the evolution of hydrogen gas at the cathode (Fig. 9(a)). The cathode and anode were made of platinum. Cyclic voltammograms of $(\text{H}_3\text{O}^+)[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$ are shown in (Fig. 9(b)), where an initial decrease is seen at 0.65 V against normal hydrogen electrode (NHE). The green arrow indicates the oxidation and reduction peaks of phosphomolybdic acid's initial reduction state. The inset of (Fig. 9(b)) shows the peak current of the anodic part with scan rate. This procedure calls for solution-phase species with diffusion control, as seen by the linear trend in the inset. To check the ECPB behavior during reduction and oxidation, a 50:50 mix of reduced ECPB species $(\text{H}_3\text{O}^+)[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$ and oxidized ECPB species $(\text{H}_3\text{O}^+)[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$ was used (Figs. 9(c) and 9(d)). It takes a

potential of +0.46 V (vs. NHE) to decrease this 50:50 ECPB solution at a current density of $100 \text{ mA}\cdot\text{cm}^{-2}$, whereas it takes a potential of -0.38 V to reduce protons to hydrogen. At $100 \text{ mA}\cdot\text{cm}^{-2}$, taken as a standard potential for reduction and oxidation of ECPB, 1.71 V is required to reduce ECPB and oxidize O_2 in the first step. In the second step, it requires 1.23 V for the re-oxidation of reduced ECPB and reduction of protons to produce hydrogen. Therefore, it requires 2.94 V to complete the overall reaction (HER/OER). Traditional water electrolysis requires 2.55 V for a single step over $100 \text{ mA}\cdot\text{cm}^{-2}$ for HER and OER. In this regard, a maximum efficiency of 87% was recorded for the two-step process over the single-step process. The extra potential is required to decouple the ECPB.

After the aforementioned decoupled water splitting setup with a three-electrode configuration was developed, a decoupled water

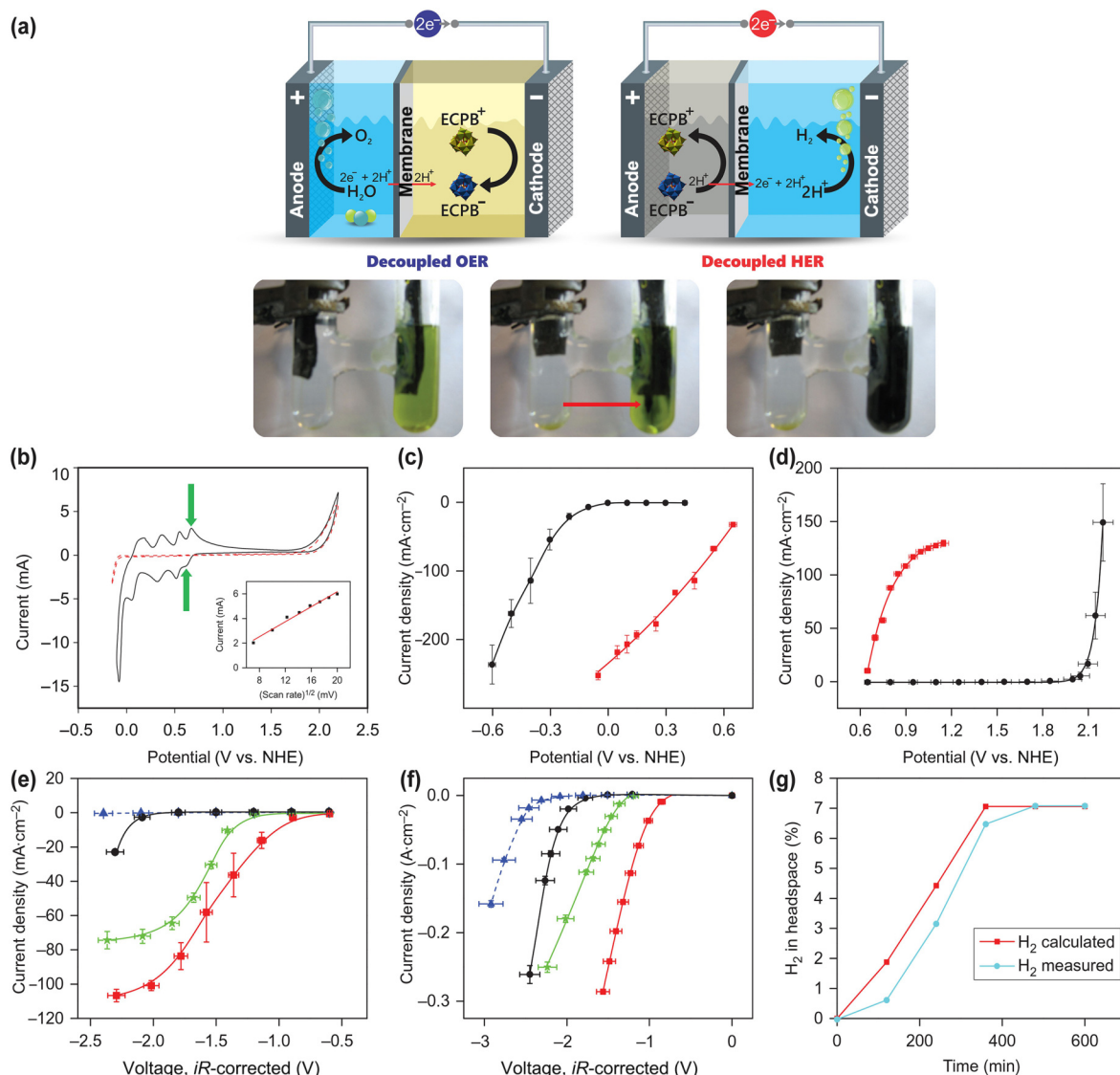


Figure 9 ECPB-based decoupled water splitting of phosphomolybdic acid $(\text{H}_3\text{O}^+)[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$. (a) Schematic diagram of DWS with a digital photograph of soluble molecular redox mediator decoupled OER/HER water splitting with switching ECPB oxidation and reduction to produce O_2 and H_2 . (b) CV curves of 0.5 M phosphomolybdic acid (black) and 1 M H_3PO_4 (red line), with green arrows indicating oxidation and reduction peaks for phosphomolybdic acid in its initial reduction form. Inset is the graph of the initial reversible two-electron wave (centered at +0.65 V) peak current vs. square root of scan rate (scan rate range: 50–400 $\text{mV}\cdot\text{s}^{-1}$). Current–voltage profiles are produced while stirring, either with or without ECPB. ((c) and (d)) Comparison of the reduction and oxidation of 0.5 M solution of 50:50 mixture of $(\text{H}_3\text{O}^+)[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$ and $(\text{H}_3\text{O}^+)[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$ (red) and 1 M H_3PO_4 (black). (e) Comparison of current densities for H_2 evolution with and without using 0.5 M 50:50 ECPB. Red (platinum with ECPB), black (platinum without ECPB), green (glassy carbon with ECPB), and blue (glassy carbon without ECPB). (f) Current densities for H_2 evolution using an ECPB. Red (platinum with ECPB), black (platinum without ECPB), green (glassy carbon with ECPB), and blue (glassy carbon without ECPB). (g) For gas chromatography of hydrogen in the presence of ECPB, H_2 was calculated (red), and H_2 was measured (blue) on the Pt electrode for HER. Reproduced with permission from Ref. [28], © Springer Nature Limited 2013.

splitting setup with a two-electrode configuration and a fixed potential was arranged further to test the performance of ECPB as a decoupling agent. In the hydrogen cell, one compartment of the cell was filled with a 50:50 mixture of oxidized (ECPB) and reduced (ECPB^{*}) species, and a second compartment with 1 M phosphoric acid (H_3PO_4). A Nafion membrane was used as the separator. When an ECPB is used in both chambers of the hydrogen cell, it gives large increasing current densities, as compared to phosphoric acid, because ECPB species quickly oxidize, resulting in the evolution of H_2O evolving bubbles of H_2 at the working electrode. Figures 9(e) and 9(f) depict a contrast between a Pt electrode and a glassy carbon electrode with and without ECPB. HER using Pt electrodes is favorable to those using glassy carbon electrodes, as shown in (Fig. 9(f)). To confirm the dependency of current densities on the electrode area, a small area electrode was employed to test the nature of HER/OER. Current densities during HER performance on the small-area electrodes were normalized. Using gas chromatography (GC) analysis, 100% FE of ECPB^{*} was recorded. ECPB^{*} can be easily oxidized to generate H_2 (Fig. 9(g)). These results show that hydrogen and oxygen are generated in different spaces and at different times. The current–voltage (I – V) curves are shown for carbon electrodes in the presence of ECPB/ECPB^{*}, which are easily oxidized with lower voltages than Pt. Using carbon electrodes as an alternative to Pt for hydrogen generation presents a promising and cost-effective approach, primarily due to their high Faradaic efficiency. A detailed analysis showed that phosphomolybdic acid is one of the best decoupling agents in water electrolysis due to its stability in maintaining pH. Due to some limitations, all the polyoxometalates (POMs) are unsuitable as decoupling agents. Decreasing the distance between electrodes and improving membrane

performance are critical factors in reducing cell resistance.

In the abovementioned strategy, twice as much time is needed to decouple water electrolysis than the one-step conventional water electrolysis to produce hydrogen and oxygen in separate time and space. To address this problem, Girault et al. [171] proposed a novel idea for the electrolyzer design using redox flow batteries (RFBs) to decouple water rapidly (Fig. 10(a)). V(III)/V(II) and Ce(IV)/Ce(III) are two soluble molecular redox mediators that were employed in this study (Figs. 10(b) and 10(c)). The cyclic voltammetry (CV) results are shown in Fig. 10(d). Its specific potential against SHE is -0.26 V for V(III)/V(II). This cathodic redox couple is stable under strong acidic conditions with $\text{pH} < 2.5$ and has a high solubility under acidic conditions. The V(III)/V(II) pair exhibits rapid kinetics under various acidic environments on the graphite-felt or carbon-felt electrodes. The redox potential of Ce(IV)/Ce(III) can vary from 1.28 V in 1 M HCl to 1.70 V in 1 M perchloric acid. As a result of the varying redox potentials, nitric acid (HNO_3), sulfuric acid (H_2SO_4), and methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$ /MSA) are frequently used as acidic media in V–Ce RFBs. V(III)/V(II) redox pair produces V(II) species suitable for electron donation in HER. Both V(II) and Ce(IV) can thermodynamically drive decoupled water-splitting processes, but cannot do so kinetically without a catalyst. Comparatively speaking, the thermodynamic cell potential of a V–Ce RFB is 1.7 V, which is significantly greater than that of an all-vanadium RFB (1.26 V). The cell potentials recorded during charging and discharging at $60 \text{ mA}\cdot\text{cm}^{-2}$ were 2.5 and 0.7 V, respectively. The anode was slightly degraded at high potentials during deep charge and discharge in the V–Ce RFB hybrid system. Small black particles were visible in the Ce anolyte, while in the catholyte solution, some vanadium particles crossed the

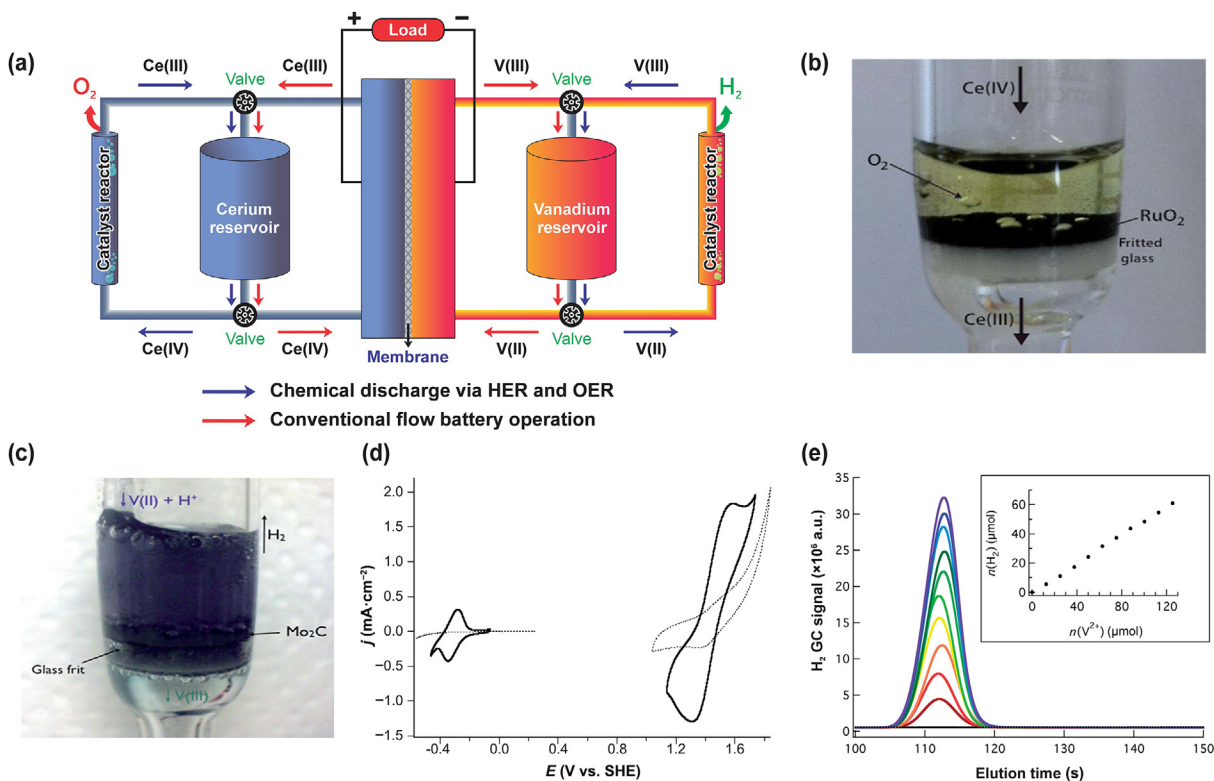
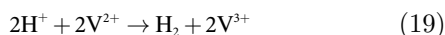


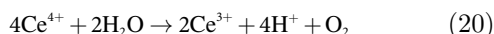
Figure 10 (a) Schematic illustration of indirect water electrolysis for V–Ce redox flow battery, where H_2 and O_2 are generated in their isolated system. (b) A photo of catalytic OER, where RuO_2 catalytic bed turns an acidic Ce(IV) solution into O_2 by oxidizing water. (c) A photo of catalytic HER, where Mo_2C catalytic bed has H_2 evolution from acidic V(II) solution. (d) Cyclic voltammograms of 50 mM V(IV)/Ce(III) sulfate in 1 M H_2SO_4 . (e) Gas chromatography of hydrogen signals for V(II) solutions in 1 M H_2SO_4 and 1 mg Mo_2C , each containing 2 mL and varying in concentration from 0 to 200 mM. The inset indicates hydrogen production for the solution's initial V(II). Reproduced with permission from Ref. [171], © The Royal Society of Chemistry 2014.

Nafion membrane. In 1 M H_2SO_4 , Ce^{3+} is oxidized to Ce^{4+} on the anode, while V^{3+} is reduced to V^{2+} . After passing over a catalytic bed of IrO_2 or RuO_2 nanoparticles, the Ce^{4+} -containing electrolyte released oxygen, and the V^{2+} -containing electrolyte released hydrogen. The V–Ce RFB has a higher energy density than the conventional electrolyzer. The complete chemical reactions are shown in Eqs. (19) and (20).

Catalyst (Mo_2C)



Catalyst (RuO_2 or $\text{IrO}_2/\text{SiO}_2$)



In terms of its stability and performance, Mo_2C is an improved electrocatalyst for the HER. At a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, the HER of a device that has been integrated with an electrode displays an overpotential of 150 mV. Mo_2C is used in the form of nanoparticles as a heterogeneous catalyst. Gas chromatography analysis shows an FE of $96\% \pm 4\%$ for HER and $78\% \pm 8\%$ for OER (Fig. 10(e)). The lower FE of OER indicates the side reactions that occur during the overall process. In this indirect electrolysis, the charged vanadium catholyte and cerium (Ce) anolyte produce hydrogen and oxygen, respectively.

In a progressive movement in 2014 to facilitate ECPB water electrolysis, Cronin et al. [172] developed a novel decoupling agent, silicotungstic acid $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, a highly soluble molecular redox mediator with a potent acidic property. Based on Pt-catalyst, it was found that this system generates hydrogen 30 times faster than PEM electrolyzers. In the aforementioned decoupling strategy, it does not matter whether the OER step is initiated by electricity or renewable energy. HER always requires electricity inputs due to a variety of redox aspects. This leads to a proposed, unique, and alternate decoupling strategy in which OER is initiated by an electrochemical step and HER by a chemical step, having a breakthrough in decoupled water splitting. The CV for $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ shown in (Fig. 11(a)) depicts a pair of reversible redox peaks, the first at +0.01 V and the second at -0.22 V vs. NHE. It is clear from the CV that HER is more favorable for the Pt electrode (green) than the carbon electrode (red) because the redox wave of Pt lies the same as $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, while for the carbon, it is far away from $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$. Complete reduction of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ to $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ without hydrogen evolution requires a positive potential greater than -0.6 V vs. NHE at the carbon cathode. To generate hydrogen efficiently, one can remove the reduced two-electron redox mediator, $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$, from the electrolysis cell and store it in hermetically sealed flasks under an argon (Ar) atmosphere. When metal foils are introduced into this solution, H_2 is evolved. Among the tested metals, Pt shows superior performance for hydrogen evolution, as illustrated in (Figs. 11(b) and 11(c)). Electrolyzers using proton exchange membranes require high current densities ($> 1 \text{ A}\cdot\text{cm}^{-2}$).

Precious metal supported on carbon electrodes evolves more hydrogen. Powdered form catalysts like Pt, Pd, Au, Ag, Cu, W, MoS_2 , and Ni_2P also play a better role in generating hydrogen from $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$. MoS_2 and Ni_2P perform superior to other powdered catalysts in generating H_2 from polyoxometalates (Fig. 11(g)). The one-electron-reduced species $\text{H}_5[\text{SiW}_{12}\text{O}_{40}]$ releases 122.4 mL of hydrogen. For the complete conversion of $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ to $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$, a two-electron transfer occurs, releasing doubled hydrogen volume, 244.7 mL, corresponding to the mediator solution volume used in the experiment. A series of

investigations was conducted using various H_2 -evolving catalysts in different ratios to determine the optimal efficiency and hydrogen production rate. A low loading of 0.1 mg of precious metal Pt/C gives the maximum rate of $2861 \text{ mmol}\cdot\text{mg}^{-1}\cdot\text{h}^{-1}$ of H_2 (Figs. 11(d) and 11(e)). Furthermore, gas chromatography was applied to check the purity of hydrogen obtained from $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$. Introducing 10% O_2 into the container fully reacts with $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$, resulting in the production of water and re-oxidized species. The presence of only 0.04% oxygen after 30 min indicates complete consumption of the introduced O_2 . This decoupling approach offers the advantage of prolonging membrane lifespan beyond that of PEM electrolyzers. The rate of H_2 evolution from the two-electron reduced species $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ is faster than that from the one-electron reduced species $\text{H}_5[\text{SiW}_{12}\text{O}_{40}]$ in the presence of a Pt/C electrode. Recycling data demonstrate that $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ remains a stable and effective redox mediator for hydrogen generation throughout the reduction and oxidation processes. Faradaic efficiencies of $95\% \pm 7\%$ were observed at the Pt cathode. During the overall reduction of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ to $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$, only 0.03% hydrogen gas was detected with a charge of 800 C (Figs. 11(f) and Figs. 11(h)–11(j)).

The aforementioned decoupled water splitting was powered by electricity using an ECPB method. This scheme can be easily adapted to photoelectrochemical water electrolysis using a photocathode and a photoanode. Given its widespread availability and low environmental impact, solar power has emerged as one of the most alluring carbon-free options. Solar-driven water splitting is one of the best strategies for using renewables efficiently. Lower current densities lead to the combination of H_2/O_2 gases, either without a headspace separator or impermeable membranes were used. Using thicker membranes decreases efficiency and increases the Ohmic resistance in an electrolytic cell. Another significant issue is hydrogen collection from a larger surface area array. With a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ for hydrogen production and the goal of generating 500 g of H_2 gas over 8 h of irradiation at 1 Sun ($1 \text{ Sun} = 100 \text{ mW}\cdot\text{cm}^{-2}$), an array of about 17 m^2 is needed [173, 174]. Solar-based decoupled water splitting can be carried out to avoid such mixing using an ECPB molecular redox mediator. Cronin et al. further demonstrated the solar-driven ECPB water splitting using phosphomolybdic acid. Tungsten trioxide (WO_3) was adopted as a photo-anode because of its stability under different pH conditions. Water oxidation at the anode and ECPB [$\text{PMo}_{12}\text{O}_{40}$] $^{3-}$ reduction at the cathode (+0.6 V vs. NHE) are in equilibrium due to the band gap of the whole process. A two-compartment cell configuration separated by a Nafion membrane was utilized. In one compartment, 1 cm^2 WO_3 -fluorine doped tin oxide (FTO) photoanode with 1 M methanesulfonic acid was introduced, while in another compartment, 0.5 M $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and an ECPB in water with carbon electrode were utilized. Gas chromatography shows $84\% \pm 6\%$ FE of OER at the WO_3 photoanode by solar radiation, while no H_2 was detected at the cathode, which indicates decoupling of the overall process. H_2 with 100% FE was obtained when rECPB [$\text{PMo}_{12}\text{O}_{40}$] $^{5-}$ was oxidized to [$\text{PMo}_{12}\text{O}_{40}$] $^{3-}$ electrochemically. Overall, the estimated solar-driven to hydrogen decoupled water splitting efficiency is 1%–2%.

A major benefit of this approach is that cheaper membranes like cellulose for large-scale applications can be used to replace expensive Nafion [174]. Sun et al. [175] reported that the concept of decoupled water splitting through ECPB was extended to a solar-driven strategy by introducing a powdered photocatalyst, BiVO_4 , with a molecular redox mediator $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (Fig. 12(a)).

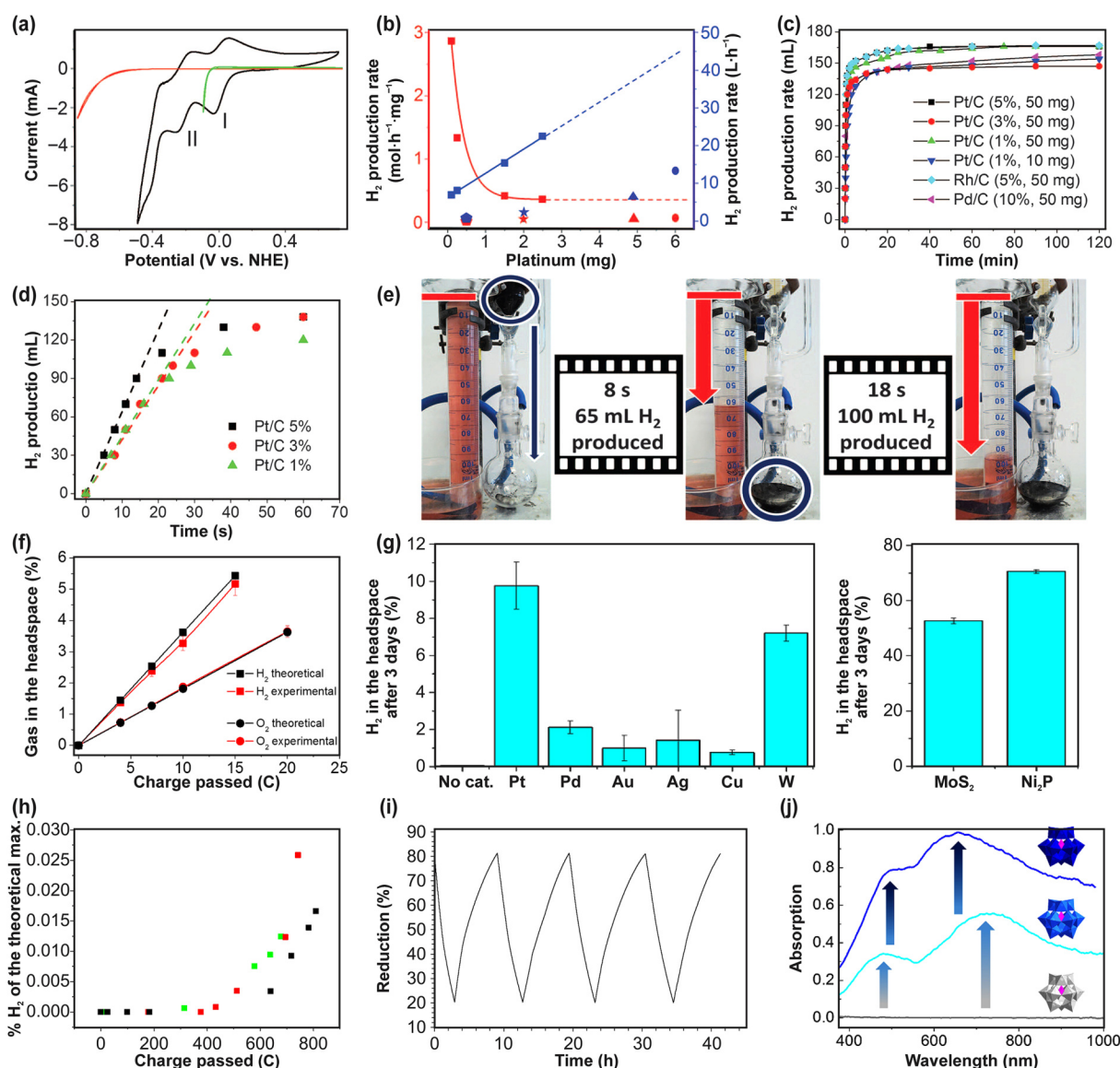


Figure 11 ECPB-based decoupled water splitting of silicotungstic acid $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$. (a) CV curves of 0.5 M $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ (black line), 1 M H_3PO_4 (green line) on a Pt electrode, and 1 M H_3PO_4 (green line) on a carbon electrode under Ar. (b) Comparison of H_2 production from the electrochemical reaction by redox-mediated silicotungstic acid with other electrolyzers; the left y-axis (red) is H_2 production per milligram of Pt; the right y-axis (blue) is hydrogen production from reduced silicotungstic acid. H_2 generation from reduced $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ by adding multiple catalysts. (c) Hydrogen production from different catalyst loadings with reduced species. (d) Hydrogen production during the first 2 min with 50 mg of Pt/C electrodes (1 wt.%, 3 wt.%, and 5 wt.%). (e) H_2 evolved when $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ directly interacted with the powdered catalyst. (f) Theoretical and experimental expected (black) and calculated (red) hydrogen and oxygen evolutions. (g) Different powdered catalysts were mixed with $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$, and the H_2 concentration in the headspace was measured after 3 days. (h) Traces of hydrogen during the reduction of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ to $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ with the overall charge of 800 C. (i) Reduction and oxidation cycles of 200 mM solution of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ in water. (j) UV-vis spectra of the reduction of $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ from one-electron reduced species $\text{H}_5[\text{SiW}_{12}\text{O}_{40}]$ to two-electron reduced species $\text{H}_6[\text{SiW}_{12}\text{O}_{40}]$ step by step in 1 mM solution of ECPB. Reproduced with permission from Ref. [172], © American Association for the Advancement of Science 2014.

The powdered form of photocatalyst BiVO_4 (size of 200–300 nm) used in this scheme lowered the cost of the cell as compared to solid-state photocatalyst. In the first step of solar radiation, the photocatalyst with ECPB oxidized water at the anode, releasing oxygen-producing protons and electrons. In the second step, the reduced phosphomolybdic acid was poured into the electrolyzer and re-oxidized to produce hydrogen at the cathode (Fig. 12(b)). The band gap of BiVO_4 is 2.4 eV, making it an n-type semiconductor. An experiment was conducted on photocatalytic water oxidation using 50 mg BiVO_4 and 10 mL of a 10 mM solution of phosphomolybdic acid in a glass-tight cell. Xenon lamps (300 W) with a transmitting glass filter greater than 400 nm were utilized. During the oxidation process, the pH was

maintained at ~ 1.67 . When oxidizing water in the presence of ECPB (OER step), BiVO_4 outperforms other n-type semiconductor photocatalysts, including WO_3 , Ag_3PO_4 , and Fe_2O_3 . In the H-cell, the Pt mesh was used as a working electrode, Ag/AgCl was used as a reference, and the Pt wire was used as a counter electrode. Both compartments were filled with partially reduced $[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$ obtained through solar radiation previously in the OER step. The Nafion membrane was used as an ion-selective separator. H_2 was obtained by oxidation of reduced species $[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^-$ to $[\text{H}_2\text{PMo}_{12}\text{O}_{40}]^-$ by applying 0.9 V vs. Ag/AgCl (Fig. 12(c)). Complete oxidation of reduced species is represented by a shift in color from dark blue to yellow in the solution. The resulting FE of 98% is comparable to the theoretical

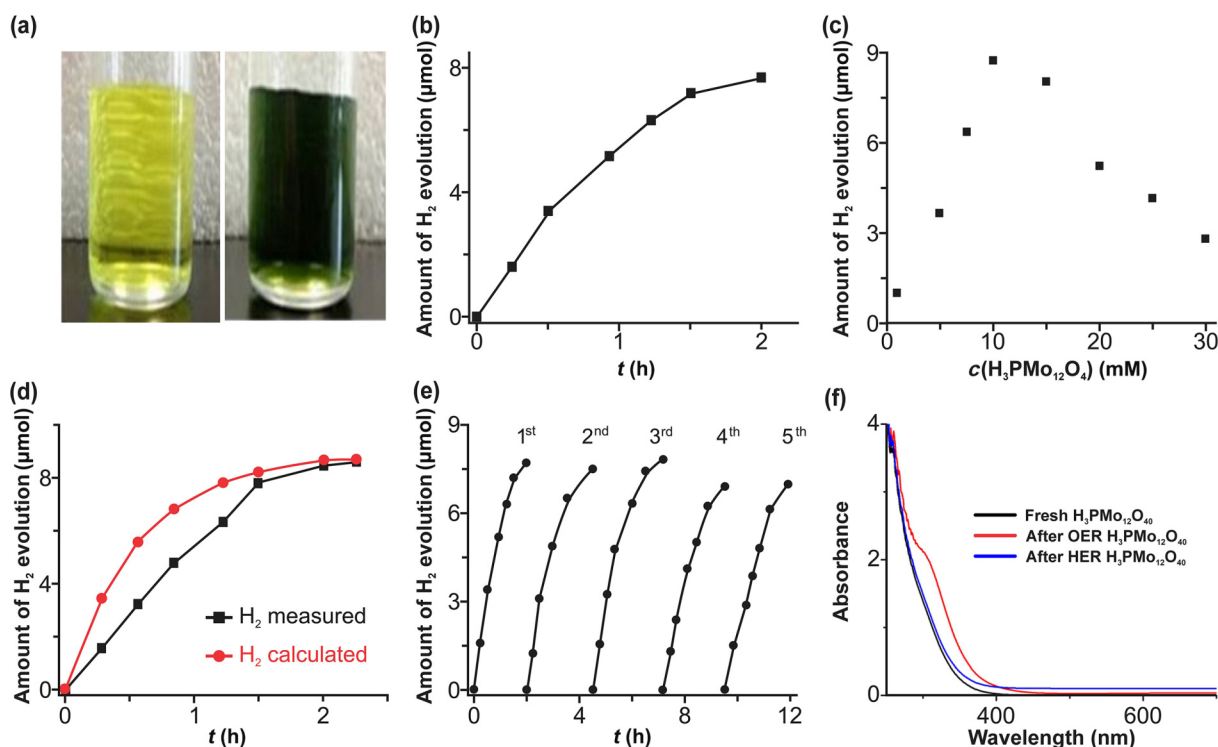


Figure 12 ECPB-based decoupled water splitting of polyoxometalate $\text{H}_3\text{PMo}_{12}\text{O}_{40}$. (a) Digital photographs of oxygen evolution of BiVO_4 under visible irradiation in aqueous $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (10 mM, pH = 1.67), where color changes from yellow to dark blue during this process. (b) Kinetics of H_2 evolution at 0.9 V with respect to Ag/AgCl. (c) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ concentration effects on hydrogen evolution in aqueous solution. (d) A three-electrode setup was used at 0.9 V vs. Ag/AgCl to calculate the Faradaic efficiency of proton reduction. Hydrogen gas diffuses slowly from the reaction solution to the headspace, which causes a lag between “ H_2 measured” and “ H_2 calculated”. (e) Hydrogen production was performed for five cycles, and 10 mM $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was used for each cycle. (f) UV-vis spectra of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ before (black) and after (red) photocatalytic OER and after HER (blue) with the resulting solution of photocatalysis. Reproduced with permission from Ref. [175], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2017.

yield. A concentration of 10 mM $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was employed to generate the maximum H_2 (Fig. 12(d)). When the electrochemical process ends after releasing H_2 , the remaining solution (mixture of BiVO_4 and ECPB) can be used again for the OER process without treatment. Figure 12(e) shows water oxidation and H_2 evolution for five cycles. The evolution of hydrogen is constant at every cycle, indicating the stability of BiVO_4 and the reversibility of polyoxometalate throughout the process. XRD patterns of powdered BiVO_4 after five cycles show no significant change. Meanwhile, ultraviolet (UV)-vis spectra indicate no major change in $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, indicating good recyclability of the catalysts for practical applications (Fig. 12(f)). The OER performance of the photocatalyst BiVO_4 is adversely affected by its dark coloration when high concentrations of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ are present [175].

HER is more feasible in acid media, as shown in the abovementioned DWS strategies. This limits the performance of OER in basic media because major earth-abundant OER electrocatalysts cannot survive in a low-pH atmosphere and do not reveal better results than basic electrolytes [176]. To achieve efficient DWS, it is essential to investigate new redox mediators that perform optimally in basic electrolytes. Sun et al. [177] introduced a cost-effective molecular redox mediator for decoupled water electrolysis in alkaline conditions (Fig. 13(a)). Photovoltaic-driven DWS, under natural solar irradiation, separates HER from OER in a neutral electrolyte, requiring only low voltage inputs. This process also facilitates the valorization of intermediates derived from biomass alongside the decoupled hydrogen evolution. Two molecular redox mediators, $\text{Na}_4[\text{Fe}(\text{CN})_6]$ and (ferrocenylmethyl) trimethylammonium chloride (FcNCl), have been identified as proton-independent ERs that operate

efficiently when powered by electricity or renewable energy sources while maintaining a nearly neutral pH. These economic mediators show favorable cyclic stability with approximately 100% FE. In alkaline conditions, 5-hydroxymethylfurfural (HMF) was oxidized to 2,5-furandicarboxylic acid (FDCA) via the $\text{Na}_4[\text{Fe}(\text{CN})_6]$ mediator, yielding both 2,5-furandicarboxylic acid and H_2 . Traditional water splitting carried out at a large voltage input ranging from 1.8–2.5 V, either in acidic or basic conditions, using PEM or alkaline electrolyzers, respectively. FcNCl acts as a decoupling agent close to the neutral electrolyte in 0.5 M Na_2SO_4 . $\text{Na}_4[\text{Fe}(\text{CN})_6]$ was also used as a decoupling agent, and its pH versatility from neutral to basic was well appreciated. Electrocatalysts, such as non-precious metal phosphide and Ni foam, were used to kick off HER and OER, respectively.

Commercial solar cells with a voltage of fewer than 1.7 V can launch the DWS process as an alternative to the higher inputs needed to drive the HER and OER processes. O_2 is not a valuable product at the anode compared to H_2 , so $\text{Na}_4[\text{Fe}(\text{CN})_6]$ electron reservoir coupled with OER produces a value-added product by organic oxidation of biomass-derived compounds like 5-hydroxymethylfurfural. HER and OER working electrodes made of transition-metal phosphide and Ni foam, respectively, were put in the same chamber with a carbon counter electrode containing an electron reservoir solution in a separate chamber. FcNCl is highly soluble in water with long-term cyclic stability in redox flow batteries under neutral pH. When the oxidation potential of a compound is lower than the OER potential, organic oxidation can be used to convert the compound to a more useful one, such as the conversion of HMF to FDCA. FcNCl solubility significantly rises to at least 4 M in water. In the first HER step, CV

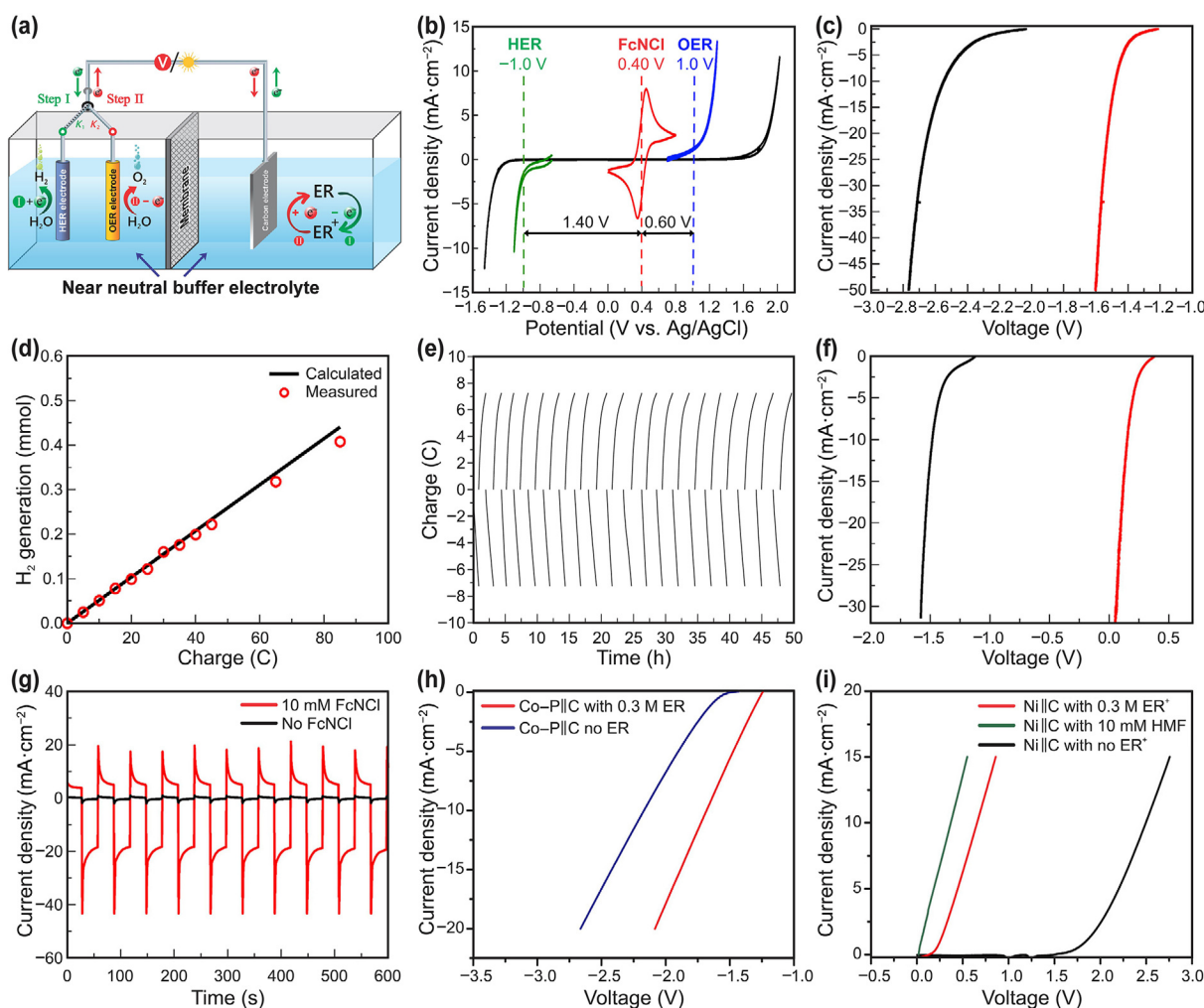


Figure 13 (a) A DWS electrolyzer that uses FcNCl or Na₄[Fe(CN)₆] electron reservoirs for step-by-step HER and OER in a near-neutral electrolyte. (b) Using a three-electrode set-up, the near-neutral CV and LSV curves of FcNCl in 0.5 M Na₂SO₄ (pH = 6.5) solution with Ag/AgCl (saturated KCl) as the reference electrode were compared. (c) LSV at a zero (black) or 50 mM (red) FcNCl reservoir at a scan rate of 5 mV·s⁻¹ (*i*R corrected) using Ni₂P/Ni/NF as the working electrode, carbon rod as a counter electrode with a 0.5 M Na₂SO₄ solution in both the working and counter chambers. (d) GC comparison of a theoretical and measured amount of H₂ released from FcNCl at -1.8 V during electrolysis. (e) Estimation of FcNCl stability as an electron reservoir via HER and OER electrolysis cycles. The working and counter electrodes were subjected to -1.6 V for HER and 1.8 V for OER voltage bias. (f) LSV under solar irradiation with (red) and without (black) an external photovoltaic cell over a carbon electrode Ni₂P/Ni/NF after being charged with 10 mM FcNCl + 0.5 M Na₂SO₄. (g) The current density of HERs on Ni₂P/Ni/NF as a function of time when exposed to sunshine. The red line indicates the addition of 10 mM FcNCl to the counter compartment, whereas the black line indicates that no FcNCl was added. An electrochemical investigation on decoupled HER, OER, and HMF oxidation, utilizing Na₄[Fe(CN)₆] as an electron reservoir. (h) LSVs for HER in two-electrode H-cell systems were acquired using Co-P as the working electrode and carbon as the counter electrode in the presence (red) or absence (blue) of 0.3 M Na₄[Fe(CN)₆]. (i) LSV for OER in two-electrode H-cell systems in which carbon is the counter electrode and nickel foam is the working electrode under various conditions. Reproduced with permission from Ref. [177], © Elsevier Inc. 2017.

demonstrates a reversible redox wave at 0.40 V vs. Ag/AgCl when using 50 mM FcNCl in 0.5 M Na₂SO₄ (pH = 6.5) solution. The HER and OER currents do not become significant until -1.2 and 1.7 V are attained without electrocatalysts (Fig. 13(b)). Earth-abundant electrocatalysts were employed to reduce the voltage input for HER and OER in a nearly neutral electrolyte. DWS was achieved with Ni₂P (Ni₂P/Ni/NF) for HER and nickel foam (NF) for OER electrocatalyst electrodes. While in the presence of electrocatalysts, overpotentials for both HER and OER were reduced in the range of -1.0 and +1.0 V vs. Ag/AgCl, respectively.

Linear sweep voltammetry (LSV) curves of Ni₂P/Ni/NF electrocatalyst in 0.5 M Na₂SO₄ are figured out using an anion exchange membrane in two-electrode configurations. At the same time, a carbon rod was taken as a counter electrode (Fig. 13(c)). Without using FcNCl, no catalytic HER activity was observed on Ni₂P/Ni/NF until -2.4 V. When 50 mM FcNCl solution was

added in the counter compartment, a rapid catalytic HER activity was observed on Ni₂P/Ni/NF nearly -1.4 V, saving almost 1.0 V voltage input. GC results showed 100% FE of FcNCl when an external bias of -1.8 V was applied to Ni₂P/Ni/NF (Fig. 13(d)). Previously, all the charges passed were utilized to evolve hydrogen. While on the counter electrode, FcNCl was oxidized to FcNCl⁺ with the release of H₂. During HER, no O₂ was detected in the headspace of the working chamber, which indicates the purity of the H₂. In the second OER step, the connection was switched off from the Ni₂P/Ni/NF electrode to the nickel foam (NF) electrode to proceed with the OER to complete the whole redox reaction. A bias voltage of 0.6 V was applied in the presence of a fully oxidized FcNCl⁺ electron reservoir. In contrast, in its absence, a voltage exceeding 2.4 V was required to initiate the OER for O₂ production. When HER and OER complete their cycle, the redox mediator comes to its original form, FcNCl. An input voltage of

2.338 V is needed for one-step water splitting without an electron reservoir like FcNCl when using a $\text{Ni}_2\text{P}/\text{Ni}/\text{NF}||\text{NF}$ electrode configuration to achieve a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ in $0.5 \text{ M Na}_2\text{SO}_4$.

However, two-step water splitting proves to be more feasible, achieving an efficiency of 96%, which is significantly higher than the efficiencies reported in previous studies, like phosphomolybdic acid (79%) [28], silicotungstic acid (93%) [178], potassium hydroquinone sulfonate (80%) [172], and $\text{Ni}(\text{OH})_2$ (92%) not including resistive factors [179]. The FE of both HER and OER is 100%. The calculated energy efficiency of FcNCl was 61% at $10 \text{ mA}\cdot\text{cm}^{-2}$ as compared to previously reported molecular redox mediators phosphomolybdic acid (59%) [180], silicotungstic acid (63%) [28], potassium hydroquinone sulfonate (61%) [178], $\text{Ni}(\text{OH})_2$ (67%) and Pt-based proton exchange membrane (PEM) electrolyzers (67%) [172]. Long-term decoupled water electrolysis was done to check the cyclic stability of FcNCl as an electron reservoir. Roughly 7 C charge was passed during the redox cycle (Fig. 13(e)). For H_2 evolution at the $\text{Ni}_2\text{P}/\text{Ni}/\text{NF}$ electrode, an input voltage bias of -1.6 V was applied at the cathode. For O_2 evolution at the NF electrode, an input voltage bias of 1.8 V was applied at the anode. The pH of the FcNCl increases from 6.5 to 9 during HER and finally back to its initial state of pH of 6.5 after OER. FcNCl shows robust cyclic stability during DWS. Further, NO_3^- was used to replace Cl in FcNCl. This ion does not change the redox feature of the FcN $^+$. FcN(NO_3) can also act as an electron reservoir in place of FcNCl, which gives equal performance to FcNCl. Due to the extraordinary performance of FcNCl as an electron reservoir, this redox mediator was employed in solar irradiation systems to produce green energy (H_2). For this purpose, a single photovoltaic (PV) module with a photovoltage $> 1.4 \text{ V}$ was applied without using external bias. LSV shows -1.58 V is required to evolve H_2 to reach a current density of $-30 \text{ mA}\cdot\text{cm}^{-2}$ without solar irradiations (Fig. 13(f)). The same current density can be attained from the PV module when fully exposed to solar irradiation, at $92 \pm 5 \text{ mW}\cdot\text{cm}^{-2}$ at zero external bias (Fig. 13(g)).

In conclusion, FcNCl was identified as a key molecular redox mediator for solar-driven DWS aimed at H_2 production. Notably, FcNCl operates effectively within a pH range of 5–9. Another redox mediator, $\text{Na}_4[\text{Fe}(\text{CN})_6]$, functions across a wider pH spectrum, from neutral to alkaline, particularly in 1.0 M NaOH solutions. $\text{Na}_4[\text{Fe}(\text{CN})_6]$ is stable, highly soluble in water (0.6 M), cost-effective, and acts as a proton-independent electron reservoir for DWS. Co–P was used as the working electrode for HER. At the same time, nickel foam (NF) was employed for OER (Fig. 13(h)). The molecular redox wave of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ is positioned between the onset potentials of HER and OER, demonstrating 100% FE and 64.6% energy efficiency. Additionally, $\text{Na}_4[\text{Fe}(\text{CN})_6]$ can be integrated with photovoltaic cells (1.1 or 1.6 V) under solar irradiation for DWS. Incorporating $\text{Na}_4[\text{Fe}(\text{CN})_6]$ as an electron reservoir to generate value-added products at the anode during the OER process would further enhance its benefits. Oxygen obtained during DWS is not as valuable as H_2 , so oxidation at the anode was integrated with biomass-derived products like HMF (Fig. 13(i)). Previous results reveal that by using Ni-based electrocatalysts through an alkaline solution, HMF can be oxidized to more valuable FDCA [70, 181]. The redox feature of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ lies between HER and OER onset (1.3 V vs. RHE), which is readily less positive than HMF oxidation on nickel foam (NF) in 1.0 M NaOH solutions. 1000 redox cycles of $\text{Na}_4[\text{Fe}(\text{CN})_6]$ show brilliant stability with a minor degradation rate in 1.0 M NaOH . Less positive potential of

0.37 V was detected on HMF oxidation over $10 \text{ mA}\cdot\text{cm}^{-2}$. Chronocoulometry electrolysis shows 100% HMF conversion to 83% FDCA after the passage of 87 C charge at 0.2 V using a non-precious catalyst. This strategy can be integrated, as HER can be launched with an electron reservoir using photovoltaics upon solar irradiation. At the same time, OER can carry out HMF oxidation to FDCA on lower voltage input approximately 0.2 V . It has been observed that FcNCl and $\text{Na}_4[\text{Fe}(\text{CN})_6]$ are inexpensive electron reservoirs redox mediators for neutral-condition DWS. Both of the abovementioned molecular redox mediators have high solubility in water at near neutral pH, flexible reversible redox wave, and low cost [177].

The abovementioned decoupling strategies give 1 to 2 electron transfers in the overall process. In addition, the Cronin group [182] synthesized the very abundant electronic species polyoxoanion $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, which has 18 electrons/ H^+ per anion and can undergo reversible reduction and protonation in water. In addition to its usage as a mediator in an electrolytic cell for producing hydrogen on demand, it is also a high-performance electrolyte for redox flow batteries. Finding a mediator that can accept as many electrons into a molecule as feasible is an urgent research priority. For example, up to 17 or 18 electrons can be stored reversibly in polyoxometalates. The specific energy density of redox flow batteries based on polyoxometalates is $15.4 \text{ Wh}\cdot\text{L}^{-1}$ [183]. $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ based redox flow battery has an energy density of $225 \text{ Wh}\cdot\text{L}^{-1}$. At a lower concentration of 2 mM , four reversible redox were obtained between $+0.6$ and -0.6 V vs. SHE (Fig. 14(a)). As pH decreases from 7 to 4, the one-electron process transfers to 2-electron process below 0 V . Increasing the concentration of polyoxometalates leads to a larger redox potential below -0.3 V compared to 2 mM concentration and 1 M sulfuric acid in the absence of polyoxometalates. The increase in the concentration of polyoxometalates in solution is directly proportional to the number of electrons. Protons and electrons generated on IrO_2 catalyst by water oxidation reduce and form highly rich electronic species polyoxoanions ($[\text{P}_2\text{W}_{18}\text{O}_{62}]^{(6+n)-}$). After a specific charge has been passed, ECPB species undergo electrochemical re-oxidation to generate hydrogen. The total charge capacity of polyoxometalates can be assessed by comparing the energy input required for reduction with the energy released during re-oxidation. The charge in the $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ cluster at lower pH concentrations will increase with polyoxometalate concentration. In a 2 mM solution, 4 electrons were recovered; while in a 50 mM solution, 16 electrons were recovered from $\text{Li}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$. These results indicate that increasing the concentration in the solution will increase the electron transfer (Fig. 14(b)). Eighteen electrons are considered standard and can be stored in polyoxometalates per molecule during the redox cycle. Galvanostatic redox cycles demonstrate that Coulombic efficiency (CE) was above 95% with 97.3% capacity retention over 100 cycles, confirming the stability of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ upon 18 electron redox process (Figs. 14(c) and 14(d)). Headspace analysis indicates that hydrogen evolved from those charges that were not recovered over the re-oxidation of polyoxometalates. 96% charge stored during reduction can be recovered during the electrochemical re-oxidation process by increasing the 100 mM concentration. The results show that 3500 mmol of H_2 was produced per hour per milligram of Pt, whereas PEM electrolyzers generated only 50 – 100 mmol of H_2 per hour per milligram of Pt (Fig. 14(e)) [184, 185]. After 400 s , the re-oxidized polyoxometalates consumed 14 of 18 electrons to produce hydrogen. The last two $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ re-oxidation potentials were

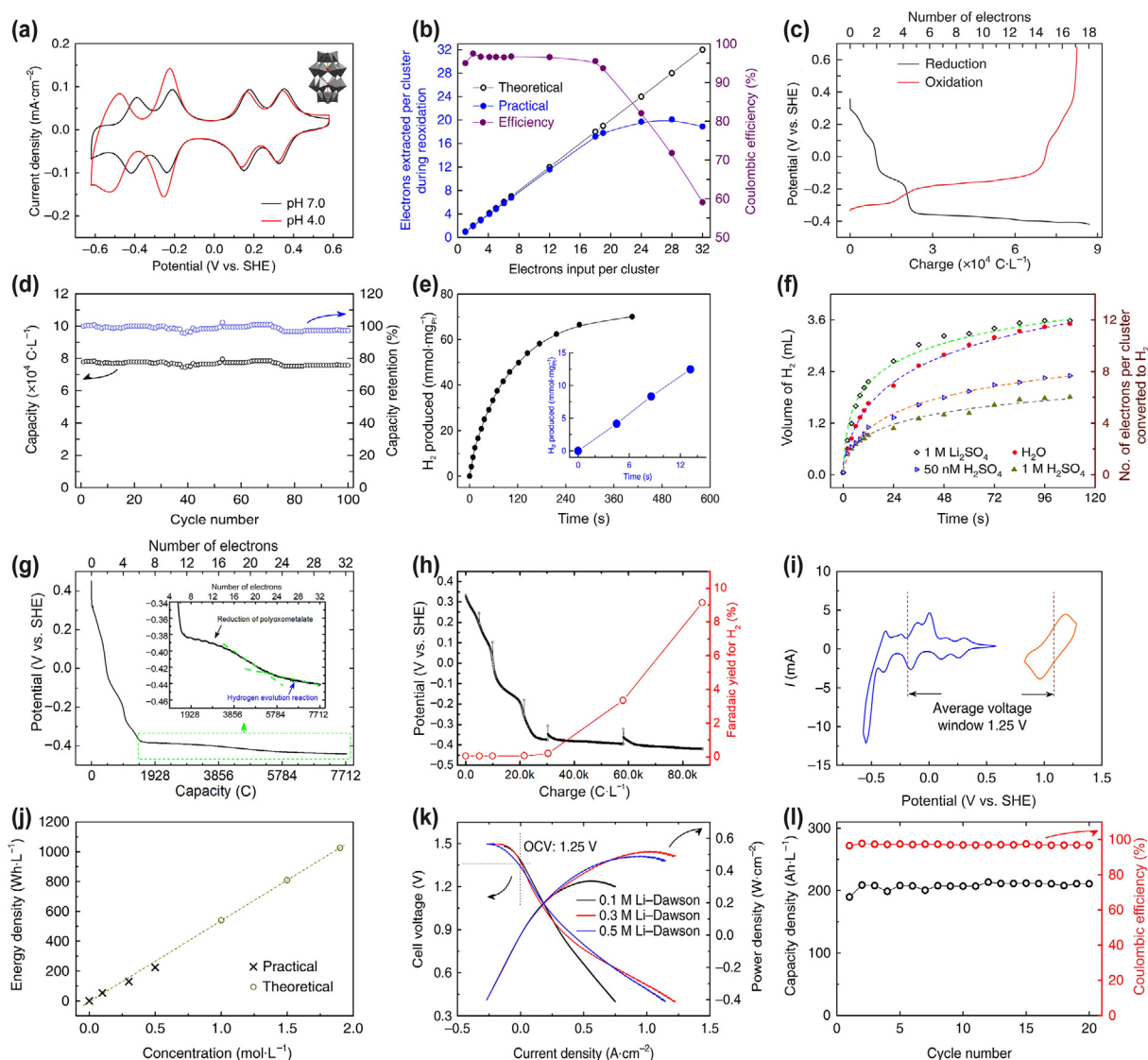


Figure 14 ECPB-based decoupled water splitting of polyoxometalate $[P_2W_{18}O_{62}]^{6-}$. (a) CV at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ of $2 \text{ mM Li}_6[P_2W_{18}O_{62}]$ solution in $1 \text{ M Li}_2\text{SO}_4/\text{H}_2\text{SO}_4$ (red, $\text{pH} = 4.0$) and $1 \text{ M Li}_2\text{SO}_4$ (black, $\text{pH} = 7.0$). The inset shows the structure of $[P_2W_{18}O_{62}]^{6-}$. (b) Following reduction with varying numbers of electrons per molecule, the number of electrons extracted from a 100 mM polyoxometalate solution shows that, beyond 18 electrons per molecule, competitive hydrogen evolution becomes significant. (c) Reduction and re-oxidation curves for the 18-electron process of a 50 mM $[P_2W_{18}O_{62}]^{6-}$ solution. (d) 100 reduction/re-oxidation cycles of 50 mM $[P_2W_{18}O_{62}]^{6-}$ solution. (e) Hydrogen production from a 0.1 M solution of 18-electron-reduced polyoxometalates (10 mL) in the presence of a 10 mg Pt/C catalyst. (f) Dilution of 50 mM 18-electron reduced polyoxometalates solution. When diluted, the pH rises, which causes more hydrogen to evolve spontaneously. (g) 25 mL of 100 mM $[P_2W_{18}O_{62}]^{6-}$ 32-electron solution reduction curve. Inset shows where significant H_2 evolution begins. (h) GC analysis of 25 mL of $50 \text{ mM Li}_6[P_2W_{18}O_{62}]$ in H_2O , with each polyoxometalate molecule reduced by 18 electrons. (i) CV at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ for $100 \text{ mM Li}_6[P_2W_{18}O_{62}]$ (blue) and 0.5 M HBr (orange) reduction in $1 \text{ M H}_2\text{SO}_4$. (j) Comparison of $\text{Li}_6[P_2W_{18}O_{62}]$ concentration with energy density for redox flow battery. (k) Polarization curves showing current density vs. power density at 20°C with OCV range of $0.4\text{--}1.5 \text{ V}$. (l) Discharge capacity density and Coulombic efficiency for $0.5 \text{ M Li}_6[P_2W_{18}O_{62}]$ in $0.1 \text{ M H}_2\text{SO}_4$ at the negative side and $4 \text{ M HBr} + 0.1 \text{ M Br}_2$ at the positive side, vs. cycles at 20°C (across the voltage window of $0\text{--}1.65 \text{ V}$ by applying a constant current of $0.1 \text{ A}\cdot\text{cm}^{-2}$). Reproduced with permission from Ref. [182], © The Author(s), 2018.

anodic. Hydrogen evolution on Pt/C electrodes continued until two electron-reduced species $[P_2W_{18}O_{62}]^{8-}$ were obtained. Using a Pt/C electrode, a maximum of 16 electrons was obtained by reducing polyoxometalates.

Upon dilution, the polyoxometalate $[P_2W_{18}O_{62}]^{(6+n)-}$ continuously evolved hydrogen gas without the need for a catalyst or electrochemical input. Different media were used to dilute a 50 mM solution of $[P_2W_{18}O_{62}]^{6-}$ ($\text{pH} = 2$), including $50 \text{ mM H}_2\text{SO}_4$ ($\text{pH} = 1.5$), $1 \text{ M H}_2\text{SO}_4$ ($\text{pH} = 1.0$), H_2O ($\text{pH} = 7$), and $1 \text{ M Li}_2\text{SO}_4$ ($\text{pH} = 7$). H_2 evolved spontaneously when diluted with $50 \text{ mM H}_2\text{SO}_4$, $1 \text{ M H}_2\text{SO}_4$, and H_2O (Fig. 14(f)). Conversely, fast kinetics were shown when a non-buffering electrolyte, $1 \text{ M Li}_2\text{SO}_4$

($\text{pH} = 7$), was used for dilution of polyoxometalates. Finally, it is concluded that increasing the pH leads to fast hydrogen evolution during the dilution process. This indicates that polyoxometalates store an average charge of up to 17.2 electrons per molecule. It is crucial to control HER during $[P_2W_{18}O_{62}]^{6-}$ reduction by using around 6 electrons to elaborate on the feasibility of an electrolytic cell. The Coulombic efficiency of the $\text{Li}_6[P_2W_{18}O_{62}]$ cluster by using 32 electrons to check reduction/oxidation (in 100 mM concentration) came out above 95%. Maximum electrons recovered during this process came out to 20 per polyoxometalate molecule due to some parasitic losses (Figs. 14(g) and 14(h)). High-resolution mass spectroscopy further confirms the stability of

$[P_2W_{18}O_{62}]^{6-}$ over 100 mM solution. The amount of H_2 produced using polyoxometalates is greater than that of conventional PEM electrolyzers.

Furthermore, the authors evaluated the performance of highly reduced species $Li_6[P_2W_{18}O_{62}]$ as an electrolyte in a redox flow battery. For this purpose, a redox flow battery was constructed with HBr/Br_2 serving as the positive electrolyte and polyoxometalate serving as the negative redox pair (Fig. 14(i)). The battery in a 0.1 M solution at $50\text{ mA}\cdot\text{cm}^{-2}$ has a CE of 96% with $43.2\text{ Wh}\cdot\text{L}^{-1}$. At 20°C , the capacity increased from 131 to $230\text{ Ah}\cdot\text{L}^{-1}$ as the concentration of $Li_6[P_2W_{18}O_{62}]$ was raised from 0.3 to 0.5 M (Fig. 14(j)). The practical energy densities are $130\text{ Wh}\cdot\text{L}^{-1}$ for 0.3 M and $225\text{ Wh}\cdot\text{L}^{-1}$ for 0.5 M solution with an energy efficiency of up to 76%. These findings suggest that redox flow batteries may produce energy densities greater than $1000\text{ Wh}\cdot\text{L}^{-1}$. At a concentration of 0.3 M at 20°C , $0.52\text{ W}\cdot\text{cm}^{-2}$ peak galvanic power density was obtained. Galvanic power density decreases slightly at higher concentrations due to viscosity (Fig. 14(k)). A Coulombic efficiency of 98% was recorded over 20 cycles with a galvanic discharge capacity nearly at $210\text{ Ah}\cdot\text{L}^{-1}$ in $0.5\text{ M } Li_6[P_2W_{18}O_{62}]$ solution for a redox flow battery system (Fig. 14(l)). In conclusion, the energy density of $Li_6[P_2W_{18}O_{62}]$ is significantly greater than that of other harmful redox flow batteries. This cluster can accept and release up to 18 electrons and protons. With a discharge energy density of $225\text{ Wh}\cdot\text{L}^{-1}$ at ambient temperature, this redox flow battery can store $\sim 9\text{ g}$ of H_2 per liter. Due to its limitation of solubility in aqueous solutions, 34.2 g of hydrogen per liter might be attained compared with cryogenic liquid H_2 (71 g of hydrogen per liter at 20 K) or might be a redox flow battery with an energy density of $1000\text{ Wh}\cdot\text{L}^{-1}$ [182].

The redox performance (at $\sim 0.02\text{ V}$ vs. RHE advanced in the negative direction) of silicotungstic acid as an ECPB was further enhanced by Wu and collaborators [186] by the use of organic solvents (ethanol, N,N -dimethylformamide (DMF), and acetonitrile) (Fig. 15(a)). A higher hydrogen yield ($\sim 85\%$) was

produced in a water–ethanol combination than in water ($\sim 45\%$). The rate of hydrogen evolution was unaffected by the addition of ethanol. However, the previously described ECPB systems only collect 45%–60% of the hydrogen [172, 186]. This is because the $1e^-$ reduced silicotungstic acid limited the reducing ability. For the semihydrogenation of organic molecules in water–organic solvent mixtures, reduced silicotungstic acid is an excellent hydrogen source. Acetonitrile, dimethylformamide, and ethanol were used to control silicotungstic acid redox behaviors in aqueous solutions. To completely reduce $H_4SiW_{12}O_{40}$ to $H_6SiW_{12}O_{40}$ through a two-electron reduction, a potential of 8.3 V was applied to the working electrodes. The reduced silicotungstic acid and H^+ ions react favorably to produce hydrogen in the presence of the catalyst when the redox wave of silicotungstic acid moves in the negative direction at $\sim 0.02\text{ V}$ vs. RHE. Hydrogen was produced using a Pt/C catalyst. It has been discovered that adding organic solvents can increase H_2 production. When compared to the yields of H_2 in water (3.62 mL , 45%), acetonitrile (6.05 mL), and DMF (6.75 mL), the water–ethanol system produces a high yield of H_2 (6.95 mL) with a FE of 85% (Figs. 15(b) and 15(c)). Without the Pt/C catalyst or redox mediator $H_6SiW_{12}O_{40}$, the amount of H_2 produced in a control experiment was negligible. The results of measuring the H_2 yield in a water–ethanol system with varying volume ratios reveal that the H_2 yield rises with increasing ethanol concentration in the present system. The ideal ethanol percentage is 50% for hydrogen production. When the ethanol concentration rises, a negative shift occurs in the redox of silicotungstic acid (Fig. 15(d)). At high ethanol concentrations, silicotungstic acid reduces well. The reaction rate and yield are critical in large-scale hydrogen synthesis from water electrolysis. Hydrogen evolution from water electrolysis is very efficient in the present ECPB system, with an initial rate of $0.8\text{ mL}\cdot\text{s}^{-1}$, resulting in a rate of 47 mmol of H_2 per hour per mg of Pt catalyst. In addition, as seen in the inset, adding ethanol causes a shift in the solution color from deep blue to light brown, suggesting that more reduced silicotungstic acid is

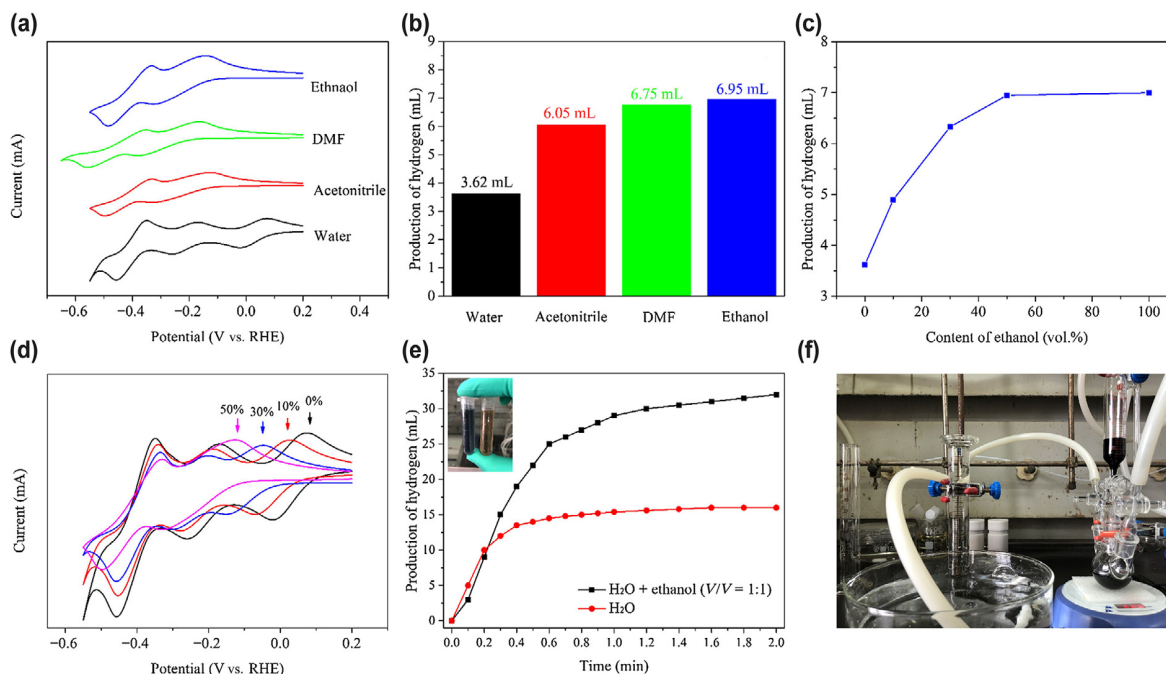


Figure 15 ECPB-based decoupled water splitting of silicotungstic acid $H_4[SiW_{12}O_{40}]$ by adding organic molecules. (a) CV and (b) production of hydrogen gas from silicotungstic acid in a combination of water and organic solvent ($V/V = 1:1$, V means volume). (c) Hydrogen yield and (d) CV curves of silicotungstic acid in the water–ethanol system at various volume ratios. (e) The reaction time-dependent generation of H_2 in the water–ethanol system. Inset: the resultant color of the solution. (f) A typical setup for measuring hydrogen gas quantities. Reproduced with permission from Ref. [186], © Elsevier Inc. 2019.

involved in hydrogen evolution (Figs. 15(e) and 15(f)). These results demonstrate that ethanol enhances silicotungstic acid capacity to generate more hydrogen. In addition, phenylacetylene and acetophenone (organic compounds that undergo semihydrogenation) were studied. When using reduced silicotungstic acid and Pt/C as the hydrogen source and catalyst, phenylacetylene may be hydrogenated to styrene efficiently. For the semihydrogenation of phenylacetylene, it is shown that styrene has a good selectivity ($\sim 80\%$) at a relatively high conversion ($\sim 97\%$). Acetophenone may be converted to 1-phenylethanol using a hydrogen source (reduced silicotungstic acid) and a catalyst (Pd/C). The selectivity for 1-phenylethanol is 82%, while the rate of acetophenone conversion is 80%. These systems produced around 2.4 mL of hydrogen and achieved 80% FE in their semihydrogenation processes. Based on these results, it appears that including organic solvents in the system increases the H_2 production and improves the potential use of polyoxometallates in the semihydrogenation of organic compounds under mild conditions. The conversion rates of phenylacetylene and acetophenone at ideal conditions are 97% and 80%, respectively, whereas those of styrene and 1-phenylethanol are 80% and 82%, respectively [186].

Chisholm and coworkers [187] presented silicotungstic acid, an electron-coupled-proton buffer in a PEM electrolyzer, as a redox flow reactor (Fig. 16(a)). Both the HER and OER steps of the decoupling process were carried out in two connected electrochemical flow cells. Both HER and OER in electrochemical cells employed a Nafion-117 membrane with a catalyst on one

side. The anodic side of HER cells was coated with IrO_2 , whereas the cathodic side of OER cells was coated with Pt/C. A conventional PEM electrolyzer was also constructed to compare with an ECPB-based PEM electrolyzer. This proposed system also works at low current densities of $25\text{ mA}\cdot\text{cm}^{-2}$ while the presence of hydrogen during O_2 production was $< 0.4\%$. While conventional PEM electrolyzers work at the same low current density, 2% hydrogen is present in the O_2 process. This mediator has two reversible redox at $+0.01$ and -0.22 V vs. NHE at pH of 0.5. A constant feed of anolyte and catholyte was applied during the whole process. With the help of the novel ECPB-based PEM configuration, over 99% of the hydrogen and oxygen were separated at a relatively high voltage of 2.0 V at a current density of $500\text{ mA}\cdot\text{cm}^{-2}$. The procedure was started at 30°C with a flow rate of $40\text{ mL}\cdot\text{min}^{-1}$ for the anodic feed and $250\text{ mL}\cdot\text{min}^{-1}$ for the cathodic peak (Fig. 16(b)). In the OER cell, oxygen was produced at the anode by cathodic reduction of ECPB ($H_4[SiW_{12}O_{40}]$ to $H_5[SiW_{12}O_{40}]$) at the cathode by one electron. One electron-reduced ECPB from the OER cell was then further moved to the anodic side of the HER cell while keeping the circuit open to stop spontaneous re-oxidation of silicotungstic acid, where complete re-oxidation of ECPB produces hydrogen gas at the cathode. At varying levels of current densities of 100, 250, and $500\text{ mA}\cdot\text{cm}^{-2}$, the decoupling percentage and cell voltage of the redox mediator are 97%/1.85 V, 98%/2.01 V, and 76%/2.35 V, respectively. It was observed that higher current densities lead to a decrease in decoupling H_2 and O_2 . The issue was resolved by increasing the catholyte flow rate from 250 to $500\text{ mL}\cdot\text{min}^{-1}$ and increasing the

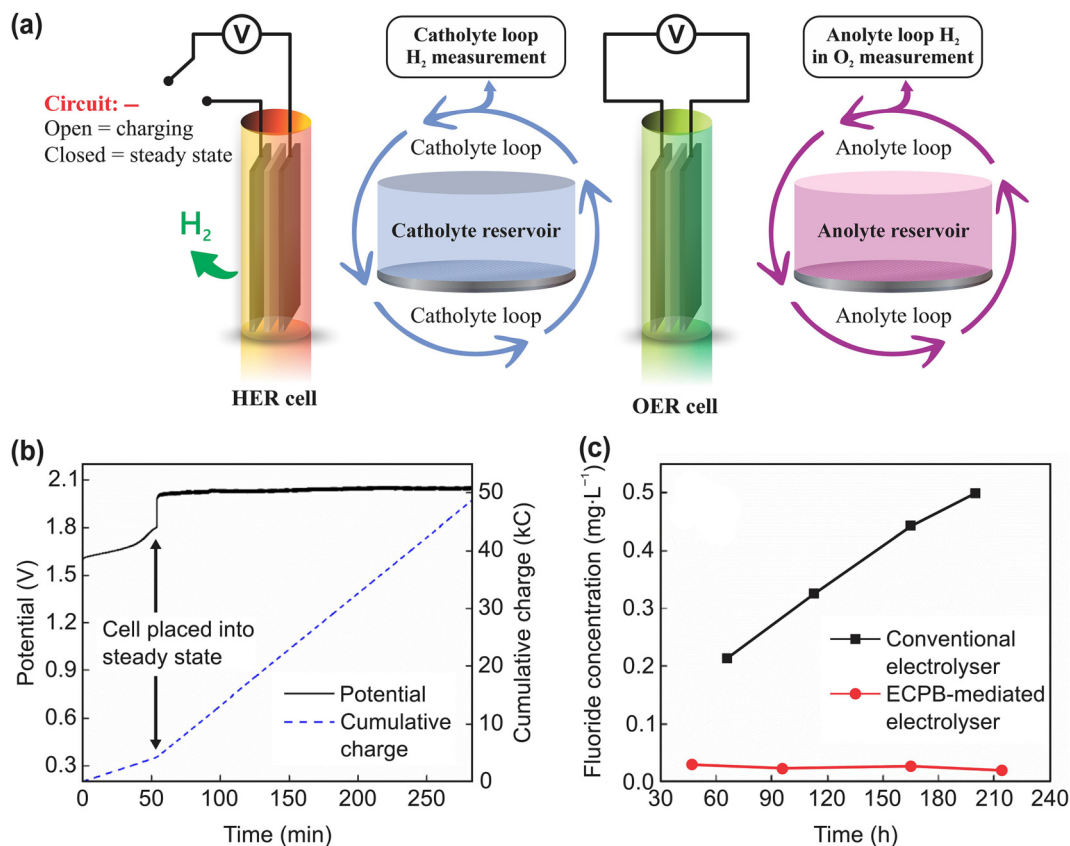


Figure 16 (a) A diagram of the device configuration utilized in this investigation. (b) Voltage–time curves. After being charged at a current density of $100\text{ mA}\cdot\text{cm}^{-2}$, the catholyte solution runs at a steady state current density of $250\text{ mA}\cdot\text{cm}^{-2}$. A total charge of 4240 C was added during the initial charging process. A further charge of 44,164 C was passed after the system was brought to a steady state (as shown by arrows). Once equilibrium was reached, the catholyte was re-oxidized, and the initial reduction of 4240 C was restored. (c) Performance comparison of ECPB-mediated electrolyzer (red) and a traditional PEM electrolyzer (black) while switching from a demineralized to a mineralized anolyte input. Reproduced with permission from Ref. [187], © The Author(s), 2019.

concentration from 0.25 to 0.4 M. This problem occurs because of ECPB depletion at the cathodic side of the OER cell. Alterations to either factor have negligible effects at lower current densities (100 and 250 mA·cm⁻²), but at 500 mA·cm⁻², 99% decoupling of ECPB is achieved at a cell voltage of 2.16 V. Experimental data show that silicotungstic acid as a redox mediator can be integrated with renewables and operated at low current densities of 25 or 50 mA·cm⁻². At a lower current density of 25 mA·cm⁻² hydrogen percentage in O₂ in conventional and ECPB electrolyzers was 1.89 (±0.02) and 0.31 (±0.07), respectively, while at 50 mA·cm⁻² hydrogen percentage in O₂ in conventional and ECPB electrolyzer was 1.47 (±0.04) and 0.31 (±0.04), respectively. It is clearly seen that the hydrogen percentage in O₂ in the ECPB electrolyzer is lower than that of the conventional PEM electrolyzer. The degradation rate of the membrane due to fluorides is lower in the ECPB membrane than in the conventional PEM electrolyzer (Fig. 16(c)).

Previously, polyoxometalates were discussed in detail and shown to be promising candidates for DWS. Phosphomolybdic acid and silicotungstic acid contribute 1–2 electron storage capacity during the reduction/oxidation process in DWS. Then, it is necessary to develop an advanced redox mediator to proceed with efficient DWS. POMs could expose the hidden properties regarding electron storage capacity. In this regard, a prosperous electronic species, up to 18 electrons, Li₆[P₂W₁₈O₆₂] was introduced. Further, Dong et al. [188] increased the performance of phosphomolybdic acid to some extent. The limit of electron transfer during the redox cycle was increased up to 4 electrons by tuning polyoxometalates H₆ZnW₁₂O₄₀ and then comparing it with well-known H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀. H₆ZnW₁₂O₄₀ acts as the best-performing molecular redox mediator to generate on-demand hydrogen. Electrochemical energy efficiency and decoupling efficiency were obtained as 83.3% and 95.5%,

respectively. Additionally, at a current density of 30 mA·cm⁻², H₆ZnW₁₂O₄₀ has a better CE of 92% and hydrogen-mediated capacity retention of 100% over 200 cycles. Keggin-type tungsten polyoxometalates, with central atom Si⁴⁺ or P⁵⁺, were replaced with heteroatoms Zn²⁺, which enhanced the reversibility and its ECPB functionality for hydrogen generation.

Cyclic voltammograms of H₆ZnW₁₂O₄₀ elaborate that its redox potential lies between -0.078 and -0.198 V vs. NHE. The storing capacity of electrons further increased to 2 in the newly introduced tuned redox mediator (Fig. 17(a)). The reversible redox cycle of H₆ZnW₁₂O₄₀ is pH dependent, whereas H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ are not. CVs of phosphomolybdic acid (H₃PW₁₂O₄₀) cannot be obtained at pH = 2.0 and 3.0 because of its instability at a pH greater than 1.5. At a current density of 5 mA·cm⁻², a CE of over 94% was attained during the reduction/reoxidation process, which proves the 4 electrons per molecule during the redox reaction. Brown solution recovered after more than 4-electron reduction, indicating some irreversible reactions occurred. Results show the hydrogen-mediated trend of H₆ZnW₁₂O₄₀ for on-demand H₂ production. Water splits to O₂ on the anode by releasing electrons and protons. These charges are reversibly stored on H₆ZnW₁₂O₄₀ instead of direct hydrogen evolution on the cathode. Reduced ECPB was then transferred to another container for on-demand H₂ production on the cathode using a suitable catalyst. At a constant potential of -0.36 V vs. NHE, the CV curve of H₆ZnW₁₂O₄₀ shows 4-electron reduction/oxidation transfer. A comparison was made between two-electron reduced H₄SiW₁₂O₄₀ and four-electron reduced H₆ZnW₁₂O₄₀ species for on-demand H₂ generation. The theoretical amount of hydrogen stored in two-electron reduced H₄SiW₁₂O₄₀ is calculated to be 44.8 mL, while it is 89.6 mL for four-electron reduced H₆ZnW₁₂O₄₀. Experimentally, 30 mL of H₂ was obtained from two-electron reduced silicotungstic acid

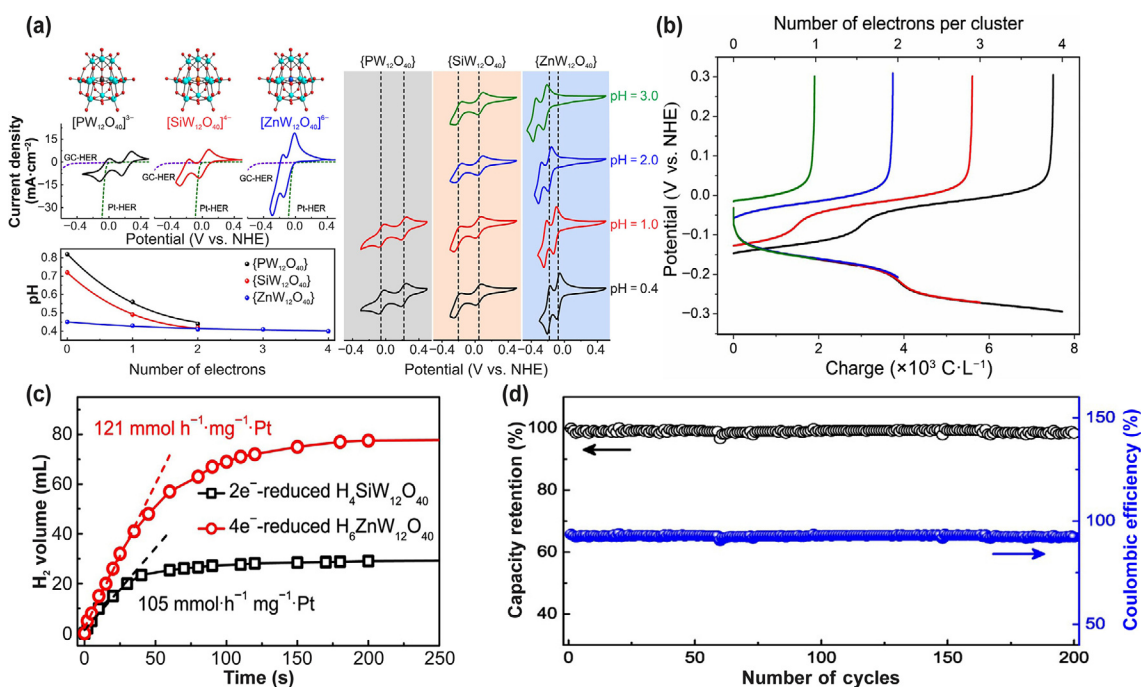


Figure 17 Tuning polyoxometalate clusters to enhance ECPB-based decoupled water splitting. (a) An example of a CV and its corresponding crystal structure of [XW₁₂O₄₀] at a scan rate of 50 mV·s⁻¹ of a 100 mM H_nXW₁₂O₄₀ (X = P⁵⁺, Si⁴⁺, and Zn²⁺) solution on a glassy carbon electrode, with a pH balance shift when reduction takes place. Right: pH-dependent CV at a scan rate of 50 mV·s⁻¹. (b) At a constant current density of 5 mA·cm⁻², various quantities of electron equivalents per cluster were used to reduce and reoxidize a 20 mM H₆ZnW₁₂O₄₀ solution. (c) H₂ evolved spontaneously from a 20 mL sample of 100 mM with 2e⁻ reduced H₄SiW₁₂O₄₀ or 4e⁻ reduced H₆ZnW₁₂O₄₀ over 5 mg 20% Pt/C. (d) A 20 mM ECPB solution was subjected to prolonged electrochemical reduction and reoxidation cycling at a current density of 30 mA·cm⁻² in an Ar atmosphere. Reproduced with permission from Ref. [188], © The Author(s), 2019.

($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) mixed with 5 mg of 20% Pt/C, representing approximately 67% of the theoretical volume (Fig. 17(b)). The first redox pair of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ occurs at a more positive potential than the onset of HER for the Pt/C catalyst, resulting in partial hydrogen release. The $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$ -mediated system theoretically releases 95.95% H_2 . The hydrogen evolution rate for the four-electron reduced $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$ is 121 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{Pt}}^{-1}$, while for the two-electron reduced species $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, it is 105 $\text{mmol}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{Pt}}^{-1}$ (Fig. 17(c)). UV-visible analysis shows the structural stability of molecular redox mediators before and after hydrogen release. The electrochemical efficiency of $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$ is 83.3%, which is higher than that of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ because of the more electrons ($4e^-$) than $2e^-$ transfer and tuned redox potentials. Due to its fruitful properties as a redox mediator, this ECPB was introduced in the flow cell system. IrO_2 as anode and carbon as cathode were applied. O_2 was generated at the anode by water oxidation, simultaneously reducing $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$. Further, the reduced $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$ with 4 electrons and protons was pumped to another compartment where it reoxidized electrochemically to produce H_2 at the cathode in the presence of a Pt/C catalyst. The reduced $\text{H}_6\text{ZnW}_{12}\text{O}_{40}$ under 200 cycles shows 100% H_2 capacity retention at a constant current density of 30 $\text{mA}\cdot\text{cm}^{-2}$ (Fig. 17(d)). Finally, it was concluded that tuning Keggin-type tungsten polyoxometalates molecular structure with heteroatoms like P^{5+} , Si^{4+} , or Zn^{2+} gives increased number of electrons with improved protonation capability and better redox potentials [188].

The original ECPB system involved the reduction of PMA followed by its reoxidation to release hydrogen, utilizing an additional electrical input. H_2 can spontaneously evolve from STA using a carbon electrode in the presence of a Pt catalyst without further energy input. This spontaneous hydrogen evolution occurs when the redox potential of the POM is more negative than the HER onset potential of the catalyst. To make the ECPB system commercially viable, cheaper and more abundant catalysts are needed. Cronin et al. [189] utilized more earth-abundant HER catalysts, i.e., Mo_2C , MoS_2 , Ni_2P , and Ni_5P_4 to decouple water

(Fig. 18(a)). Glassy carbon serves as the working electrode for the cyclic voltammetry of STA. The (*) symbol indicates the reduction potential corresponding to the second electron reduction peak of the mediator. Glassy carbon does not evolve hydrogen until potentials are more negative than -0.225 V vs. RHE of the second STA reduction peak. This demonstrates that STA can be reduced by two electrons on a carbon electrode without any competing HER (Fig. 18(b)). Additionally, phosphotungstic acid (PTA), PMA, and silicomolybdic acid (SMA) were investigated as redox mediators. PTA does not release as much hydrogen as STA because PTA has positively shifted redox peaks (redox potential voltage ($E_{1/2}$) = -0.036 and 0.237 V) compared to STA ($E_{1/2}$ = -0.195 and 0.042 V) (Figs. 18(b) and 18(c)). Lower concentrations of STA (0.1 M STA) evolve hydrogen more efficiently than higher concentrations due to mass transport limitations. A higher concentration of STA causes the active sites of the Pt catalyst saturation and decreases the reaction rate (Fig. 18(d)). Decrease in ΔG indicates a slower rate and lower volume of hydrogen evolution with PTA (~ 30 mL for STA compared to ~ 18 mL for PTA after 5 min) due to the reduced availability of two-electron. STA showed faster rates and higher hydrogen production than PTA. The rates of hydrogen produced per mass of catalyst are as follows: Ni_5P_4 (STA: 1.198 and PTA: 0.205), Mo_2C (STA: 1.006 and PTA: 0.226), MoS_2 (STA: 0.438 and PTA: 0.038), and Ni_2P (STA: 0.250 and PTA: 0.039) having unit of $\text{mmol}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$. While in terms of volume, hydrogen produced as follows: Ni_5P_4 (STA: 60.2% and PTA: 44.6%), Mo_2C (STA: 49.7% and PTA: 26.6%), MoS_2 (STA: 42.9% and PTA: 18.4%), and Ni_2P (STA: 51% and PTA: 42.9%). PMA and SMA did not spontaneously evolve hydrogen, even in the presence of a Pt catalyst. Because ΔG and the onset potential of PMA ($E_{1/2}$ = 0.57 V) and SMA ($E_{1/2}$ = 0.509 V) are more positive than that of Pt catalyst, leading to non-spontaneous hydrogen evolution (Figs. 18(e) and 18(f)).

Silicotungstic acid is regarded as a promising candidate as a soluble redox mediator (ECPB) in DWS, owing to its high solubility and reversible redox characteristics. However, noble

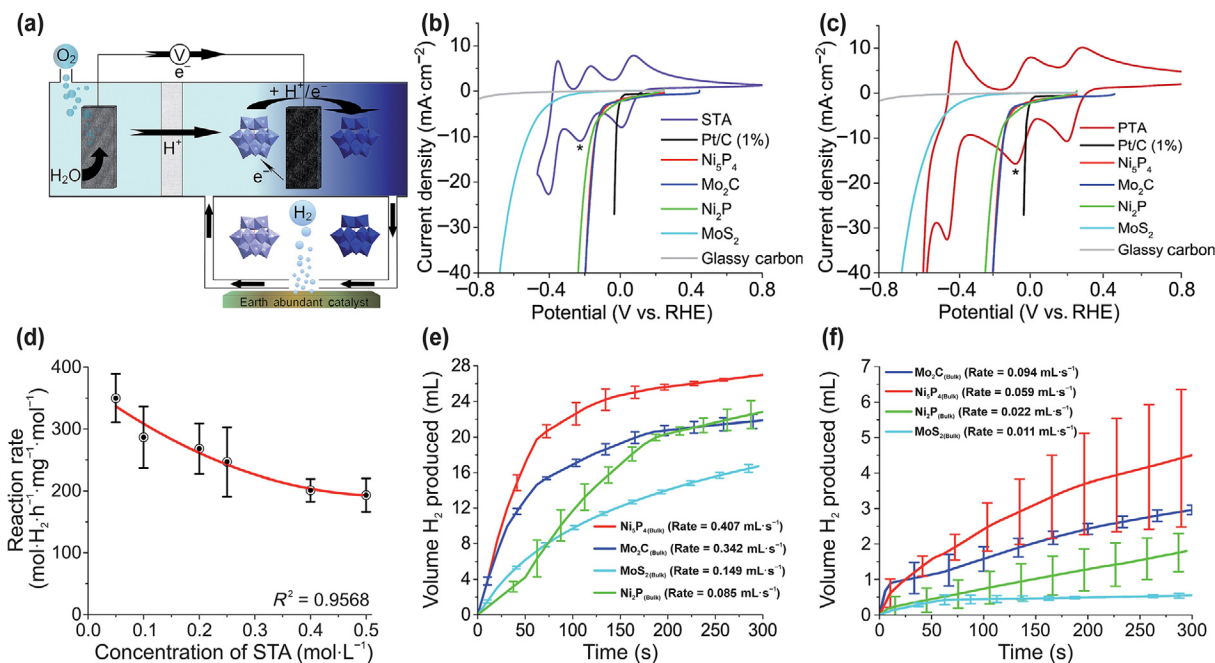


Figure 18 (a) A schematic illustration of a decoupled hydrogen evolution system using earth-abundant catalysts. LSV and CV curves of (b) STA and (c) PTA. (d) Moles of STA vs. concentration of STA for hydrogen evolution. ((e) and (f)) H_2 produced vs. time from earth-abundant catalysts with 0.1 M reduced STA and PTA. Reproduced with permission from Ref. [189], © The Royal Society of Chemistry 2017.

metal catalysts like Pt are typically used for the HER. In contrast, earth-abundant transition metal phosphides have attracted considerable interest as they offer a more sustainable alternative for splitting water into hydrogen using electrical energy, reducing the dependency on expensive noble metals [190]. Lu et al. [191] introduced nanocrystalline transition metal phosphides, specifically cobalt phosphide (CoP) and nickel phosphide (Ni_2P), as non-noble metal catalysts for the HER in silicotungstic acid. Among these, CoP demonstrated significantly higher catalytic activity compared to Ni_2P , as illustrated in (Fig. 19(a)). This highlights the potential of CoP as a more efficient and cost-effective alternative to noble metal catalysts for HER. H_2 evolution for CoP is $32 \text{ mmol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$ initially, having a turnover frequency (TOF) of 2.9 min^{-1} . Theoretically, 74.6 mL (3.3 mmol) of H_2 should be produced, as the two-electron-reduced silicotungstic acid can provide 6.7 mmol of electrons for hydrogen evolution. However, the authors obtained only half of this amount (37 mL). This discrepancy is attributed to the low reducing ability of one-electron-reduced silicotungstic acid ($\text{H}_5\text{SiW}_{12}\text{O}_{40}/\text{H}_4\text{SiW}_{12}\text{O}_{40} = 0.01 \text{ V vs. RHE}$). Notably, the CoP sample exhibited catalytic activity comparable to that of the commercial Pt/C catalyst. The CoP catalyst was directly added to one compartment of a two-compartment H-cell containing one-electron-reduced $\text{H}_5\text{SiW}_{12}\text{O}_{40}$. Then, a potential of 8.3 V across the working electrodes was applied. H_2 and O_2 evolved continuously at a molar ratio of 2:1 (H_2 : $\sim 49 \text{ mL} \cdot \text{h}^{-1}$ and O_2 : $\sim 23 \text{ mL} \cdot \text{h}^{-1}$), closely matching the theoretical value of 2 for the overall water splitting. After 12 h of working, the system still has 100% FE, which shows good stability of the catalyst (Fig. 19(b)). $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ is reduced first to $\text{H}_5\text{SiW}_{12}\text{O}_{40}$, and then the introduction of the CoP catalyst generates $48 \text{ mL} \cdot \text{h}^{-1}$ hydrogen. Theoretically, only half of the hydrogen can be produced without electrolyte and redox mediator. The η_{10} (overpotentials required to achieve a current

density of $10 \text{ mA} \cdot \text{cm}^{-2}$) for the samples are 28 mV for Pt/C, 65 mV for CoP, and 150 mV for Ni_2P . At a current density of $100 \text{ mA} \cdot \text{cm}^{-2}$, the CoP sample exhibits a high cathodic current in the range of 0.1 to 0.2 V vs. RHE , requiring only 130 mV , which is lower than that of 200 mV needed for the Pt/C catalyst (Fig. 19(c)). Polarization curves measured before and after 50 cycles at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ for the CoP sample demonstrate the excellent stability of the CoP for HER in acidic water electrolysis (Fig. 19(d)). Finally, it is observed that the CoP sample displayed significantly higher catalytic activity ($32 \text{ mmol} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$) compared to the Ni_2P sample and commercial Pt/C.

Alkaline water electrolysis is viable for large-scale hydrogen production using noble-metal-free electrocatalysts. Lu et al. [192] introduced a decoupled electrolysis system, utilizing a bipolar membrane (BPM) specifically designed for alkaline water electrolysis, with phosphomolybdic acid serving as an electron-coupled proton buffer. Phosphomolybdic acid also exhibits significant six-electron redox activity, which enhances both the energy and capacity density of the system. Bipolar membranes, which have been commercially available since the late 1980s, are widely used in fuel cell applications, further demonstrating their versatility and efficiency in energy conversion processes [193–195]. These bipolar membranes consist of an anion-exchange layer, a cation-exchange layer, and a hydrophilic interface. During the OER, hydroxide ions (OH^-) are oxidized at the anode, producing oxygen and water. Concurrently, the hydrophilic interface facilitates the splitting of water molecules into hydrogen (H^+) and hydroxide (OH^-) ions. The OH^- ions migrate to the anode through the anion-exchange layer, while the H^+ ions pass through the cation-exchange layer towards the cathode, where the ECPB phosphomolybdic acid is reversibly reduced and protonated by these H^+ ions and electrons. During

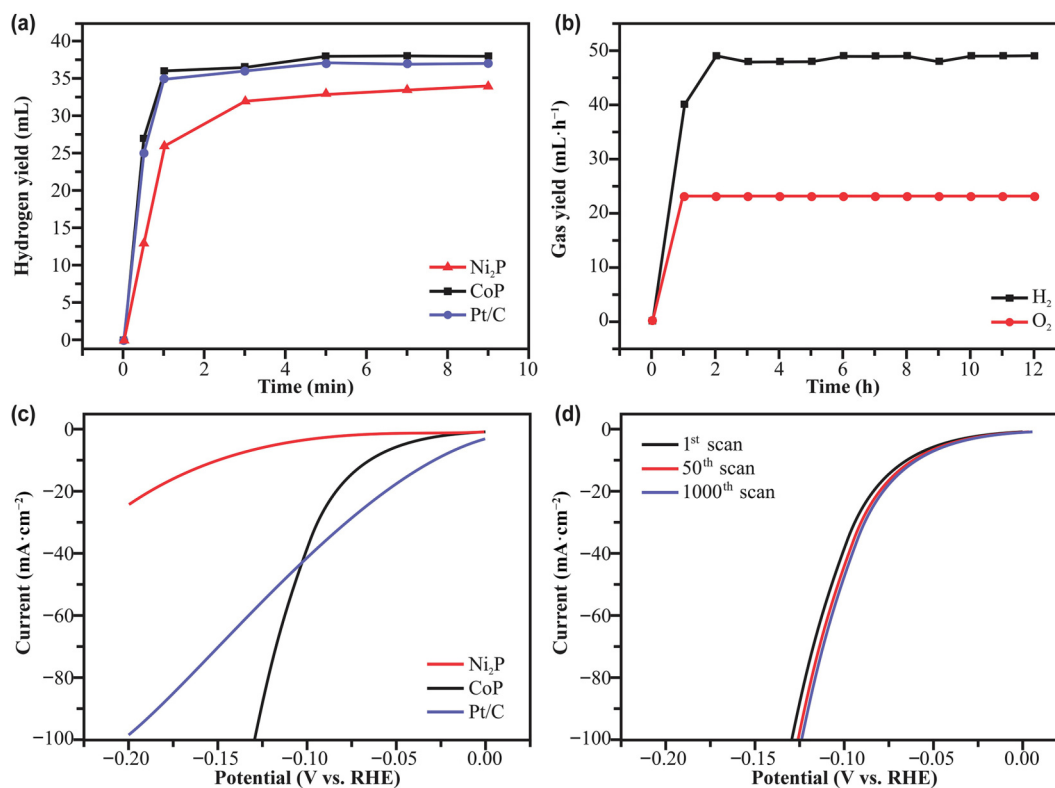


Figure 19 (a) H_2 production vs. reaction time for catalysts. (b) H_2 and O_2 production for the CoP catalyst. (c) Polarization curves of all catalysts. (d) Polarization curves for the CoP catalyst before and after 1000 cycles. Reproduced with permission from Ref. [191], © The Royal Society of Chemistry 2018.

reduction, golden phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) is converted into blue phosphomolybdic acid ($\text{H}_5\text{PMo}_{12}\text{O}_{40}$). In the reverse process, during the HER, the reduced phosphomolybdic acid is reoxidized at the anode, while water is reduced to H_2 at the cathode. The generated H^+ and OH^- ions traverse their respective exchange layers and neutralize at the hydrophilic interface to form H_2O . The reduction of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ to $\text{H}_5\text{PMo}_{12}\text{O}_{40}$ occurs at approximately 0.35 V vs. Ag/AgCl at a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$. During this process, OH^- ions are oxidized to form O_2 and H_2O at the anode. As the current density increases, the reduction potential becomes more negative, reaching about 0.05 V vs. Ag/AgCl at $150 \text{ mA}\cdot\text{cm}^{-2}$. These reduction potentials exceed the hydrogen evolution potential ($E(\text{H}^+/\text{H}_2) = -0.23 \text{ V}$ vs. Ag/AgCl), thereby preventing hydrogen production during water oxidation. Additionally, the reoxidation of reduced phosphomolybdic acid occurs at potentials between 0.60 and 0.85 V vs. Ag/AgCl, with current densities ranging from 50 to $150 \text{ mA}\cdot\text{cm}^{-2}$. The oxygen evolution potential ($E(\text{O}_2/\text{H}_2\text{O})$) is approximately 1.0 V vs. Ag/AgCl. Chronopotentiometric measurements show stable cycles at $100 \text{ mA}\cdot\text{cm}^{-2}$, with no significant changes. While $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is an attractive candidate, its capacity is typically limited to two electrons per molecule. Despite the instability of the 6e-reduced $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, which transforms into a heteropolyacid in solution, this heteropolyacid can be reoxidized back to the 2e-reduced phosphomolybdic acid, facilitating the process of alkaline water electrolysis mediated by phosphomolybdic acid. H-type electrolytic cell filled with 30 mL of 1.5 M NaOH solution, while the other, containing 30 mL of 0.5 M phosphomolybdic acid in water, was used. The voltages for OER and HER at $100 \text{ mA}\cdot\text{cm}^{-2}$ were 2.78 and 2.39 V, respectively, using a Pt mesh as the catalyst. GC analysis indicates that O_2 (1.2%) and H_2 (2.5%) evolution occurred in a 1:2 ratio. NiFe layered double hydroxide (LDH)/Ni foam and Ni_3S_2 /Ni foam were employed as OER and HER catalysts, respectively. The voltage for the bulk Ni

foam was measured at 1.78 V at $50 \text{ mA}\cdot\text{cm}^{-2}$. NiFe LDH on Ni foam reduced the OER voltage to 1.40 V, significantly lower than Pt mesh (2.33 V) and commercial IrO_2 (1.78 V). Ni_3S_2 on Ni foam also slightly decreased the voltage for HER. However, the electrolytic voltage remained relatively low (1.67 V) when Ni_3S_2 /Ni foam was used as the HER catalyst, replacing the Pt mesh. Moreover, NiFe LDH/Ni foam and Ni_3S_2 /Ni foam demonstrated good stability, confirming their activity as effective OER and HER electrocatalysts. These results highlight the potential of earth-abundant, noble-metal-free electrocatalysts for efficient energy conversion in electrolysis systems.

Conventional polymer electrolyte membrane (PEM) electrolyzers face significant challenges, particularly when operated with intermittent energy sources. Gas crossover can lead to inefficiencies, especially under fluctuating energy conditions, and the high cost of electricity continues to impede large-scale deployment. One issue with PEM electrolyzers powered by renewable energy sources is the production of explosive gas mixtures due to unsustainable levels of gas crossover between oxygen and hydrogen, resulting in hazardous conditions. To address these challenges, different types of decoupled systems were proposed by many scientists [171, 179, 180, 196–200]. Ce-mediated decoupled electrolysis system has been developed by Modestino et al. [201] to produce hydrogen and store energy in redox couples. The system consists of two distinct subcells: a charging subcell dedicated to the HER and a discharging subcell for the OER, both interconnected by a Ce(III)/Ce(IV) redox shuttle (Fig. 20(a)). This setup allows for efficient separation and coordination of the two reactions, facilitating controlled energy storage and release during the water splitting process. In the charging subcell, cerium undergoes a redox reaction as Ce^{3+} is oxidized to Ce^{4+} at the anode ($E^0 = 1.6 \text{ V}$ vs. SHE), while water is split into protons (H^+) and oxygen at the anode ($E^0 = 1.23 \text{ V}$ vs. SHE). The cathode facilitates HER, producing H_2 ($E^0 = 0 \text{ V}$ vs.

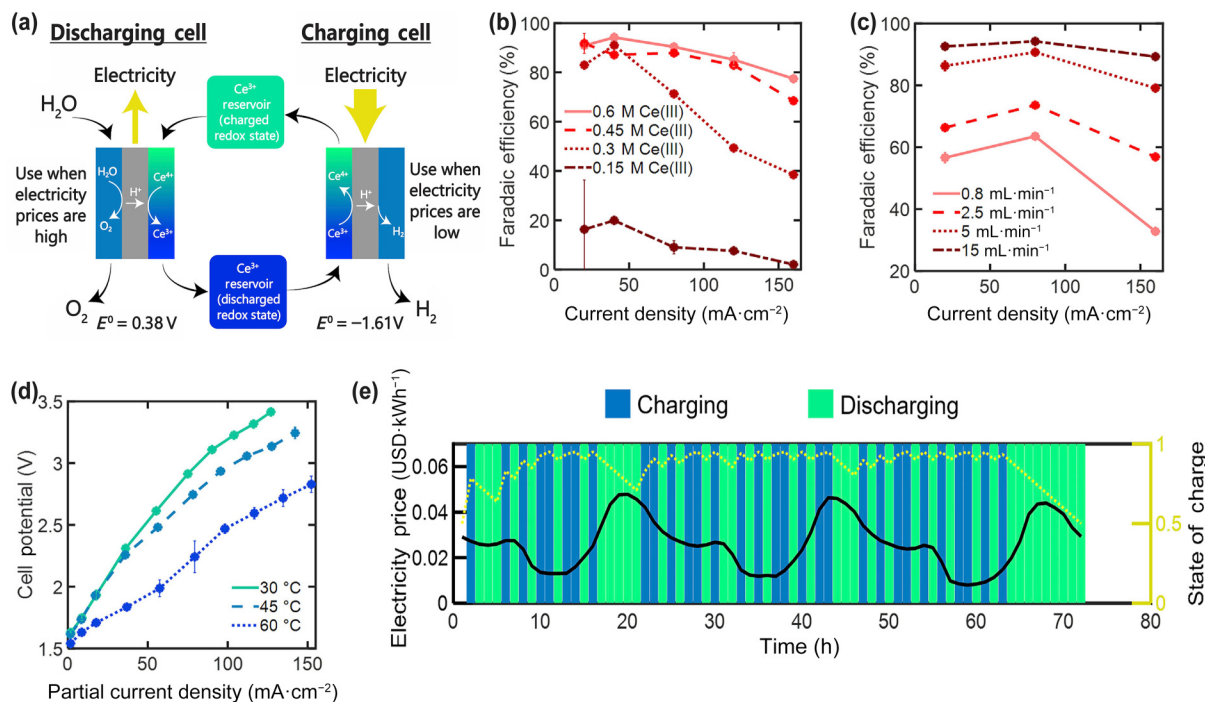


Figure 20 (a) Ce-mediated decoupled hydrogen production during discharging and charging of a redox flow cell. (b) Faradaic efficiency for Ce(IV) vs. charging current density at various concentrations. (c) Faradaic efficiency for Ce(IV) vs. charging current density at various flow rates. (d) Cell potential vs. partial current density for Ce(III) oxidation at various flow rates in terms of different temperatures. (e) Grid-scale illustration of charging and discharging operation schedule using the high solar renewable energy source. Reproduced with permission from Ref. [201], © The Author(s), 2020.

SHE), with an overall cell potential of 1.6 V. In the discharging subcell, the reverse reaction takes place. At the anode, water is oxidized to oxygen and protons, and at the cathode, Ce^{4+} is reduced to Ce^{3+} ($E^\circ = 1.6 \text{ V vs. SHE}$), with an overall cell potential of 0.37 V. This configuration allows for H_2 generation during charging and O_2 production during discharging, creating an efficient energy storage and decoupled H_2 production system. This Ce-mediated system optimizes energy storage and hydrogen production, making it a promising solution for addressing the issues with PEM electrolyzers, especially when used with renewable energy sources. The use of Pt as an electrode for Ce oxidation and reduction is common due to its high activity, though it risks unwanted oxygen evolution during charging. Nevertheless, Pt mesh was used for Ce redox reactions in this study, with Pt/C and Ir/C catalysts employed for HER and OER, respectively. RFBs have also gained attention due to their long cycle life and high round-trip efficiency ($\sim 85\%$). However, their high cost and lower energy density remain obstacles to wide-scale adoption. During the operation of the cerium-mediated decoupled electrolysis system, the Ce(III) concentration in the charging subcell decreases dynamically, influencing overpotential and FE. The overpotential represents the excess voltage required beyond the theoretical cell potential to achieve a specific current density. As the concentration of Ce(III) decreases, the mass transport of Ce ions slows, leading to an increase in the OER and a lower FE for Ce oxidation (Fig. 20(b)). This becomes evident when Ce(III) concentration drops from 0.3 to 0.15 M, causing the FE to decrease by at least 75% across all current densities as OER becomes dominant.

In experiments, the highest accessible Ce(III) concentration was 0.6 M in 4 M MSA, given the limited solubility of the redox ions in aqueous electrolytes. This limitation impacts the system efficiency due to the mass transport restrictions of redox ions to the anode surface. Increasing the electrolyte flow rates enhances convective mass transfer, reducing the diffusion boundary layer and improving the flux of Ce ions to the electrode (Fig. 20(c)). As a result, increasing the flow rate positively impacts FE and partial current densities for Ce oxidation in the charging subcell. However, mass transport effects are less significant in the discharging subcell, where current densities remain low, and transport processes do not significantly hinder the Ce(IV) reduction reaction. Thermal effects also play a critical role in enhancing electrochemical performance. Higher temperatures lead to improved mass transport and lower reaction overpotentials. For instance, at 60°C , the highest power density achieved during discharge was $1.5 \text{ mW}\cdot\text{cm}^{-2}$, marking a 400% improvement compared to room temperature performance (Fig. 20(d)). These improvements in power density, mass transport, and FE suggest that the reduction reaction of Ce(IV) is kinetically limited and can be further optimized through enhanced electrocatalysis. The optimization model showed that state-of-charge (SOC) plays a key role in the system operation. At higher SOC, FE decreases as OER becomes more significant, reducing the Ce(III) oxidation rate. This allows for longer charging periods, generating more H_2 before reaching the SOC limit. However, during high electricity prices, the system discharges to generate power instead of H_2 , balancing energy production with economic factors (Fig. 20(e)). Despite the small effect of electricity price variability on H_2 production costs, the study suggests that reducing overpotential, increasing current densities, and lowering stack costs can make the Ce-mediated system competitive with state-of-the-art PEM electrolyzers. This analysis highlights the

importance of further research and development (R&D) in reducing capital costs, improving power density, and enhancing overall energy conversion efficiency in decoupled electrolysis systems. While increased renewable energy penetration reduces the electricity cost component of hydrogen production in spatiotemporally decoupled water electrolysis systems, the overall economic viability remains constrained by high capital costs, particularly for dual-stack architectures like Ce-mediated electrolysis. These systems currently exhibit lower power density and efficiency compared to conventional PEM electrolyzers, necessitating larger stacks and greater energy input for equivalent hydrogen output. However, targeted R&D could address these limitations: A 50% reduction in overpotential (e.g., from 800 to 400 mV) would lower electricity costs by 18%, while doubling current density at fixed voltage could reduce capital costs by 46.5% through enhanced hydrogen production rates. Further capital cost reductions achievable via advanced manufacturing techniques, flow field-free bipolar plates, or scaled production of high-surface-area electrodes would amplify the economic benefits of temporal energy arbitrage by enabling extended operation during low-price periods. For instance, a 50% decrease in stack costs, combined with improved redox mediators (e.g., higher oxidation potentials), could render decoupled systems cost-competitive with PEM electrolysis. Beyond direct hydrogen production, ancillary services, such as grid flexibility, frequency regulation, or seasonal energy storage, could diversify revenue streams, though their economic value remains uncertain due to limited real-world deployment. Ultimately, achieving cost parity requires prioritizing R&D in three areas: (1) enhancing energy conversion efficiency through overpotential minimization and current density optimization, (2) reducing stack costs via material innovations and manufacturing scalability, and (3) integrating hybrid operational modes that leverage both energy markets and grid-support services. These advancements would position decoupled electrolysis as a versatile, economically viable pathway for low-carbon hydrogen production in renewable-dominated energy systems.

Choi et al. [202] developed an asymmetric cell for DWS consisting of a $3 \text{ M H}_2\text{SO}_4 | \text{V(II)/V(III)} | 1 \text{ M KOH}$ configuration with nickel foam electrodes. The process is split into two stages, utilizing vanadium ions as redox mediators. This system achieves water splitting at an average cell voltage of 1.3 V with a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, even when using anion exchange membranes, and demonstrates excellent cycling stability. The combination of an acid/alkaline dual electrolyte and the V(II)/V(III) redox mediator optimizes the cell thermodynamic potential for efficient water electrolysis. The process involves two interconnected half-reactions HER at the cathode and OER at the anode, which theoretically occur at 1.23 V. HER is kinetically favored in acidic electrolytes due to the lower overpotential required for hydrogen production. In contrast, OER occurs rapidly in alkaline solutions. For decoupled electrolysis using a redox mediator, the mediator redox potential must lie between the onset potentials of OER and HER. Notably, although the V(II)/V(III) redox potential (-0.255 V vs. SHE) is slightly negative compared to HER onset potential (0 V vs. SHE), membrane resistance (iR_m drop of 0.198 V) and internal resistance (iR_s) cause the HER onset potential to shift further into the negative, satisfying the conditions for decoupled electrolysis. In Step 1, hydrogen is produced by the oxidation of V(II) to V(III) in 3 M H_2SO_4 , as shown: $2\text{V}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{V}^{3+}(\text{aq}) + \text{H}_2(\text{g})$. In Step 2, OER occurs in 1 M KOH, where V(III) is reduced back to V(II) : $4\text{V}^{3+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{V}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$. Nickel foam

electrodes provide catalytic sites for HER and OER, while carbon felt stabilizes the V(II)/V(III) redox reactions. AEM prevents vanadium cation crossover. During hydrogen generation at $10 \text{ mA}\cdot\text{cm}^{-2}$ for 50 min, V(II) is oxidized at the nickel foam cathode in the $3 \text{ M H}_2\text{SO}_4$ electrolyte ($\text{pH} = 0$). The mode is then switched to oxygen generation at the Ni foam anode in 1 M KOH ($\text{pH} = 14$), where V(III) is reduced to V(II) under the same current density. The HER and OER potentials range from 0 to 0.2 and -1.1 to -1.3 V , respectively, demonstrating stable cycling without degradation. The average cell voltage remains 1.3 V , comparable to the theoretical 1.23 V for conventional water electrolysis. The cell operates stably for 100 h, with electrolyte replacements every 20 h to prevent pH variation and nickel electrode dissolution. After 100 h, the cathode potential required for HER increases by 124 mV , while the anode potential for OER rises by only 7 mV . The performance decay during HER is attributed to slight nickel dissolution at grain boundaries in the acidic electrolyte. In contrast, the Ni electrode used for OER shows low dissolution and is slightly activated by the KOH electrolyte, which forms a Ni oxide or hydroxide layer. This porous structure enhances the electrode's stability and activity for OER, as confirmed by surface analysis.

Chen et al. [203] designed a DWE system that integrates a proton exchange membrane electrolyzer cell (PEMEC) for the generation of high-pressure H_2 and an H-cell for the generation of low-pressure O_2 . This configuration allows for the independent production of hydrogen and oxygen at different pressures, optimizing the process for energy efficiency and storage while maintaining the benefits of DWS. The system employs an electrolyte containing the $\text{VO}_2^+/\text{VO}^{2+}$ redox couple as the redox mediator (Fig. 21(a)). The DWE system enables H_2 production at a pressure of 35 MPa without mixing with O_2 . Crossover rate (r_c) increases with pressure and decreases with lower current densities, reaching approximately $1 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ at 35 MPa . The solution, containing H^+ and the $\text{VO}_2^+/\text{VO}^{2+}$ redox couple, serves as the mediator electrolyte. In Step 1 of H_2 generation, the VO^{2+} oxidation reaction (VOR) and HER are conducted in a high-

pressure PEMEC (HP-PEMEC) with a continuous flow of the $\text{VO}_2^+/\text{VO}^{2+}$ redox mediator electrolyte (VRME), driven by a pump. The generated H_2 is confined in the cathode, increasing the gas pressure. In Step 2, for O_2 generation, an H-cell consisting of an OER cell and a VO_2^+ reduction reaction (VRR) cell is used. The OER occurs on an IrO_2 -coated Ti-mesh electrode, while the VRR occurs on a carbon-felt electrode. These two steps can be performed simultaneously due to the separated electrodes for the VRR and VOR. The electrochemical performance of the VRME (a solution of $1.5 \text{ M H}_2\text{SO}_4$ and $2 \text{ M VO}_2\text{SO}_4$) was first tested in a three-electrode system. Before conducting electrochemical tests, chronopotentiometry for HER and VOR was performed for 3000 s at a current of 50 mA , producing a proper concentration of VO_2^+ (approximately 13 mM) in the VRME, ensuring stable potential curves for subsequent VRR experiments. CV confirmed that the redox peaks of the $\text{VO}_2^+/\text{VO}^{2+}$ couple were located around $0.78/1.37 \text{ V}$ vs. RHE.

The LSV curves of the HER and OER in $1.5 \text{ M H}_2\text{SO}_4$ indicated that the redox potential window, located between the HER onset potential (-37 mV vs. RHE) and the OER onset potential (1.45 V vs. RHE), suggested that the VRME is feasible for use in the DWE system (Fig. 21(b)). Chronopotentiometry measurements were carried out in the H-cell at varying currents. The average cell voltages for Steps 1 and 2 were 1.24 and 0.76 V at a current of 5 mA , increasing to 1.47 and 1.43 V , respectively, when the current was raised to 50 mA (Fig. 21(c)). GC analysis at 20 MPa revealed a distinct hydrogen peak, which increased further when the cathodic pressure was raised to 35 MPa . Importantly, no oxygen peaks were detected, indicating that OER, a common side reaction during the VOR, did not occur. During Step 2, O_2 peaks were detected as expected in the OER cell (Fig. 21(d)). The cell voltage in Step 2 displayed a more significant variation than in Step 1 at higher currents, which might be attributed to differences in reaction kinetics. In Step 1, the cell voltage decreased by approximately 100 mV as the concentration of VO_2SO_4 increased from 0.01 to 2 M , indicating that increasing the concentration of the VRME enhances efficiency. Conversely, when the VO_2^+

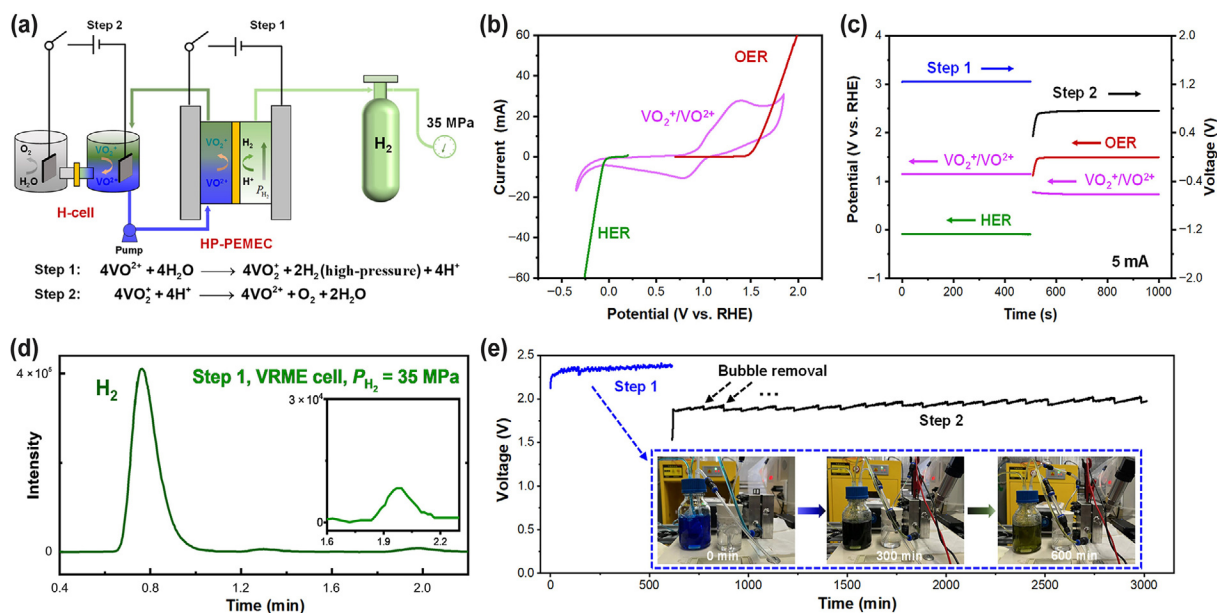


Figure 21 (a) Schematic illustration of the high-pressure DWE system. (b) CV and LSV curves of the $\text{VO}_2^+/\text{VO}^{2+}$, Pt, IrO_2 -coated Ti-mesh electrode at scan rate $10 \text{ mV}\cdot\text{s}^{-1}$ in $1.5 \text{ M H}_2\text{SO}_4$. (c) Potential vs. time curves of the WE/CE and cell voltage-time curves of Steps 1 and 2 at 5 mA . (d) GC results of the gas extracted from the VRME tank at cathodic pressures of 35 MPa in Step 1, and the headspace of the OER cell in Step 2. (e) Voltage vs. time curves of Steps 1 and 2, and the inset is the color change of the VRME during Step 1. Reproduced with permission from Ref. [203], © American Chemical Society 2023.

concentration was reduced from 0.75 to 0.0625 M, the cell voltage in Step 2 increased slightly from 1.85 to 1.94 V, suggesting that lower VO_2^+ concentrations in the VRME during electrochemical tests lead to higher cell voltages for Step 2. The voltage efficiencies are 61% and 42% for a current of 5 and 50 mA, respectively. The FE for hydrogen production decreased from 92.1% to 70.5% as cathodic pressure increased. The voltage–time curve for Step 1 indicated an increase of 130 mV (from 2.25 V at 30 min to 2.38 V at 620 min) as the cathodic pressure increased, which is slightly higher than the theoretical increment of 117.5 mV. The color of the VRME changed significantly during the VOR, from blue (VO^{2+}) to green (VO_2^+), demonstrating the conversion process (Fig. 21(e)). The newly designed DWE system, using the flowed VRME as a mediator, successfully achieved decoupled H_2 generation at 35 MPa and O_2 generation at atmospheric pressure, without H_2 – O_2 mixing.

Lu et al. [204] reported an aqueous Zn–phosphomolybdc acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) battery that simultaneously generates reduced phosphomolybdc acid and electricity (Fig. 22(a)). This Zn–phosphomolybdc acid battery exhibits an open circuit voltage (OCV) of approximately 1.50 V, with a high CE (> 90%). The reduced phosphomolybdc acid also functions as an active electron-coupled proton buffer, enabling efficient, decoupled hydrogen production from alkaline water electrolysis. This process is facilitated by ultrafine platinum nanoparticles (~ 2.0 nm) dispersed on nickel-cobalt hydroxide nanosheets, with a low Pt loading (0.4 mg-cm⁻²) on a free-standing electrode. Transition metal compounds (such as manganese, vanadium, and lead), halogens, and organic compounds (such as polyaniline (PANI), polyacrylamide, and quinone) have been previously reported as cathodes for aqueous zinc-ion batteries [205–214]. Excellent solubility and multi-electron redox capabilities of heteropolyacids

in water offer advantages in capacity densities in aqueous zinc-ion batteries. Consequently, heteropolyacids are promising candidates for cathode materials in these batteries. The electrocatalytic activity of the free-standing Pt-based electrocatalyst for HER was evaluated in 1 M NaOH. LSV curves show that Pt–Ni/Co–Ni foam samples demonstrated superior current density compared to commercial Pt mesh, Ni foam, and Ni/Co–Ni foam samples. Specifically, the Pt–Ni/Co–Ni foam achieved a current density of 100 mA-cm⁻² at an overpotential of 105 mV, which is significantly lower than the values for commercial Pt mesh (315 mV), Ni foam (370 mV), and Ni/Co–Ni foam (325 mV) (Fig. 22(b)). Additionally, the Pt–Ni/Co–Ni foam functions as an effective HER electrode as compared to commercial Pt/C catalyst. A long-term stability test at a current density of 50 mA-cm⁻² of the Pt–Ni/Co–Ni foam shows that no significant changes were observed in HER potential curves over 20 h. Additionally, post-experiment morphological analysis revealed no substantial variations, confirming the sample's excellent stability as a porous electrode for HER. The decoupled electrolysis system also demonstrates high efficiency and stability over multiple oxygen and hydrogen evolution cycles (Fig. 22(c)). GC analysis measured the evolved O_2 and H_2 gases, with volume contents of 1.3% and 2.5%, respectively, indicating near-stoichiometric evolution of O_2 and H_2 in a 1:2 ratio. Cycling performance of the Zn–phosphomolybdc acid battery during discharging and decoupled H_2 production from alkaline water electrolysis at a current density of 20 mA-cm⁻² over 60 h of operation, the average discharge voltage of the battery was approximately 0.85 V, enabling the simultaneous production of reduced phosphomolybdc acid and electricity (Fig. 22(d)). The electrolytic voltage for HER remained low (~ 1.0 V) when using the free-standing Pt-based electrode for alkaline water electrolysis. The

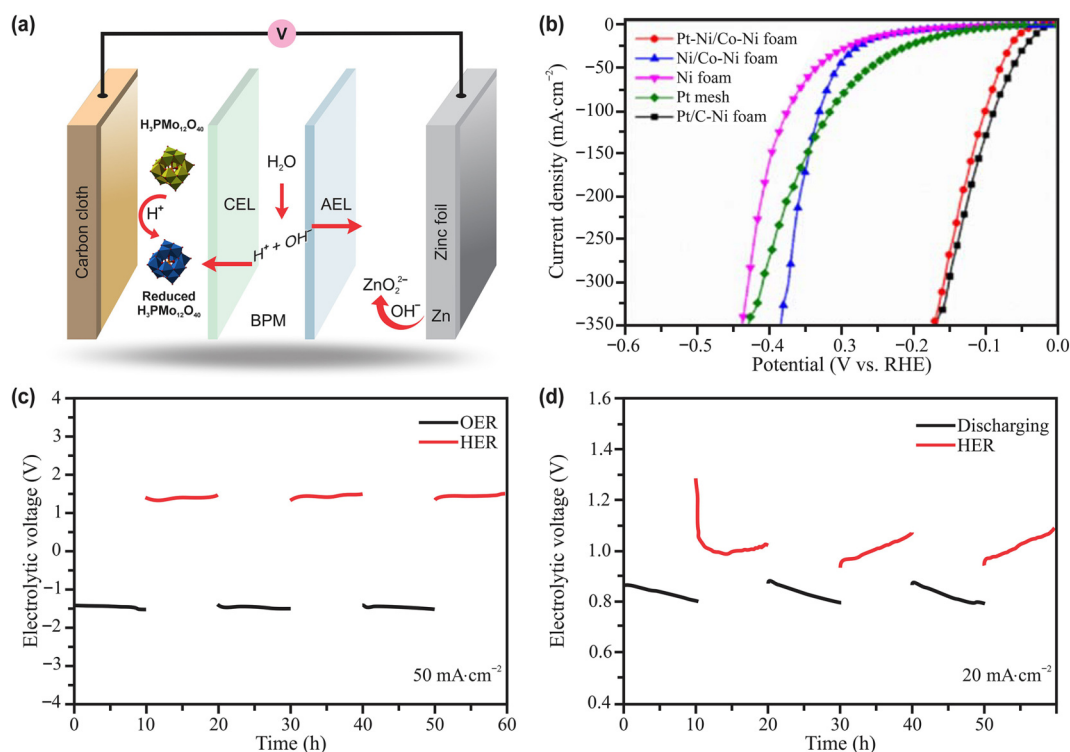


Figure 22 (a) A conceptual diagram depicting the aqueous Zn–phosphomolybdc acid battery. (b) Polarization curves of the fabricated electrodes in 1 M NaOH aqueous solution. (c) Electrolytic voltage–time curves for decoupled alkaline water electrolysis using phosphomolybdc acid (0.5 M) as an electron-coupled proton buffer. (d) Cycles of discharge for the Zn–phosphomolybdc acid battery and decoupled hydrogen production from alkaline water electrolysis at a current density of 20 mA-cm⁻², with phosphomolybdc acid pre-reduced for 2 h. Reproduced with permission from Ref. [204], © The Royal Society of Chemistry 2024

Zn-polyoxometalate battery, with an open circuit voltage of about 1.50 V, effectively replaces the OER with the generation of reduced phosphomolybdic acid and electricity. The battery maintained a high CE (> 90%) and demonstrated strong stability throughout the process.

High efficiency has been achieved in batch processes involving thermal swings, though they encounter substantial operational challenges. Rothschild et al. [215] demonstrated a system with high Faradaic and electrolytic efficiency alongside high-rate operation in a near-neutral NaBr electrolyte. In this system, bromide ions (Br^-) are electro-oxidized to bromate (BrO_3^-) while hydrogen is evolved in one cell. In another cell, bromate is chemically reduced back to bromide, catalytically producing oxygen (Fig. 23(a)). Instead of using a nickel (oxy)hydroxide anode, this study proposes the use of a solid redox couple (SRC), which enables continuous operation in an isothermal process with high efficiency and a fast reaction rate. In this system, the reduced form of the SRC undergoes electrochemical oxidation ($\text{red} \rightarrow \text{ox} + n\text{e}^-$, where n represents the number of electrons) to support hydrogen evolution without generating oxygen or other volatile byproducts. In the presence of a suitable catalyst, the oxidized form (ox) spontaneously evolves oxygen in a chemical reaction that regenerates the reduced state ($\text{ox} \rightarrow \text{red} + \text{O}_2$). The bromide (Br^-)/bromate (BrO_3^-) redox couple, with a standard reduction potential of 1.42 V vs. the reversible hydrogen electrode (RHE), was selected due to its high solubility in water, 946 $\text{g}\cdot\text{L}^{-1}$ for NaBr and 394 $\text{g}\cdot\text{L}^{-1}$ for NaBrO_3 at 25 °C. This combination facilitates a high-efficiency, high-rate water splitting process with reduced operational difficulties. Bromine (Br_2), produced at the anode, has a high density (3.1 $\text{g}\cdot\text{cm}^{-3}$) and good solubility in water (34 $\text{g}\cdot\text{L}^{-1}$ at 25 °C), which minimizes the risk of evaporation. This makes the $\text{Br}^-/\text{BrO}_3^-$ redox couple more favorable than the $\text{Cl}^-/\text{ClO}_3^-$ couple, as the latter generates volatile chlorine (Cl_2), which has low

solubility (6.3 $\text{mg}\cdot\text{L}^{-1}$ at 25 °C), leading to significant Faradaic losses. The overall reactions involved are: at the cathode: ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) and at the anode: ($2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$). The catalytic cell comprises a column filled with a catalyst that facilitates the decomposition of bromate (BrO_3^-) into bromide (Br^-) and oxygen, as described by the reaction ($2\text{BrO}_3^- \rightarrow 2\text{Br}^- + 3\text{O}_2$). Two operational modes for the electrolytic process were examined. The first mode involved bromate electrolysis in a 1.5 M NaBr aqueous electrolyte with the addition of 3.8 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, heated to 60 °C, and stirred continuously. In this mode, the FE was $98\% \pm 2\%$, effectively suppressing side reactions, such as the OER. The absence of OER during bromide electrolysis, as confirmed using a Hoffman apparatus, indicated no oxygen evolution at the cathode. In the second mode, electrolysis was conducted without $\text{Na}_2\text{Cr}_2\text{O}_7$ at room temperature and without stirring. The FE in this mode dropped to $10\% \pm 1\%$, highlighting the critical role of $\text{Na}_2\text{Cr}_2\text{O}_7$ in preventing side reactions, likely by forming a protective polyoxide barrier on the cathode. When operating in this mode (Fig. 23(d)), without $\text{Na}_2\text{Cr}_2\text{O}_7$, the FE was $72\% \pm 2\%$ without stirring but declined to $13\% \pm 1\%$ with stirring, demonstrating the effectiveness of spontaneous phase separation in reducing cathodic losses. Additionally, a precoated cathode with $\text{Na}_2\text{Cr}_2\text{O}_7$ yielded a FE of $80\% \pm 2\%$ in subsequent tests conducted without $\text{Na}_2\text{Cr}_2\text{O}_7$. However, the first mode, involving $\text{Na}_2\text{Cr}_2\text{O}_7$ and heat, achieved the highest FE, reaching $98\% \pm 2\%$. These measurements were conducted using two-electrode galvanostatic voltammetry at current densities ranging from 5 to 1000 $\text{mA}\cdot\text{cm}^{-2}$, both with and without the addition of a borate buffer. The results demonstrated complete conversion (100%) of the electrolytically generated bromate to bromide and oxygen within approximately 3 h, confirming a full cycle of hydrogen evolution and the electro-oxidation of bromide to bromate in the electrolytic cell with nearly 100% FE. Following this, bromate was fully converted back to

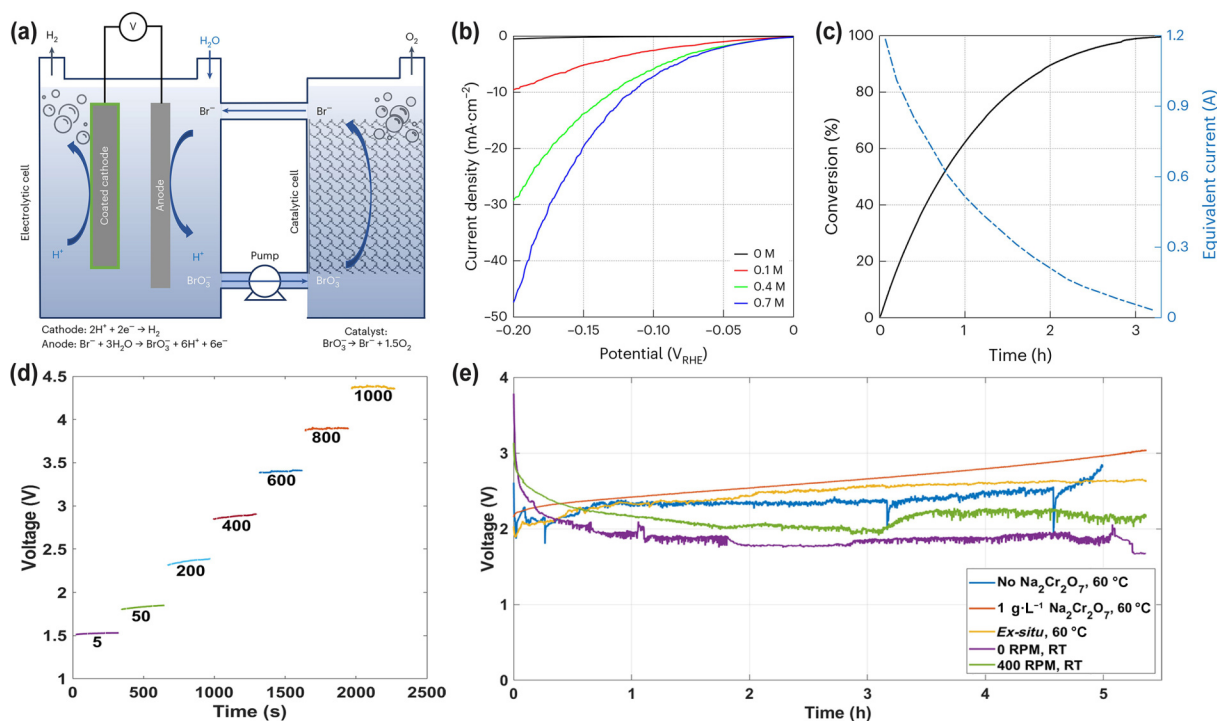


Figure 23 (a) Schematic of the DWE process. Decoupled H_2/O_2 generation in separate cells using $\text{Br}^-/\text{BrO}_3^-$ as a soluble redox couple. (b) LSV curves at a scan rate of 1 $\text{mV}\cdot\text{s}^{-1}$, where Pt foil was used as cathode, and $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ DSA as anode. (c) Catalytic conversion of BrO_3^- to Br^- and O_2 . (d) Chronopotentiometry curves at different current densities in NaBr electrolyte with a borate buffer. Electrolyte contains 0.7 M borate buffer, 1.5 M NaBr, and 3.8 mM $\text{Na}_2\text{Cr}_2\text{O}_7$. (e) Bromide electrolysis long-term stability at a current of 600 mA in different electrolytes. Reproduced with permission from Ref. [215], © The Author(s), 2024.

bromide with stoichiometric oxygen evolution in the catalytic cell. In a near-neutral NaBr aqueous electrolyte, bromate was chemically reduced to bromide in a separate cell, producing oxygen through a catalytic reaction. The FE in this process reached $98\% \pm 2\%$ in a 1.5 M NaBr electrolyte with the addition of 3.8 mM $\text{Na}_2\text{Cr}_2\text{O}_7$, which played a crucial role in mitigating cathodic loss reactions. $\text{Na}_2\text{Cr}_2\text{O}_7$ formed a protective barrier layer on the cathode, preventing the electro-reduction of oxidized bromine species. The introduction of a borate buffer enhanced the HER and reduced the cell voltage to 1.5 V at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$ or 2.4 V at a current density of $1 \text{ A}\cdot\text{cm}^{-2}$. These voltage values corresponded to electrolytic efficiencies of 97.6% (higher heating value (HHV)) at $5 \text{ mA}\cdot\text{cm}^{-2}$ and 61.7% HHV at $1 \text{ A}\cdot\text{cm}^{-2}$, reflecting the improved energy efficiency of the system under different operational conditions.

Although the electrolytic efficiency of this system is slightly lower than that reported for E-TAC water splitting, the process offers the advantage of continuous operation without the need for thermal swings, in contrast to the batch-mode operation and thermal cycling required by E-TAC. Another notable advantage of our process is its operation in a near-neutral electrolyte, which contrasts with previous reports on DWS that typically operate in acidic or alkaline electrolytes. We have to focus on several key goals: (1) Replacing the Pt cathode and $\text{RuO}_2\text{-TiO}_2/\text{Ti}$ dimensionally stable anode (DSA) anode and catalyst (RuO_2 Adams) with Earth-abundant, cost-effective alternatives to reduce reliance on expensive and rare materials. (2) Finding non-toxic alternatives to $\text{Na}_2\text{Cr}_2\text{O}_7$, which currently serves as an additive to prevent cathodic losses but poses environmental and health hazards. (3) Integrating the electrolytic and catalytic subprocesses into continuous processes to enhance operational efficiency and the system's long-term stability. LSV results in a three-electrode setup were carried out using 1.5 M NaBr electrolyte with varying borate buffer concentrations without the addition of $\text{Na}_2\text{Cr}_2\text{O}_7$. The results reveal that the cathodic reaction (HER) requires a significantly higher overpotential than the anodic reaction (bromide electro-oxidation), indicating that HER is the main contributor to polarization losses in our system. However, adding borate buffer enhances HER kinetics and substantially reduces cathodic overpotential (Fig. 23(b)) while having a minimal impact on anodic polarization. This borate buffer attributes its role as a proton source in the near-neutral NaBr electrolyte, helping to mitigate local pH gradients at the cathode surface. The electrolytic and catalytic subprocesses were submerged into a batch-to-batch process. Specifically, we transferred 7 mL of the oxidized electrolyte from the best-performing electrolytic test to a catalytic cell containing 50 mg of RuO_2 Adams catalyst. This catalyst effectively decomposed bromate anions back into bromide and oxygen. The volume of the effluent gas (oxygen) was measured, and the corresponding fraction of bromate-to-bromide conversion was plotted as a function of reaction time (Fig. 23(c)). The results confirmed complete conversion (100%) of bromate to bromide and oxygen within approximately 3 h. This demonstrates the efficiency and practicality of our system, where hydrogen evolution and bromide electro-oxidation occur with near 100% FE in the electrolytic cell, followed by stoichiometric oxygen evolution and complete bromate-to-bromide conversion in the catalytic cell (Figs. 23(d) and 23(e)).

Seawater electrolysis driven by renewable energy presents a sustainable approach to extracting abundant hydrogen resources from the ocean. However, the chlorine electro-oxidation reaction (ClOR) poses a major challenge by reducing the efficiency of the electrolysis process and causing progressive anode corrosion. Xie

et al. [216] present a redox-mediated strategy to mitigate ClOR, enabling the development of a decoupled seawater electrolysis system that incorporates a separate O_2 evolution reactor. In this system, the ferricyanide/ferrocyanide ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) redox couple acts as an electron mediator between the electrolysis cell and the O_2 evolution reactor, replacing the conventional OER with a more favorable half-reaction. This design simplifies the anodic process to a single-electron transfer without gas evolution, effectively preventing the formation of chlorine-containing byproducts. The system operates efficiently at low voltages ($\sim 1.37 \text{ V}$ at $10 \text{ mA}\cdot\text{cm}^{-2}$ and $\sim 1.57 \text{ V}$ at $100 \text{ mA}\cdot\text{cm}^{-2}$) and exhibits stability even in Cl-saturated seawater electrolytes, showcasing significant potential for chlorine-free decoupled seawater electrolysis. The ClOR, which competes with OER, produces corrosive ions and harmful gases, such as ClO^- , Cl_2 , and HOCl . These byproducts not only pose significant environmental hazards but also accelerate electrode corrosion, undermining the efficiency and sustainability of seawater electrolysis [217, 218]. Although the OER has a kinetic advantage of approximately 490 mV over the ClOR under alkaline conditions due to its favorable redox potential, the continuous influx of seawater into electrolyzers leads to the accumulation of Cl^- ions. This accumulation ultimately causes anode corrosion and degrades the entire system during operation [219, 220]. An alternative to seawater desalination electrolysis (SDE) involves replacing the OER with more thermodynamically favorable anodic reactions to mitigate ClOR. These reactions utilize species more readily oxidized than water, thereby lowering system voltage and preventing ClOR. However, this approach incurs high costs due to the consumption of raw chemicals and the need for product purification. Decoupled water electrolysis presents a more promising solution by facilitating stepwise reactions with a redox mediator, which acts as an electron/ion buffer, effectively separating the HER and OER in both space and time. The inherently slow, four-electron kinetics of the OER is the major factor contributing to high overpotentials, limiting the energy efficiency and stability of seawater electrolyzers. The decoupled SDE (DSDE) system overcomes these challenges by combining a redox-flow seawater electrolysis cell with a separate O_2 evolution reactor. This design effectively prevents ClOR and eliminates chlorine-containing byproducts without relying on additional chemicals. The ferricyanide/ferrocyanide ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) redox mediator, dissolved in alkaline seawater, serves as a charge carrier, circulating between the electrochemical cell and the O_2 evolution reactor. In the electrochemical cell, HER occurs at the cathode, while ferricyanide undergoes electro-oxidation at the anode, providing both thermodynamic and kinetic advantages over ClOR. In the separate O_2 evolution reactor, $[\text{Fe}(\text{CN})_6]^{3-}$ reacts with OH^- to facilitate oxygen generation via reduction, supported by a Fe-Ni(OH)₂/NF catalyst. An anion exchange membrane separates the anode and cathode, ensuring efficient ion transport. The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple demonstrates reversible redox kinetics and excellent stability in seawater, making it highly effective for this system. At cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$, at anode: $2[\text{Fe}(\text{CN})_6]^{4-} \rightarrow 2[\text{Fe}(\text{CN})_6]^{3-} + 2\text{e}^-$, and overall chemical reduction reactor: $4[\text{Fe}(\text{CN})_6]^{3-} + 4\text{OH}^- \rightarrow 4[\text{Fe}(\text{CN})_6]^{4-} + 2\text{H}_2\text{O} + \text{O}_2$.

The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple is renowned for its robustness, stability, and non-toxicity, making it an ideal candidate for a wide range of applications, including electrochemical studies, high-performance redox-flow batteries, and other advanced energy systems [221, 222]. CV experiments conducted on 10 mM $[\text{Fe}(\text{CN})_6]^{3-}$ in three different electrolytes-alkaline freshwater, simulated seawater, and real seawater-revealed distinct and

reversible redox peaks at ~ 1.27 V (vs. RHE), underscoring its reliability under diverse conditions. The redox behavior remained stable even after 5000 CV cycles, with less than 5% variation in seawater, demonstrating exceptional electrochemical reversibility and durability. Additionally, the oxidation reaction of $[\text{Fe}(\text{CN})_6]^{4-}$ exhibited stability for over 16 h. Reaction potentials for $[\text{Fe}(\text{CN})_6]^{4-}$ in alkaline seawater and simulated seawater were marginally lower than in alkaline freshwater. In alkaline seawater alone, the potential increased continuously, leading to electrochemical corrosion and failure of the carbon felt electrode within 6 h. However, the inclusion of $[\text{Fe}(\text{CN})_6]^{4-}$ stabilized the potential, maintaining an average voltage of approximately 1.45 V. Importantly, no hypochlorite ions (ClO^-) were detected during electrolysis in $[\text{Fe}(\text{CN})_6]^{4-}$ containing alkaline seawater, as confirmed by iodometric analysis. Long-term stability tests conducted over 120 h revealed only a slight potential increase, with an overall average potential of 1.50 V. These results demonstrate the remarkable electro-oxidation efficiency and stability of $[\text{Fe}(\text{CN})_6]^{4-}$ in carbon felt electrodes, highlighting its potential for sustainable seawater electrolysis applications. The HER electrocatalyst, $(\text{NiMo})_{1-x}\text{Co}_x\text{P/NF}$, demonstrated exceptional stability in seawater, maintaining nearly the same overpotential after 100 h of testing. In the system, $[\text{Fe}(\text{CN})_6]^{4-}$ is oxidized to $[\text{Fe}(\text{CN})_6]^{3-}$ at the anode. As the concentration of $[\text{Fe}(\text{CN})_6]^{3-}$ increases and that of $[\text{Fe}(\text{CN})_6]^{4-}$ decreases, the equilibrium potential of the redox mediator gradually rises. Once the potential reaches the onset potential of the OER, $[\text{Fe}(\text{CN})_6]^{3-}$ undergoes a spontaneous chemical reaction in the presence of a catalyst, reducing back to $[\text{Fe}(\text{CN})_6]^{4-}$ and generating O_2 , thereby completing the overall water-splitting process. In 1 h reduction reaction conducted in alkaline seawater, 22.93 mL of oxygen was produced, a volume slightly greater than that observed in alkaline freshwater and simulated alkaline seawater. This result underscores the system's efficient oxygen evolution and its adaptability to real seawater conditions. It demonstrates the effectiveness of the DSDE system, utilizing $[\text{Fe}(\text{CN})_6]^{4-}$ to enhance electrochemical efficiency while mitigating the challenges posed by ClOR. The system integrates a custom-designed redox-flow cell with a separate reactor, where $(\text{NiMo})_{1-x}\text{Co}_x\text{P/NF}$ serves as the cathode and graphite felt (GF) is used at the anode. The catholyte consists of a 4 M KOH + seawater solution, while the anolyte is a mixture of 0.15 M $[\text{Fe}(\text{CN})_6]^{3-}$ and 0.15 M $[\text{Fe}(\text{CN})_6]^{4-}$ dissolved in a 4 M KOH + seawater solution. The DSDE system demonstrated impressive performance, requiring only $3.3 \text{ kWh}\cdot\text{m}^{-3} \text{ H}_2$ to achieve a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, highlighting the superior efficiency of single-electron kinetics compared to the traditional OER. GC tests revealed a gradual decline in O_2 evolution, indicating the system stability and performance over time. FE stabilized at approximately 85% after 240 h of operation. In a Cl^- -saturated alkaline seawater environment, resulting from continuous seawater feeding, the DSDE system demonstrated enhanced anticorrosion properties while maintaining stable electrochemical performance. Even at a high Cl^- concentration of 3.16 M, the system exhibited only a modest voltage increase, reaching 1.59 V at $100 \text{ mA}\cdot\text{cm}^{-2}$ and 1.70 V at $200 \text{ mA}\cdot\text{cm}^{-2}$. Chronopotentiometry results confirmed long-term stability over 250 h, with an average voltage of 1.70 V, and no generation of hypochlorite ions was detected during the process. Importantly, no structural corrosion was observed in the carbon-felt electrode after extended electrolysis in Cl^- -saturated alkaline seawater. The $\text{Fe-Ni}(\text{OH})_2/\text{NF}$ catalyst effectively facilitated the catalytic reduction of $[\text{Fe}(\text{CN})_6]^{3-}$, ensuring high chemical efficiency. These

advancements highlight the potential of the DSDE system to efficiently and sustainably harness seawater as a clean energy source, paving the way for future energy solutions with minimized environmental impact.

3.2 Organic molecular redox mediators

Broadening the ECPB concept for DWS with superior outputs, the Cronin group [178] further demonstrated organic compounds like quinones and their derivatives for decoupled water splitting (Fig. 24(a)) because those as mentioned earlier decoupling inorganic agents phosphomolybdic acid ($1843 \text{ g}\cdot\text{mol}^{-1}$) and silicotungstic acid ($2880 \text{ g}\cdot\text{mol}^{-1}$) have higher molecular weights, and for bulk water electrolysis they are not low-cost elements. In this regard, inspired by the natural photosynthetic process, an organic redox mediator was introduced by the Cronin group, resolving the previous issues, having low molecular weight, lower cost, high solubility in aqueous solution, providing a feasible redox chemistry. These organic compounds are also used as electrolytes in dye-sensitized solar cells. The aromatic sulfonation of 1,4-hydroquinone yields potassium hydroquinone sulfonate, employed as the redox mediator in ECPB. Pure quinone is not extraordinarily soluble in water, which is why sulfonation of 1,4-hydroquinone was carried out to increase the solubility in water (0.5 M), both in reduced and oxidized forms. The redox wave between the HER and OER should be reversible in an ideal ECPB. In cyclic voltammetry, the sulfonate derivative organic redox couple is roughly equivalent to +0.65 V against NHE in 1.8 M H_3PO_4 at pH of 0.7 on the carbon electrode, while the redox couple of pure 1,4-hydroquinone/p-benzoquinone is around +0.7 V vs. NHE under standard circumstances (Fig. 24(b)). When a 0.5 M solution of hydroquinone sulfonate in 1.8 M H_3PO_4 (pH = ~ 0.7) was oxidized, a 50:50 mixture of the oxidized and two-electron-reduced species was produced. At $50 \text{ mA}\cdot\text{cm}^{-2}$, 0.23 V is required to reduce ECPB to ECPB* on the carbon electrode, while -0.39 V is required to produce hydrogen by reducing protons at the Pt electrode. Further oxidation of the reduced species ECPB* requires 0.90 V on the carbon electrode, and 2.23 V is required to oxidize water on the Pt electrode. A comparison of current densities at Pt and carbon electrodes is shown in (Figs. 24(c) and 24(d)).

Two-step hydrogen gas evolution requires larger current densities than one-step evolution, in which both oxygen and hydrogen are created at the same time. It takes $+2.23 - 0.23 = 2.00$ V in the first phase of a two-step process to oxidize water and reduce ECPB at a standard $50 \text{ mA}\cdot\text{cm}^{-2}$; in the second step, reoxidation of ECPB* to produce H_2 requires $+0.9 - (-0.39) = 1.29$ V. It is clearly seen that an overall voltage to decouple water splitting by summing both the voltage $2.00 + 1.29 = +3.29$ V is required as compared to single step water splitting $+2.23 - (-0.39) = 2.62$ V, which shows that to decouple water it requires a little bit higher voltage but produce H_2 and O_2 in different space and time. For hydrogen production at the carbon cathode, -0.77 V is required to reduce protons. The overall efficiency of ECPB-mediated water splitting is 91%, and it only takes +3.0 V to produce hydrogen at the carbon cathode and oxygen at the Pt anode at $50 \text{ mA}\cdot\text{cm}^{-2}$ current density. Two-step water splitting is more dominant than a single step because of these reasons: (1) It requires single precious metal Pt electrodes when ECPB is used, while it requires two Pt electrodes when utilized in one step. (2) It requires two smaller inputs in two-step water splitting, but others require one large input. An ideal situation was also observed in the two-electrode configuration system. In one compartment of the H-

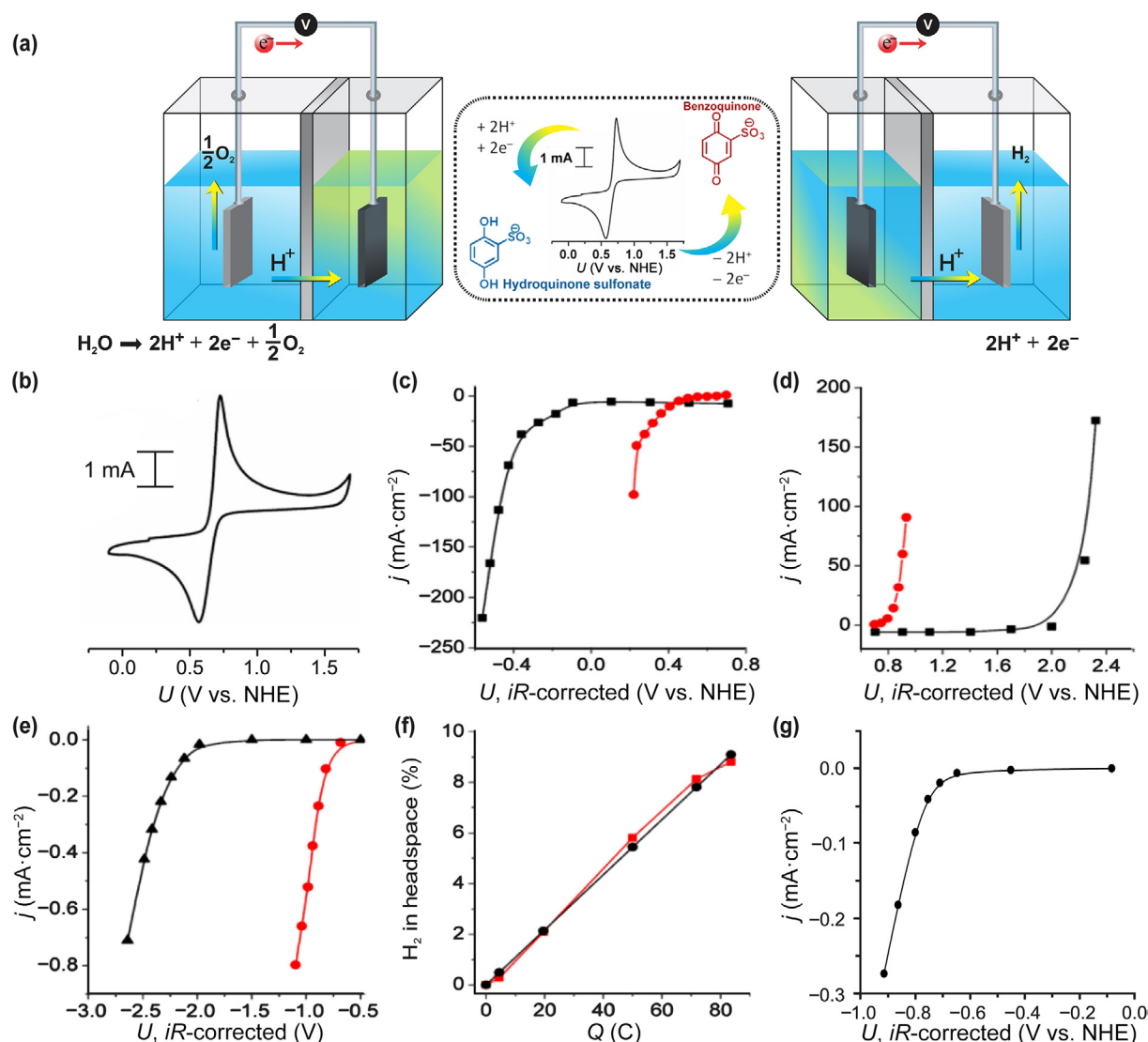


Figure 24 ECPB-based decoupled water splitting of hydroquinone. (a) Schematic diagram of DWS. At a black carbon electrode, the colorless hydroquinone is oxidized into the red benzoquinone. Two protons and two electrons are released by each hydroquinone molecule that crosses the membrane as the electrons travel through the outside circuit, and these are reunited on the Pt electrode (gray) to form H₂. In the opposite way, H₂O is oxidized into O₂. (b) CV curves of hydroquinone sulfonate (10 mM) in 1.8 M H₃PO₄ at pH of 0.7. Three-electrode configuration current-voltage curves of (c) ECPB reduction and (d) ECPB* oxidation. (e) Current-voltage curves for two-compartment cell in a two-electrode configuration. (f) Headspace H₂ measured by GCHA (red line and squares) vs. the calculated value (black line and circles) based on the amount of charge transferred. (g) Current-voltage curve for one compartment cell in a three-electrode configuration with an electrolyte of 1.8 M H₃PO₄ (pH = 0.7). Reproduced with permission from Ref. [178], © American Chemical Society 2013.

cell, 1.8 M H₃PO₄ (pH = 0.7) was placed with a Pt electrode, while in the second compartment, 0.5 M of ECPB/ECPB* in 1.8 M H₃PO₄ with carbon electrode was placed. A Nafion membrane was used to separate the two solutions. 0.98 V was applied to achieve 0.5 A·cm⁻² current density with the oxidation of ECPB. In the absence of reduced species, ECPB* current densities greater than 2.5 V are required to achieve 0.5 A·cm⁻² (Fig. 24(e)). Gas chromatography hydrogen analysis (GCHA) shows the amount of H₂ produced with a FE of (98% ± 7%) for the HER, and the amount of impurity that evolved during this reaction was less than 2% (Figs. 24(f) and 24(g)). This indicates that ECPB-DWS gives better outputs than conventional water splitting.

One advantage of this hydroquinone sulfonate as a mediator is that it controls the pH during the process and can simultaneously donate and accept electrons and protons. 91% ± 5% FE was recorded for OER with no detection of H₂. The redox mediator potassium hydroquinone sulfonate is completely oxidized and

reduced to determine its stability in a two-compartment cell arrangement. A drop of around 1% each cycle was seen in the ability to re-reduce the oxidized ECPB (over 20 cycles). The degradation rate is higher in concentrated solutions than in dilute solutions. Reduced ECPB* can be stored for a long time without degradation and oxidation in the dark. More than 98% charge would be recovered from stored 0.5 M solution of reduced ECPB* to produce H₂ in the dark. Nafion membrane was used as an impermeable barrier for larger ions, but it could not hinder ECPB/ECPB* molecule from crossing the membrane at the rate of ~ 2.7 × 10⁻⁶ mol·h⁻¹, determined by UV-vis spectra. Therefore, larger quinone derivatives are expected to cross the membrane. The above analysis suggests that the organic compound potassium hydroquinone sulfonate is promising for low molecular weight ECPB decoupled water splitting mediator. Potassium hydroquinone sulfonate also has some drawbacks, like ordinary stability for large-scale practical applications, decrease in

storage capacity, and permeation through Nafion membrane, which minimizes the overall efficiency during DWS, leading to the development of other more efficient organic redox mediators [178].

The Cronin group first developed an organic molecular redox mediator called anthraquinone-2,7-disulfonic acid (AQDS) in replacement of potassium hydroquinone sulfonate with excellent properties (Fig. 25(a)), with a low cost of only 1.02% compared to previously reported polyoxometalates, silicotungstic acid. An ideal

ECPB should have these properties: (1) highly soluble in water, (2) reversible redox between HER and OER, (3) stable in reduced and oxidized forms, (4) buffer the pH of the system during the electrolysis, and (5) low cost. Cyclic voltammograms of AQDS show a reversible redox pair that peaks at +0.214 V vs. NHE (Figs. 25(b) and 25(c)). Redox couple reversibility was examined in AQDS solution over 100 cycles (Fig. 25(d)), showing an overall rate of charge capacity decrease of 5.75%, which equates to 0.06% per cycle. The previously reported organic ECPB potassium

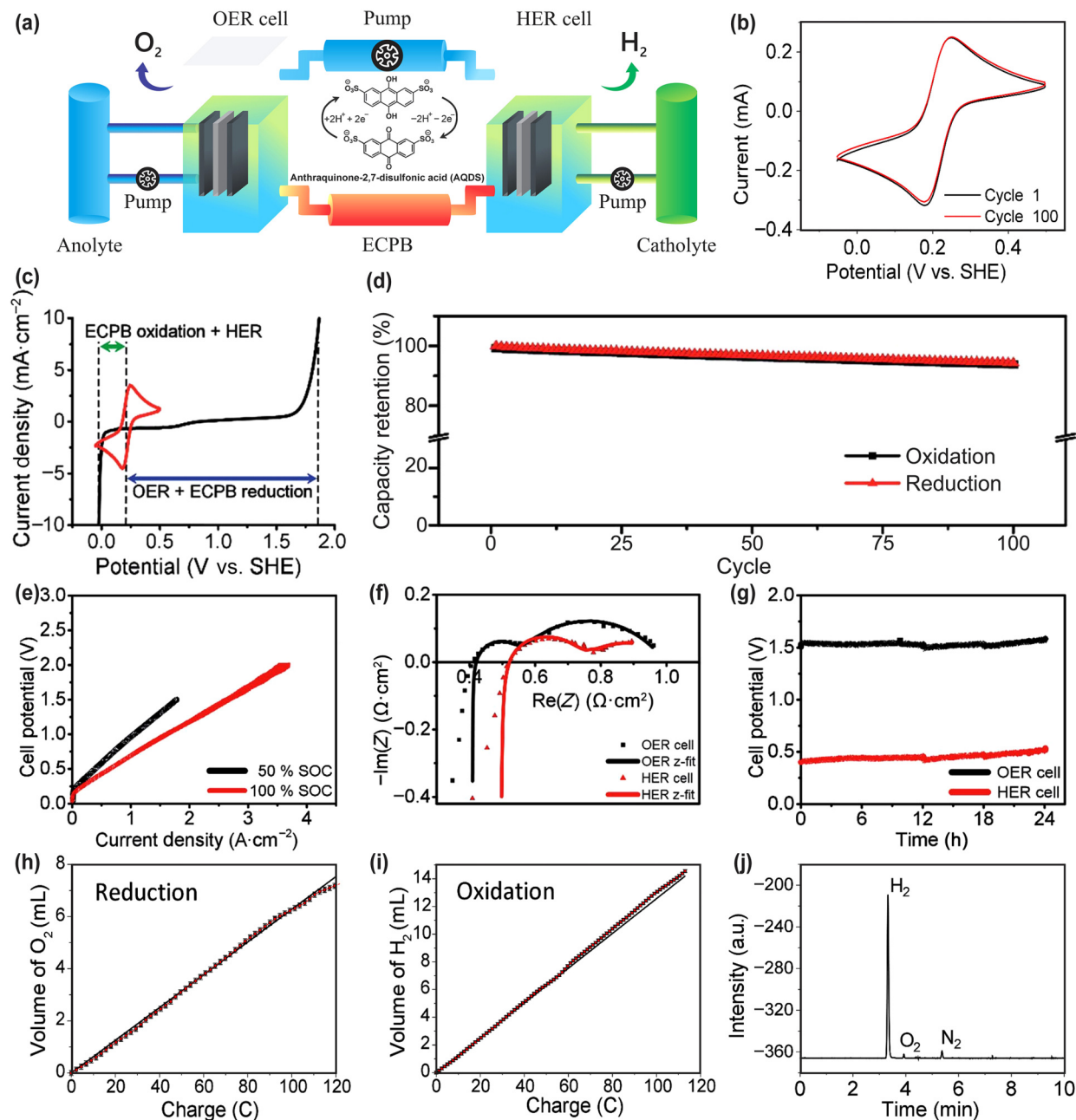


Figure 25 ECPB-based decoupled water splitting of AQDS. (a) Schematic diagram of DWS electrolyzer. The idea is to use ECPB to divide water into two different electrolyzers. In the left-hand side OER cell, water is oxidized while ECPB is reduced. When ECPB is reduced, it travels to HER cells and is re-oxidized to generate hydrogen gas. (b) The CV curves of anthraquinone-2,7-disulfonic acid were recorded at 25 mV·s⁻¹ using a glassy carbon working electrode immersed in 1 M H₂SO₄. (c) OER and HER are shown at Pt electrodes in 1 M H₂SO₄ (black), together with the AQDS CV recorded from a glassy carbon electrode (red). (d) Charge stability of 100% through 100 cycles of complete reduction/oxidation of the AQDS in a two-chamber hydrogen cell. (e) The efficiency of AQDS at 50 °C in a hybrid ECPB electrolyzer. HER cell polarisation curves at 50% (black) and 100% state of charge (red). (f) HER (red, triangles) and OER (black, squares) Nyquist plots, using markers and a solid line z-fit to represent experimental data. (g) The HER cell voltage (red) and the OER cell voltage (black); this test compares the two cells' stability over 24 h while running at a constant current of 0.25 A·cm⁻². Volumetric gas measurements for AQDS (h) reduction and (i) oxidation. The experimental and theoretical volumes of gas evolved depending on the charge passed during electrolysis, which are represented by the red and black lines. (j) GC of the gas streams that come out of the hybrid electrolyzer. Reproduced with permission from Ref. [223], © The Royal Society of Chemistry 2018.

hydroquinone sulfonate shows a loss of charge of approximately 1% per cycle. The result shows 100% FE of AQDS. Its large molecular size makes it less able to penetrate cell membranes. Extending the concept of ECPB, AQDS was used in combination with PEM electrolyzers and flow battery technology to decouple oxygen and hydrogen. Simply, a separate two-cell device decouples water using a redox mediator. The setup price increases, but the components last longer, the cell degrades less quickly, and lower individual power inputs are used. Every cell has an effective surface area of 12.96 cm^2 . During the passage of charges, H_2 is directly proportional to the oxidation of the ECPB. The HER onset potential was 0.20 V, reaching 0.96 V at a current density of $1.00 \text{ A}\cdot\text{cm}^{-2}$ (Fig. 25(e)). In contrast, the OER onset potential was 1.30 V, reaching $1.00 \text{ A}\cdot\text{cm}^{-2}$ at 2.01 V. A maximum current density ($3.71 \text{ A}\cdot\text{cm}^{-2}$) was attained at 2.00 V when the HER cell was operating at 100% state of charge to verify the demonstration of hydrogen cell with lower energy input and quicker rate of production. Potentiostatic electrochemical impedance spectroscopy (PEIS) confirms the Ohmic resistance for HER is $0.492 \Omega\cdot\text{cm}^2$, while for OER, $0.408 \Omega\cdot\text{cm}^2$, as shown in the Nyquist plot (Fig. 25(f)). This Ohmic resistance is higher than that of conventional PEM electrolyzers. Due to cell separation, there is no restriction on the membrane; a conductive and cheaper membrane can be used as an alternative. Regarding the stability of the cells, they were operated for 24 h at a current density of $0.25 \text{ A}\cdot\text{cm}^{-2}$. When the potential of each cell was measured, there was an increase in voltages of 103 and 33 mV for HER and OER, respectively (Fig. 25(g)). Volumetric gas measurements for AQDS reduction and oxidation with the experimental and theoretical gas volumes evolved depending on the charge passed during electrolysis are represented by the red and black lines, respectively (Figs. 25(h) and 25(i)). GC analysis shows the gas streams that come out of the hybrid electrolyser, and the H_2 comes out of the HER cell (Fig. 25(j)) [223].

As reported previously, organic redox reservoirs (RRs), i.e., quinone and its derivatives, are promising candidates for DWS, but some factors limit their utilization. A newly reported tetramercaptopropanesulfonate quinone (TMQ) shows robust stability compared to anthraquinone-2,7-disulfonate reported previously [223], confirmed by symmetric flow-battery experimentations. Reduced tetramercaptopropanesulfonate hydroquinone (TMHQ) does not undergo decomposition, while oxidized TMQ undergoes slow decomposition. Organic redox reservoirs are usually made of earth-abundant elements and may be modified for stability, solubility, redox potential, and electrochemical kinetics [224, 225]. DWS is more favorable than direct water splitting because it requires two smaller inputs compatible with alternative energy sources like solar and wind power, rather than a single high input voltage. Previously reported hydroquinone monosulfonate (HQMS) by Cronin and coworkers shows its low redox capacity, which limits its practical use. Further innovations by this group show that anthraquinone-2,7-disulfonate (AQDS) is more stable than QMS. Under acidic conditions, reduced anthrahydroquinone-2,7-disulfonate (AHQDS) produces redox inactive derivatives. Due to the appealing properties of quinone and its derivatives as RRs, the TMHQ/TMQ combination, as recently reported by Stahl et al. [226], is significantly more effective than the hydroquinone/quinone and its derivatives. TMHQ/TMQ shows better and improved stability than AHQDS/AQDS in decoupled water splitting. An ideal RR should have these properties: (1) buffers the pH of the solution, (2) high solubility in aqueous solutions, (3) low

cost, and (4) reversible redox potential between HER and OER.

Cyclic voltammetry of TMHQ/TMQ shows 0.61 V vs. SHE redox potential halfway between HER and OER. In a symmetric redox flow battery, the TMHQ/TMQ pair is more stable than the AHQDS/AQDS combination. Capacity-limiting side (CLS) and non-CLS (NCLS) were achieved by employing the same redox electrolytes at different concentrations. Nuclear magnetic resonance (NMR) results show that oxidized TMQ decomposed more rapidly than reduced TMHQ, while, on the contrary, reduced AHQDS decomposed more rapidly than oxidized AQDS. For this reason, efficient redox reservoirs may store in either a reduced or oxidized state. The CLS and NCLS sides of the cell each took an equal quantity of oxidized and reduced quinones/hydroquinones electrolytes. The redox reservoir concentration was measured at 0.25 M in 1 M H_2SO_4 electrolyte solution at a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$. Symmetric flow battery results show that the charge capacity of the TMHQ/TMQ pair is more than that of AHQDS/AQDS. TMHQ/TMQ has less decay percentage ($< 1.5\%$) with no byproduct formation as compared to AHQDS/AQDS with $\sim 26\%$ decay percentage with byproduct formation after 9 days, which shows improved stability of TMHQ/TMQ redox reservoir. When TMQ is broken down, it produces TMHQ and a symmetric disulfide with a molar ratio of 2.2:1. For redox mediator-based DWS, Pt/C and IrRuO_x electrocatalysts were used as HER and OER, respectively. In contrast, carbon paper was used as the working electrode. DWS was compared to direct water splitting using a TMHQ/TMQ combination as the redox mediator at 50°C and a flow rate of $200 \text{ mL}\cdot\text{min}^{-1}$. The RR tank used a redox mediator of 0.25 M TMHQ/TMQ in a 1 M H_2SO_4 solution. In contrast, the HER and OER used only 1 M H_2SO_4 . Polarization curves imply that a $\sim 1.50 \text{ V}$ onset voltage is required for direct water splitting (Fig. 26(a)). In contrast, redox mediator-based DWS requires 0.60 and 0.85 V for HER and OER, respectively, which is lower than direct water splitting. The results of a chronopotentiometry test at a current density of more than $250 \text{ mA}\cdot\text{cm}^{-2}$ probed the device's practical performance in direct and DWS (Figs. 26(b) and 26(c)). During 24 h, direct water splitting cell voltage increases slowly from 1.77 to 1.88 V, which indicates the deactivation of IrRuO_x as an OER catalyst. In DWS, HER cell voltage remained stable (0.97 V) over 62 h throughout the experiment, which signifies its stability over time. It can be concluded that the TMHQ/TMQ redox mediator and Pt/C HER catalyst used in this experiment are both stable.

The overlapping of polarization curves provides more evidence for the system reliability. Cell voltage in OER cells used in DWS rises from 1.40 to 1.60 V during 62 h. This instability arises due to the slow deactivation of the IrRuO_x OER catalyst. Such deactivation of OER electrode was also observed in direct water splitting. Furthermore, non-overlapping polarization curves of OER in chronopotentiometry examination confirm its deactivation. Volumetric data from DWS reveal that the hydrogen and oxygen generated have a FE of $\sim 100\%$ (Fig. 26(d)). PEIS measurement of direct and decoupled HER/OER water-splitting cells was taken at 0 V. Overall, TMHQ/TMQ efficiency is 62.4% when HER/OER cells are operating independently at $250 \text{ mA}\cdot\text{cm}^{-2}$ in 1 M H_2SO_4 at 50°C . This is the highest energy efficiency that has been achieved through RRs for DWS. Finally, results support that TMHQ/TMQ is a fascinating molecular redox mediator for DWS as compared to AHQDS/AQDS due to many properties, i.e., long-term stability over $> 60 \text{ h}$, easily accessible from inexpensive products, appropriate redox potential, and high

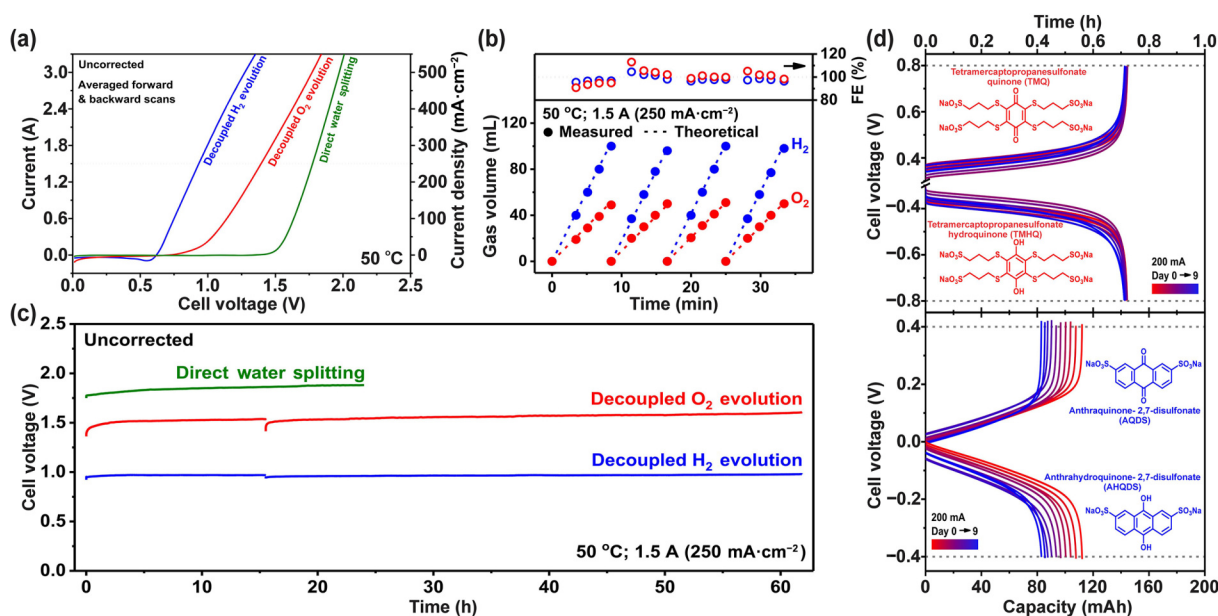


Figure 26 ECPB-based decoupled water splitting of TMQ. (a) Comparison of the polarization curves of the direct water splitting cell (green trace) without iR correction to those of the decoupled HER and OER cells (blue and red traces). (b) Four 10 min chronoamperometry experiments at $250 \text{ mA}\cdot\text{cm}^{-2}$ and 50°C were used to measure H_2/O_2 gas yields and FEs for DWS. (c) Chronopotentiometry plots of direct water splitting (green) and decoupled HER/OER (blue and red) cells, both operating at a constant current density of $250 \text{ mA}\cdot\text{cm}^{-2}$ and 50°C without iR correction. (d) Comparative studies of the redox flow-battery stability of TMHQ/TMQ and AHQDS/AQDS. Reproduced with permission from Ref. [226], © American Chemical Society 2021.

solubility in aqueous solutions [226].

Wang et al. [227] reported a system that enables the decoupling of both HER and OER reactions from the electrodes, redirecting them to two spatially separated catalyst bed reactors in alkaline solutions. The system operates in electrochemical–chemical cycles, with 7,8-dihydroxy-2-phenazinesulfonic acid (DHPS) and Pt/Ni(OH)₂ catalyst for HER, while ferricyanide and NiFe(OH)₂ catalysts for OER as redox mediators to minimize overpotentials due to the adsorption of the generated gases on the electrodes. This adsorption of gas bubbles can block the electrocatalyst surface and reduce ion conductivity in the electrolyte (Fig. 27(a)) [226, 227]. During operation, the mediators are electrochemically charged at the electrode and then chemically discharged through catalytic HER and OER reactions in their respective reactors. DHPS acts as both a proton and an electron carrier. In Step 1, the reduction of DHPS at the cathode generates DHPS-2H, and then hydrogenated DHPS-2H initiates the HER as it passes through the catalyst bed in the reactor. In Step 2 on the Pt catalyst in the gas production reactor, DHPS-2H undergoes dehydrogenation, releasing H_2 and regenerating DHPS for another cycle as it circulates back to the anodic compartment. DHPS and $[\text{Fe}(\text{CN})_6]^{4-}$ are continuously regenerated as the electrolyte circulates, while H_2 and O_2 are produced in separate reactors. LSV was conducted with a comparison to 4 M NaOH using the same set of catalysts; direct electrolytic water splitting in an alkaline solution requires 1.57 V at a current of $20 \text{ mA}\cdot\text{cm}^{-2}$, which is higher than the thermodynamic limit of 1.23 V. In contrast, only 1.39 V is required to drive the redox reactions of DHPS and $[\text{Fe}(\text{CN})_6]^{4-}$ at the same current. The initial oxidation peak at $\sim 1.38 \text{ V}$ (vs. RHE) corresponds to the oxidation of Ni^{2+} to Ni^{3+} in $\text{NiFe}(\text{OH})_2$ (Fig. 27(b)). HER process of DHPS on a Pt-Ni(OH)₂ catalyst was further investigated using a double-layer electrode (DLE). DHPS acts as an electron and proton carrier and shuttles between the CC electrode and Pt-Ni(OH)₂ through the porous spacer. DHPS is reduced on the CC electrode as in (Eqs. (21) and (22))



The hydrogenated DHPS-2H diffuses through the porous separator and undergoes catalytic dehydrogenation on the Pt-Ni(OH)₂ catalyst, releasing H_2



5 mM DHPS in the electrolyte significantly increases the current density with nearly a fivefold enhancement at -0.40 V (vs. RHE). DHPS reduction kinetics on the carbon felt were superior to the HER, with a synergistic effect between DHPS and Pt-Ni(OH)₂ existing despite the latter not being in direct electrical contact with the electrode (Fig. 27(c)). The green curve in (Fig. 27(c)) represents the difference in current between the DLE and bare CC electrode in the DHPS electrolyte, which estimates the catalytic off-electrode HER (or DHPS-2H dehydrogenation) reaction contribution on Pt-Ni(OH)₂. This steady-state behavior indicates an electrochemical–chemical process involving DHPS, confined between the CC electrode and Pt-Ni(OH)₂ through the thin spacer layer.

Gas chromatography analysis of the produced H_2 gas revealed minimal O_2 detection, especially when compared to conventional electrolyzers, demonstrating the flow cell's effectiveness in generating pure hydrogen (Fig. 27(d)). The long-term stability of the decoupled water electrolyzer system at a constant current density of $20 \text{ mA}\cdot\text{cm}^{-2}$, the cell voltage remained stable at around 1.53 V for over 80 h with no significant degradation (Fig. 27(e)). Density functional theory (DFT) shows that H_2 involves two surface-adsorbed H^* atoms on Pt, which is energetically more favorable than reactions involving one H^* and one DHPS-2H or other intermediates. The DHPS/DHPS-2H and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couples, functioning as electrolyte-borne charge carriers, undergo swift catalytic HER and OER reactions in their respective reactor tanks and electrochemical regeneration at the electrodes. This system, leveraging the robustness and superior kinetics of these redox mediators along with the decoupled flow cell design,

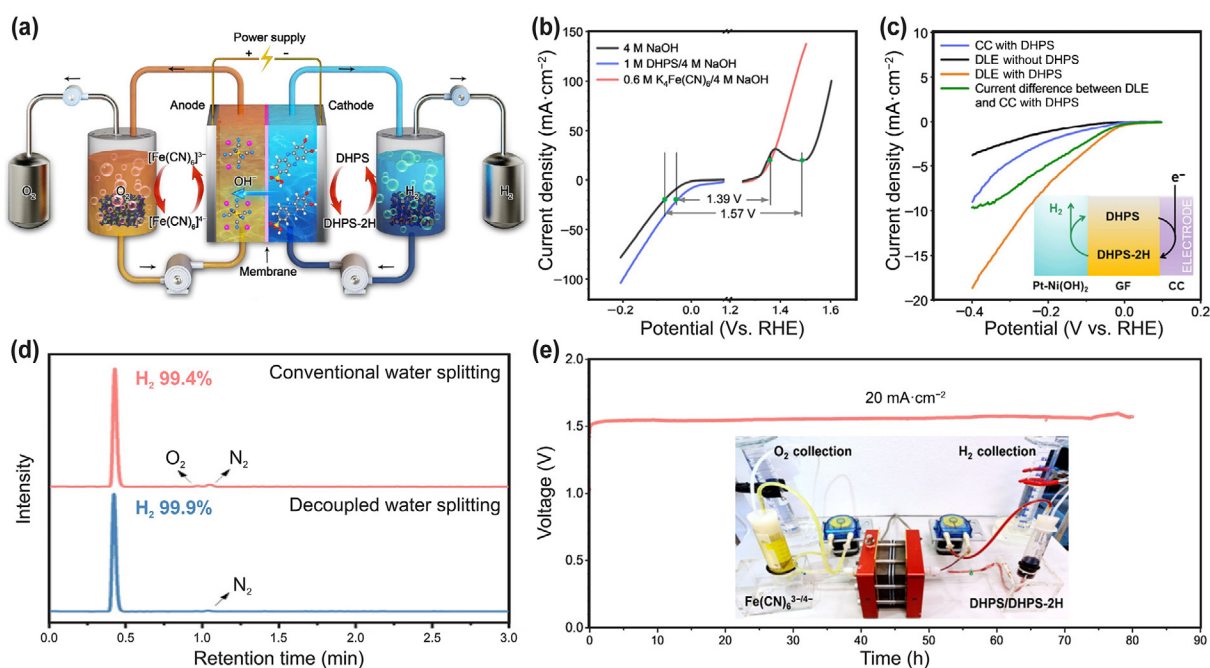


Figure 27 (a) Schematic illustration of a redox-flow electrolytic cell. (b) LSV curves of DLE in a 4 M NaOH solution with/without 5 mM DHPS, and that of a CC electrode in DHPS/NaOH solution by an anion-exchange membrane. (c) LSV curves of DLE in 4 M NaOH solution with/without 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$, and that of a CC electrode in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ /NaOH solution at a scan rate of 0.1 mV s^{-1} . (d) GC curves of the electrolytic flow cell and a conventional electrocatalytic cell. (e) Flow cell upon continuous H_2 production for 82 h at 20 mA cm^{-2} . Reproduced with permission from Ref. [227], © American Chemical Society 2020.

achieved near-unity FE and sustained hydrogen production. The energy required to break the H–OH bond in water is 0.96 eV, increasing to 1.87 eV when accounting for pH effects. In contrast, the dehydrogenation barriers of DHPS-2H and DHPS-H are 0.95 and 1.48 eV, respectively. This indicates that DHPS-2H dehydrogenation is energetically more favorable than direct water dissociation on the same Pt surface, supporting the faster kinetics of the DHPS-mediated HER. Summary of recent studies on soluble molecular redox mediators for decoupled water splitting can be seen in Table 3.

4 Insoluble solid-state redox mediators

Insoluble solid-state redox mediators (Fig. 8(b)) are redox-active compounds that cannot dissolve in water. They are broadly classified into two categories: inorganic and organic solid-state redox mediators, both of which are explored in detail.

4.1 Inorganic solid-state redox mediators

Insoluble solid-state redox mediators are promising decoupling agents for hydrogen generation during water electrolysis because of the membrane-free characteristics. Even in an alkaline environment, solid-state redox mediators can be utilized. Xia et al. [179] discovered an alkaline electrolyte-based solid-state redox mediator, nickel hydroxide $\text{Ni}(\text{OH})_2$ (Fig. 28(a)). $\text{Ni}(\text{OH})_2$ was oxidized to NiOOH at the cathode, resulting in the evolution of hydrogen. While at the anode, oxygen was produced by the reduction of NiOOH to $\text{Ni}(\text{OH})_2$. Furthermore, NiOOH is combined with a zinc anode to create a NiOOH –Zn battery, which may then be used to produce hydrogen. Alkaline water electrolysis has cutting-edge advantages over acidic water electrolysis due to the non-precious catalyst used and porous separators like anion exchange membranes. $\text{Ni}(\text{OH})_2$ has been extensively used on a large scale in rechargeable batteries. NiOOH has a greater reduction potential (0.45 V) at the cathode than Zn

anodic oxidation potential (–1.15 V) vs. Hg/HgO . A NiOOH –Zn battery arrangement, in which hydrogen is produced from the discharged nickel hydroxide ($\text{Ni}(\text{OH})_2$), is formed when NiOOH and Zn are combined. The 1.0 M KOH alkaline electrolyte was used with a carbon nanotube (CNT)-supported $\text{Ni}(\text{OH})_2$ particle working electrode, a platinum plate counter electrode, and a Hg/HgO reference electrode. $\text{Ni}(\text{OH})_2$ reversible redox peaks were identified at 0.43/0.49 V vs. Hg/HgO in CV at a scan rate of 5 mV s^{-1} . Nickel hydroxide $\text{Ni}(\text{OH})_2$ redox mediator was also compared to a Pt-coated Ti-mesh electrode for HER and a $\text{RuO}_2/\text{IrO}_2$ -coated Ti-mesh electrode for OER. The reversible redox wave of nickel hydroxide can be seen in the CV to be located between the HER onset potential and the OER of the electrodes, as mentioned above (Fig. 28(b)). The chronopotentiometry curves indicate the overall HER at 1.6 V and OER at 0.4 V vs. Hg/HgO with 100% CE (Fig. 28(c)).

Alternatively, we can use solar irradiation to produce hydrogen during the day with a larger input voltage than OER, which produces a lower input voltage. Non-precious electrodes, a Ni-foam-based for HER and Co_3O_4 -based for OER, were utilized for two-step DWS. *In-situ* mass spectrometry analysis at 200 mA was performed to independently verify the H_2 and O_2 purity throughout time and space. In Step 1, pure H_2 was obtained, although no detection of O_2 was observed within 30 min, while a rest step was observed between Steps 1 and 2, lasting within the range of 130 min, introducing pure Ar steam to remove the remaining H_2 . In Step 2, O_2 evolved till 1700 s with a small difference of 100 s compared to H_2 (1800 s). This slight difference (100 s) was supposed to be the self-discharge of NiOOH in the rest step. During the HER step, nearly 12 mL of hydrogen was evolved over 1000 mA applied current for 100 s, which was approximately close to the theoretical value (12.67 mL) by employing a drainage method with 94.67% FE (12/12.67 mL) (Figs. 28(d) and 28(e)). Nickel hydroxide demonstrates long cyclic life and high efficiency (Fig. 28(f)). The efficiency of two-step water electrolysis was

Table 3 Summary of recent studies on soluble molecular redox mediators for decoupled water splitting

Soluble molecular redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		$E_{1/2}$ (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
H ₃ PMo ₁₂ O ₄₀	Pt and RM		BiVO ₄	HNO ₃ solution for HER and 10 mM RM for OER and redox reaction	1.67	—	—	0.9 vs. Ag/AgCl	98	—	0.5	5 cycles and 12 h	[175]
H ₃ PMo ₁₂ O ₄₀	Carbon felt for redox mediator		WO ₃ photoanode	1 M CH ₃ SO ₃ H for OER and 0.5 M RM for redox reaction	0.1	0.6 vs. NHE	1.2 vs. NHE	0.35	100	84 ± 6	2.5	2000 s	[174]
H ₃ PMo ₁₂ O ₄₀	Pt	Pt	Pt	1 M H ₃ PO ₄ for HER and OER, and 0.5 M H ₃ PMo ₁₂ O ₄₀ /H ₅ PMo ₁₂ O ₄₀ for redox	0.3	1.23	1.71	~ 0.1, 0.35, 0.55, and 0.65 vs. NHE	100	100	100	5 cycles	[28]
H ₄ [SiW ₁₂ O ₄₀]	Pt/C	Pt	Pt	1 M H ₃ PO ₄ for OER and 0.5 M H ₅ [SiW ₁₂ O ₄₀]/H ₆ [SiW ₁₂ O ₄₀] for HER	0.5	0	2.37	0.01 and -0.22 vs. NHE	95 ± 7	100	50	9 cycles	[171]
H ₄ [SiW ₁₂ O ₄₀]	Pt/C	IrO ₂ /C		0.4 M redox mediator (silicotungstic acid)	0.5	—	2.16	—	100	95 ± 7	500	200 h	[187]
H ₄ [SiW ₁₂ O ₄₀]	Pt/C and Pd/C	Carbon felt		10 mmol of H ₄ SiW ₁₂ O ₄₀ and 13.3 mmol H ₃ PO ₄	—	—	—	~ 0.02 vs. RHE	85	—	—	—	[186]
[P ₂ W ₁₈ O ₆₂] ⁶⁻	Pt	IrO ₂		Water for HER and OER, and 0.1 M [P ₂ W ₁₈ O ₆₂] ⁶⁻ for redox	1	—	—	~ -0.5, -0.25, 0.15, and 0.35 vs. SHE	> 95	> 95	50	100 cycles	[182]
Li ₆ [P ₂ W ₁₈ O ₆₂]	ECPB	C	C	HBrr/Br ₂	0.3–0.16 (HER) and 14.21 (OER)	—	—	-0.5–+0.35	100	100	100	10 h	[182]
H ₄ XW ₁₂ O ₄₀	Pt/C	Ir/Ru		0.5 M H ₃ PO ₄	0.4	0	1.78	-0.078 and -0.198 vs. SHE	95.5	—	20	200 cycles	[188]
PTA-H ₃ PW ₁₂ O ₄₀	Pt/C	IrO ₂		0.5 M H ₂ SO ₄	0.4	—	—	-0.17 and -0.05 vs. RHE	95.5	—	30	200 cycles and 48 h	
STA-H ₄ [SiW ₁₂ O ₄₀]	Pt/C	Earth-abundant catalysts (Ni ₃ P ₄ , Ni ₂ P, Mo ₂ C, and MoS ₂)		Reduced POM	0.42	—	—	-0.036 and 0.237 vs. RHE	44.6	—	—	—	
SMA-H ₄ SiO ₄ ·12MoO ₃	Pt/C			Reduced POM	0.6	—	—	-0.195 and 0.042 vs. RHE	100	—	—	9 cycles	[189]
Silicotungstic acid	CoP and Ni ₂ P	—	—	Reduced H ₄ SiW ₁₂ O ₄₀ and 0.5 M H ₂ SO ₄	0.7	—	—	0.509 vs. RHE	—	—	—	—	
Zn-phosphomolybdic acid (H ₃ PMo ₁₂ O ₄₀) battery	Free-standing Pt based electrode (Pt-Ni/Co-Ni foam)		Zn	0.5 M phosphomolybdic acid as anolyte and 1.5 M NaOH as the anolyte	—	-0.1–0.2 vs. RHE	—	—	100	100	—	12 h	[191]
					—	~ 1.0	—	—	> 90	—	50	20 h	[204]

(Continued)

Soluble molecular redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		E _{1/2} (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
V ³⁺ /V ²⁺		Mo ₂ C	RuO ₂	1 M H ₂ SO ₄	0	-0.26	1.72	-0.25 vs. SHE	96 ± 4	—	10	—	
Ce ⁴⁺ /Ce ³⁺		Mo ₂ C	RuO ₂	1 M H ₂ SO ₄	0	-0.26	1.72	1.05, 1.65 vs. SHE	—	78 ± 8	60	—	[171]
Ce(III)/Ce(IV)		Pt/C	Ir/C and Pt-mesh for Ce	0.6 M Ce(III) in 4 M MSA	—	-1.5 and -1.7	0.27-0.47	—	100 ± 1	100	20	72 h	[201]
V(II)/V(III)		Ni-foam	Carbon felt	3 M H ₂ SO ₄ and 1 M KOH	Acidic (0) and alkaline (13.74)	0-0.2	-1.1, -1.3, and 1.3	-0.057 and 0.857 vs. SHE	—	—	10	> 100 h	[202]
VO ₂ ⁺ /VO ²⁺		MEA coated with conductive blacks and Pt/C	IrO ₂ -coated Ti-mesh, carbon felt	1.5 M H ₂ SO ₄ and 2 M VO ₂ SO ₄		-0.037 vs. RHE	1.45 vs. RHE	—	92.1	—	100	~ 26 h	[203]
V ^{3+/2+}	M ⁿ⁺ ↔ M ⁽ⁿ⁺¹⁾⁺ , M = V, Ce, and Fe	Carbon cloth	Ni	2 M H ₂ SO ₄ with 0.36 M V ₂ (SO ₄) ₃ for HER and 2.5 M KOH for OER	-0.16 (HER) and 14.21(OER)	-0.765 vs. SCE	—	-0.3 vs. SHE	> 99.8	> 99.8	10	200 h	[203]
V ^{5+/4+}		Mo ₂ C/ceramic catalyst	—	1.6 M of vanadium and 2 M H ₂ SO ₄	0	—	—	0.99 vs. RHE	—	—	110	120 h	[228]
FeCNl		Ni ₂ P/Ni/NF	NF	0.5 M Na ₂ SO ₄ for OER and HER, and 0.5 M Na ₂ SO ₄ + 50 mM FeCNl for redox	6.5	-1.478	0.954	0.6 vs. SHE	100	100	10	20 cycles and 50 h	
Na ₄ [Fe(CN) ₆]		Co-P/NF	NF	0.5 M Na ₂ SO ₄ and 0.5 M sodium phosphate buffer (HER and OER), and 0.3 M [Fe(CN) ₆] ⁴⁻ + 0.5 M Na ₂ SO ₄ + 0.5 M Na-phosphate buffer for redox	0	~ 1.3	~ 1	0.9 vs. RHE	100	100	10	20 cycles and 41 h	[177]
Fe(CN) ₆ ³⁻ /Fe(CN) ₆ ⁴⁻		Pt and Ni ₂ P	Carbon-cloth	0.1 M KOH, 1.0 M H ₂ SO ₄ , 0.25 M K ₃ Fe(CN) ₆ and 0.25 M K ₄ Fe(CN) ₆	7.2	-1.10	—	0.77 vs. SHE	99.88	—	—	> 20 cycles	[229, 230]
Br ⁻ /BrO ₃ ⁻	—	RuO ₂ -TiO ₂ /Ti	Pt foil	1.5 M NaBr with 3.8 mM Na ₂ Cr ₂ O ₇	8	—	—	2.4@1 A·cm ⁻²	With Na ₂ Cr ₂ O ₇ : 98 ± 2, without Na ₂ Cr ₂ O ₇ : 72 ± 2, and overall: 100	—	600	5.5 h	[215]
Ferricyanide/ferricyanide [Fe(CN ₆)] ^{3-/4-}	—	(NiMo) _{1-x} C _x /NF	GF and Fe-Ni(OH) ₂ /NF	10 mM [Fe(CN) ₆] ³⁻ , 1 M KOH, 1 M KOH + 0.5 M NaCl, 1 M KOH + seawater, catholyte 4 M KOH + seawater solution, and 0.15 M [Fe(CN) ₆] ³⁻ and 0.15 M [Fe(CN) ₆] ⁴⁻ dissolved in a 4 M	13.59 ± 0.13, 13.54 ± 0.14, and 13.49 ± 0.19	—	—	~ 1.57	~ 100	85	200	250 h	[216]

(Continued)

Soluble molecular redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		$E_{1/2}$ (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
Hydroquinone sulfonate (HQS)		Pt	Pt	1.8 M H ₃ PO ₄ for HER and OER, and 0.5 M hydroquinone sulfonate in 1.8 M H ₃ PO ₄ for redox	0.7	1.29	2.0	0.65 vs. NHE	98 ± 7	91 ± 5	50	20 cycles	[178]
AQDS	(ECPB) keto-enol tautomerism	Pt/C	IrO ₂	1 M H ₂ SO ₄ for HER and OER, and 0.5 M AQDS in 1 M H ₂ SO ₄ for redox	0	0.96	2.01	0.214 vs. SHE	100	100	1000	100 cycles and 24 h	[223]
TMQ		Pt/C	IrRuO _x	1 M H ₂ SO ₄ and 0.25 M TMHQ/TMQ	—	0.97	1.4–1.6	0.61 vs. SHE	~100	~100	250	62 h	[226]
DHPS and electrochemical-chemical cycle		Pt-Ni(OH) ₂	NiFe(OH) ₂	4 M NaOH and Fe(CN) ₆ ^{4-/3-} for OER, DHPS for HER	14.6	—	1.91	-0.05 vs. Ag/AgCl	100	100	100	82 h	[227]
(Fe(III)/TEA)-K ₂ MnO ₄	—	Pt/C on carbon cloth	Carbon felt	Fe(III)/TEA in 1.5 M NaOH for HER	14	0	—	1.45 vs. RHE and -0.01 vs. RHE	70	100–85	5	~4 h	[231]
2,6-dimethyl-1,4-benzoquinone (DMBQ)/[Fe(CN) ₆] ^{4-/3-}	—	PtCrO _x -ZrO ₂ /TaON	PS II	10 mM Fe(CN) ₆ ^{4-/3-} for HER and 5 mM DMBQ for OER	6	—	—	-0.35, 0.39, 0.88, and 0.19	90	90	0.25	25 h	[232]

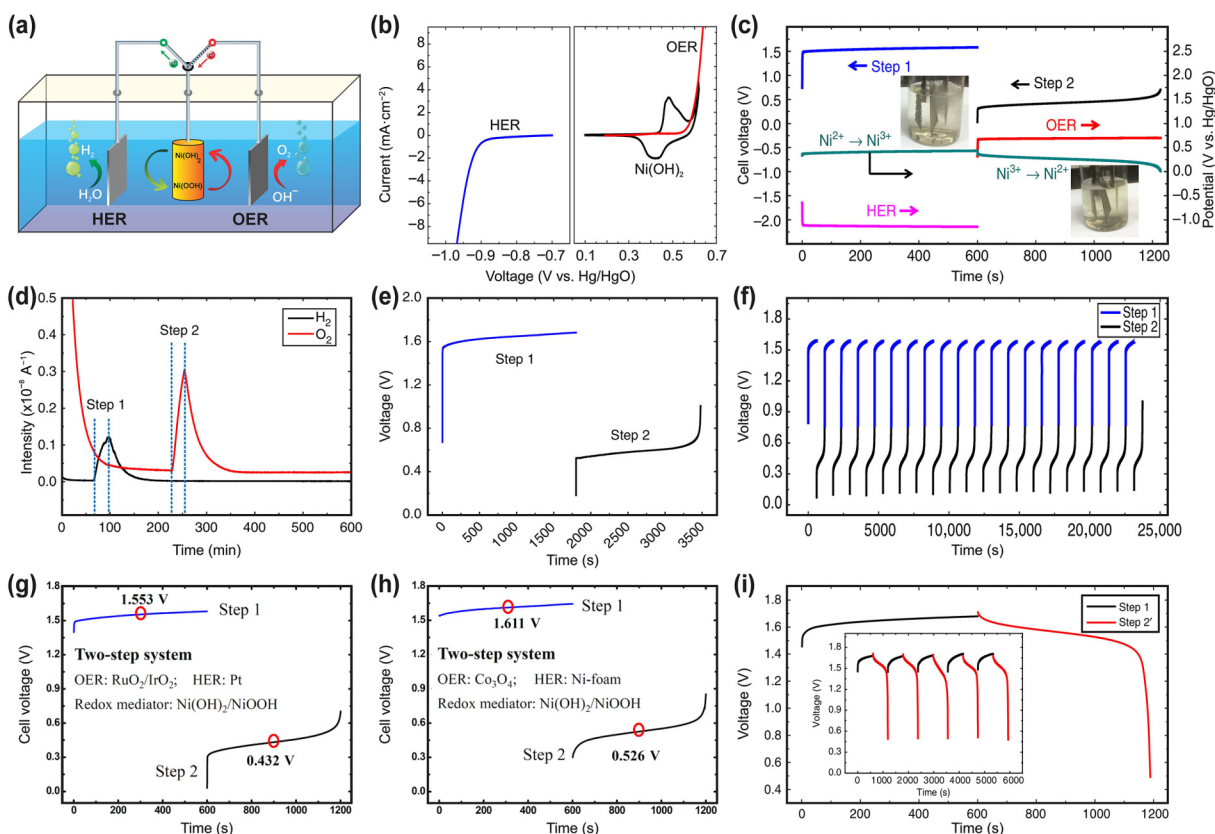


Figure 28 Solid-state redox mediator-based decoupled water splitting of nickel hydroxide. (a) A schematic diagram of the electrolysis of alkaline water occurs in two steps. (b) LSV curves of RuO₂/IrO₂-coated Ti-mesh and Pt-coated Ti-mesh electrodes for OER (red)/HER (blue) at a scan rate of 5 mV·s⁻¹ in 1.0 M KOH. CV of the Ni(OH)₂ film electrode in 1 M KOH at a scan rate of 5 mV·s⁻¹ (black). (c) The cell chronopotentiometry curves, with the voltages for H₂ production in Step 1 (blue) and O₂ generation in Step 2 (black), with an applied current of 200 mA. (d) The H₂ evolution (black line) and O₂ evolution (red line) during overall water electrolysis were measured using *in-situ* DEMS. Between stages 1 and 2, there is a break of 130 min. (e) The *in-situ* DEMS test consists of two phases, as shown by the electrolytic cell chronopotentiometry curve. Step 1 (blue): 30 min of H₂ production. Step 2 (red): 30 min of O₂ production (black). According to the electrolytic cell chronopotentiometry curve, H₂ generation occurs at 1000 mA for 100 s. (f) Chronopotentiometry curves (voltage vs. time) of the H₂/O₂ generation cycle over a step time of 600 s. One-step and two-step system-driven voltage comparison at 200 mA. ((g) and (h)) One-step (inset) vs. two-step precious and non-precious electrode electrolysis. (i) H₂-production chronopotentiometry curves (black) and NiOOH-Zn battery discharge curves (red). Inset: cycle performance of H₂-production above 200 mA. Reproduced with permission from Ref. [179], © The Author(s), 2016.

concluded at 92% for both precious (1.829/1.985 = 92%) and non-precious (1.973/2.137 = 92%) electrodes. This efficiency is higher (92%) than PEM water electrolysis (79%), as reported previously (Figs. 28(g) and 28(h)). The lowering in FE was caused by some hydrogen mixing in an aqueous solution and impendancy (Fig. 28(i)). Conversely, nearly 6 mL of oxygen was produced over 1000 mA applied current in the OER step. Finally, it was observed that hydrogen produced during HER is two times more than oxygen produced during OER with a ratio of 2:1. Further advances, the DWS author integrates the OER step with NiOOH-Zn battery. Step 1 of HER involves the production of H₂ by the oxidation of nickel hydroxide, a solid-state redox mediator (Ni(OH)₂ → NiOOH). In contrast, Step 2 (OER) was coupled with a NiOOH-Zn battery in which the NiOOH-Zn electrode was reduced by anodic oxidation of zinc (Zn → ZnO₂⁻). Hydrogen produced with charge in Step 1 leads to the discharge of NiOOH-Zn battery.

Developing earth-abundant and high-performance electrocatalysts for alkaline media HER is highly desirable. Sun et al. [233] reported that a manganese-doped Ni₂P nanosheet array on nickel foam (Mn-Ni₂P/NF) is an efficient and durable HER electrocatalyst in alkaline media. This Mn-Ni₂P/NF requires an overpotential of only 103 mV to achieve a current density of 20 mA·cm⁻² in 1 M KOH, 82 mV less than that needed for

Ni₂P/NF. Moreover, the catalyst demonstrates strong electrochemical durability, maintaining its catalytic activity for at least 25 h. The electrocatalytic activity of Mn-Ni₂P/NF for HER (Fig. 29(a)) was evaluated in 1 M KOH using a typical three-electrode system. The Pt/C electrode exhibited the highest electrocatalytic activity for HER. To reach a catalytic current density of 20 mA·cm⁻², Mn-Ni₂P/NF required a HER overpotential of just 103 mV, a significant improvement compared to Ni₂P/NF (185 mV). Notably, the HER performance of Mn-Ni₂P/NF surpasses that of other Ni phosphides reported in 1 M KOH, such as Ni₂P nanoparticles ($\eta_{20\text{mA}\cdot\text{cm}^{-2}} = 250$ mV) [234], Ni₂P ($\eta_{20\text{mA}\cdot\text{cm}^{-2}} = 205$ mV) [235], porous Ni₂P polyhedrons ($\eta_{10\text{mA}\cdot\text{cm}^{-2}} = 146$ mV) [236], NiP₂ ($\eta_{20\text{mA}\cdot\text{cm}^{-2}} = 125$ mV) [237], Ni₂P ($\eta_{20\text{mA}\cdot\text{cm}^{-2}} = 120$ mV) [238], reported elsewhere. The HER kinetics of the synthesized samples were analyzed by fitting the Tafel equation to the linear region, revealing Tafel slopes of 138, 135, and 98 mV·dec⁻¹ for Ni₂P/NF, Mn-Ni₂P/NF, and Pt/C, respectively (Fig. 29(b)). Mn-Ni₂P/NF is also effective under neutral and near-neutral conditions, demonstrating good conductivity, mass transport, and mechanical robustness [239, 240]. Additionally, the durability tests of Mn-Ni₂P/NF (Fig. 29(c)) showed negligible loss after 500 cycles of CV. A long-term durability test at a fixed potential of 140 mV for at least 25 h further confirmed the excellent stability of Mn-Ni₂P/NF

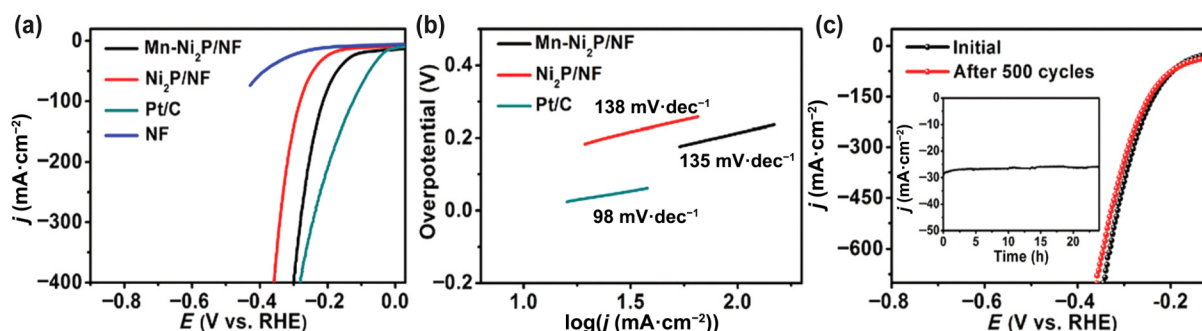


Figure 29 (a) LSV curves of Mn-Ni₂P/NF, Ni₂P/NF, Pt/C, and NF at a scan rate of 5 mV·s⁻¹ for HER in 1 M KOH. (b) Tafel plots of Mn-Ni₂P/NF, Ni₂P/NF, and Pt/C. (c) LSV curves of Mn-Ni₂P/NF catalyst before and after 500 CV cycles in 1 M KOH and time-dependent current density curve (inset). Reproduced with permission from Ref. [233], © The Royal Society of Chemistry 2017.

(Fig. 29(c), inset). The substitution of Ni with Mn in Ni₂P significantly enhances HER performance, making Mn-Ni₂P/NF a promising low-cost catalyst for water splitting devices aimed at large-scale hydrogen production.

A novel PEM electrolyzer design was recently developed, using a soluble molecular redox mediator to promote ECPB between the OER and the HER [172]. This decoupling method has also had significant drawbacks. Its electrochemical and FE for H₂ evolution were relatively low, nearly 63% and 68%, respectively, resulting in an overall efficiency of only 43%, which is also lower than the PEM electrolyzers, having up to 68.3% [14, 241]. To address these issues, Rothschild and coworkers [180] developed a solid-state redox system capable of mediating ion exchange between the anode and cathode in alkaline aqueous solutions, which can be cycled multiple times. NiOOH/Ni(OH)₂, a solid-state redox mediator, was utilized as the auxiliary electrodes (Fig. 30(a)). The AEs were activated through charge–discharge cycles. Discharge capacity increased from 59% in the beginning to 99.6% by the end of the activation process. During 20 h of continuous operation, the current polarity was reversed when the voltage reached a threshold of ±3 V to prevent OER in the hydrogen cell and *vice versa*. The applied voltage gradually increased from 1.8 V at the beginning of each cycle to 2.3 V near the end. The sharp increases at the end of each cycle indicate complete AE discharge, necessitating recharging to continue the process. The first electrolysis cycle lasted 30 min before reaching the threshold voltage, decreasing by 0.3% per cycle to 26 min after 40 cycles (Fig. 30(b)). This decline is attributed to incomplete charging of the AEs in the hydrogen cell. Cycle duration depends on the initial charge of the AEs and the electrolysis current. Throughout the 125 h test, gas bubbles formed on the primary electrodes but not on the AEs. GC analysis confirmed that H₂/O₂ was produced in separate cells with nearly 100% FE and no cross-contamination up to approximately 80% of the charged capacity of the AEs (Fig. 30(c)). Furthermore, the author demonstrates the application of this concept to design a hydrogen refueling station (Fig. 30(d)). In a case study for conventional photoelectrochemical solar cells to produce 400 kg·day⁻¹ hydrogen gas, 30 K·m² area for a solar cell is required with the conversion efficiency of 10%. The 10 cm × 10 cm largest reported PEC cells have an array of 3,000,000 cells [242]. The safety precautions result in massive efforts and expenditures that make conventional solar cells economically nonviable [243, 244]. That is why the author introduced the AEs in a PV-coupled electrolysis system that simulates a PEC–PV tandem cell. The system includes a silicon PV module, Ni foil, Pt-plated stainless steel mesh electrodes, and activated NiOOH and Ni(OH)₂ AEs. This open-cell design minimizes gas bubble formation on the

front window, reducing light intensity at the photoelectrode. Consequently, the efficiency of our PEC cell architecture is comparable to, or even exceeds, that of conventional PEC cells.

Although the standard potential of OER is 1.23 V vs. RHE, it requires a minimum onset overpotential of 200–400 mV due to the sluggish four-electron transfer, with typical values ranging between 350 and 500 mV at a current density of 10 mA·cm⁻². In contrast, the one-electron Ni(OH)₂ is kinetically more favorable, exhibiting lower overpotentials at higher current densities. Furthermore, the reversible potential of Ni(OH)₂-based anodes can be lower than the standard value, depending on their structure and chemical composition. Higher mass loadings and Ni(OH)₂ to carbon/nickel mass ratios are crucial in E-TAC anodes to manage heat during the thermal swing of the E-TAC process. The electrodes operate at room temperature during hydrogen generation, but the entire anode must be heated to approximately 95 °C for oxygen generation. The active Ni(OH)₂ material must release sufficient heat via the exothermic reaction to enable this temperature swing. However, these high mass loadings result in poor rate performance, which is unsuitable for E-TAC water splitting, where the hydrogen production rate needs to match that of conventional electrolyzers. Therefore, neither supercapacitor nor battery-grade Ni(OH)₂ electrodes are suitable as anodes for the E-TAC process. Grader et al. [245] demonstrated that electrochemical thermally activated chemical (E-TAC) water splitting can be effectively achieved using Ni(OH)₂ electrodes electrochemically deposited onto nickel foams. These electrodes exhibited significantly higher electrochemically active surface areas compared to commercial battery electrodes. Additionally, they featured relatively high mass loadings of 50–100 mg·cm⁻², which surpassed the typical mass loadings found in supercapacitor electrodes. This enhanced surface area and mass loading contribute to the improved performance and efficiency of the E-TAC water-splitting process [200].

This study aimed to significantly improve the anode performance in the unique E-TAC process to increase high-surface-area, cobalt-doped nickel nanofibers (NFs) via electrospinning, followed by electro-oxidation to grow a Ni(OH)₂ shell on the fiber surface. Metallic nickel (Ni⁰) and its native oxide (NiO) can be electro-oxidized to β-Ni(OH)₂ in alkaline aqueous solutions by applying an anodic potential above 0.5 V vs. RHE. Electro-oxidation was chosen as the synthesis method because it is simple, requires no additional nickel or cobalt sources, preserves the substrate's high porosity, and promotes excellent adhesion. These structures show significant improvements in charge regeneration capacity, rate capability, and utilization efficiency, leading to enhanced performance in DWS. The cyclic

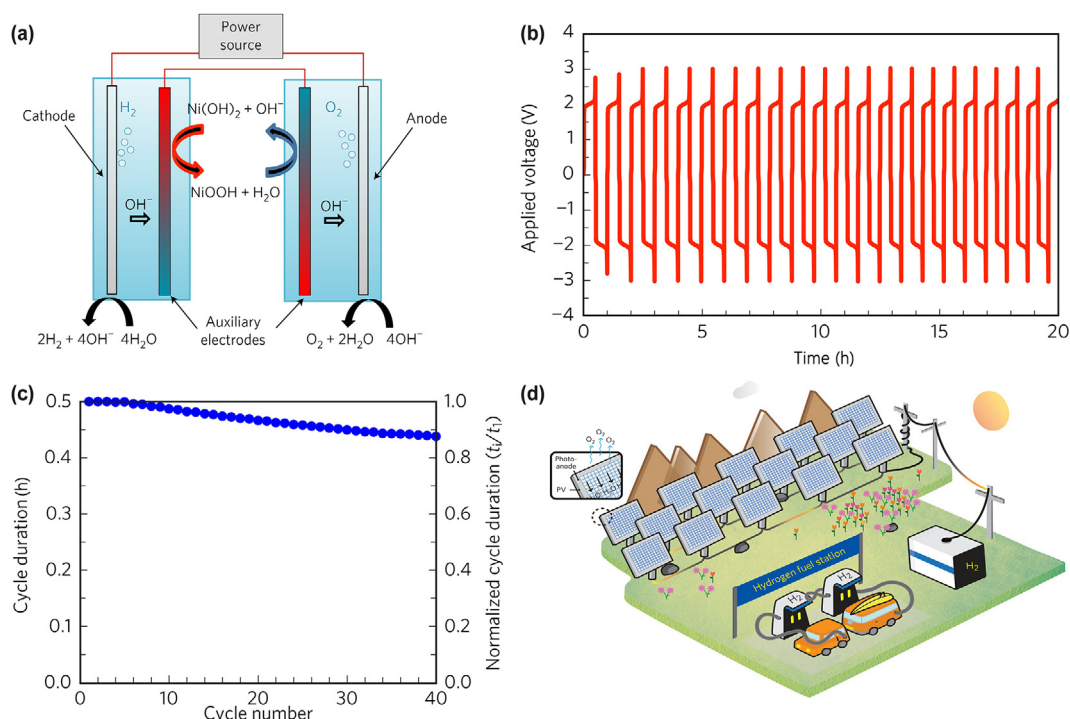


Figure 30 (a) Membrane-free configuration for alkaline water electrolysis. (b) Applied voltage vs. time for 20 h operation at a constant current of 45 mA ($5 \text{ mA}\cdot\text{cm}^{-2}$). (c) The cycle duration vs. the cycle number. The measurement was carried out in 1 M NaOH alkaline aqueous solution. (d) A conceptual representation of solar hydrogen refueling. Reproduced with permission from Ref. [180], © Springer Nature Limited 2017.

voltammetry scan of the undoped Ni/Ni(OH)₂ nickel foam anode (NFA) displayed a single redox wave centered around 1.34 V vs. RHE, providing a reasonable estimate of the anode's reversible redox potential. This reversible potential is a critical electrochemical characteristic for Ni(OH)₂ anodes used in E-TAC water splitting, as the cell voltage during hydrogen generation is closely linked to the oxidation potential of Ni(OH)₂. The thermoneutral voltage for water splitting is 1.48 V, and it is advantageous for the oxygen generation step to proceed faster than the hydrogen generation step to increase hydrogen production. Electrochemically deposited anodes (EDAs) exhibited a capacity loss of $31\% \pm 14\%$.

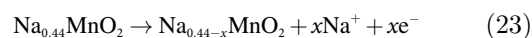
In contrast, the undoped NFAs and cobalt-doped NFAs showed significantly lower capacity losses, with reductions of only $12\% \pm 4\%$ and $13\% \pm 4\%$, respectively. This indicates the superior stability of both undoped and cobalt-doped NFAs in comparison to EDAs. Notably, doubling the hydrogen production time from 100 to 200 s with the cobalt-doped NFA increased hydrogen throughput by 33%, with a capacity loss of less than 4%. This work demonstrates stable and highly efficient DWS using core/shell Ni/Ni(OH)₂ anodes prepared via surface oxidation of electrospun Ni and cobalt-doped Ni NFs. High-rate capabilities can be achieved by increasing the substrate surface area. A discharge voltage was obtained from the NiOOH–Zn battery, which can be cycled similarly to a rechargeable battery. This methodology gives another advantage in that the first step can be initiated with solar irradiation to produce hydrogen during the daytime (charge process). In contrast, the NiOOH–Zn discharge step can operate the electronic devices at night. The redox mediator-based NiOOH–Zn battery can operate a 1.6 V electric fan after the hydrogen production step [179, 245].

In the recently inspiring DWS technology era, the chlor-alkali cell process plays an essential role in decoupling water in a new direction. Chlor-alkali cells often employ asbestos, diaphragms,

mercury, or fluorine ion exchange membranes to separate hydrogen and chlorine. The short lifetime and high cost of membranes led Hou [246] and coworkers to introduce a membrane-free architecture for DWS. Na_{0.44}MnO₂/Na_{0.44-x}MnO₂, a solid-state redox mediator, was applied using the Na⁺ de-intercalation/intercalation technique. Decoupling of water consists of two steps; in the first step, H₂ and NaOH are produced by anodic oxidation of solid-state redox mediator (Na_{0.44}MnO₂ → Na_{0.44-x}MnO₂) with Na⁺ de-intercalation in NaOH alkali solution. In the second step, Cl₂ is produced by cathodic reduction of solid-state redox mediator (Na_{0.44-x}MnO₂ → Na_{0.44}MnO₂) by Na⁺ intercalation in a saturated solution of NaCl. The chlor-alkali industry is traditionally not environmentally friendly due to its high energy consumption and harmful toxic emissions [247–250]. It is hoped that a more sustainable chlor-alkali process may be developed. In the chlor-alkali sector, three new processes were presented: (1) mercury cell, (2) diaphragm cell, and (3) membrane cell from 1888 until now [251, 252]. In fact, the old mercury cell is also a membrane-free chlor-alkali technology, but it cannot be further employed due to its poisonousness. Overall, the reaction mechanism of the DWS can be described in (Eqs. (23)–(26)).

Step 1:

Anode



Cathode

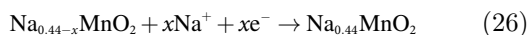


Step 2:

Anode



Cathode



The chlor-alkali approach has many advantages: (1) It is an environmentally friendly redox mediator, (2) it does not use a membrane, (3) it is easy to handle gases due to separate evolution, (4) it is low cost, and (5) it can easily be integrated with renewables. A Pt-coated Ti-mesh electrode was used for the HER in the alkaline electrolyte (NaOH). In contrast, in a brine electrolyte (NaCl), a RuO₂/IrO₂-coated Ti-mesh electrode was used for the chlorine evolution reaction (CER). CV shows reversible redox waves, indicating Na_{0.44}MnO₂ is suitable for DWS (Fig. 31(a)). It is clearly seen during HER in alkaline electrolyte five desodiation peaks at -0.04, +0.08, +0.28, +0.34, and +0.49 V (vs. Hg/HgO) in the range between -0.2 and 0.55 V vs. Hg/HgO on horizontal-axis were attained. Moreover, in a negative sweep in a range from +0.55 to 0.2 V vs. Hg/HgO during CER in NaCl electrolyte, where five peaks at +0.38, +0.25, +0.16, -0.08, and -0.16 V vs. Hg/HgO were attained. The difference between desodiation and sodiation peaks gives ~ 0.11 V potential voltage, suitable for decoupled chlor-alkali-based water splitting. The specific capacity of the redox mediator may be seen in the galvanostatic charge-discharge curves at 0.1 A·g⁻¹. Chronopotentiometry results show that in Step 1, the average cell voltage was ~ 1.3 V for HER, while in Step 2, it is ~ 1.07 V for CER at 100 mA applied current with a step time of 600 s

(Fig. 31(b)). Further investigations of electrolysis cells at higher times and applied currents, i.e., 3600 s and 100, 200, 500, and 1000 mA, respectively, are done to show the performance of the electrolytic cell. At a higher current, 1000 mA, the average voltage on Steps 1 and 2 is ~ 3.65 V. The mediator electrode electrolysis performance may be optimized by regulating the electrode surface area.

In the abovementioned methodology, Steps 1 and 2 were performed in separate cells. These steps can be done collectively in a single cell, but face some issues that no pure NaOH steam would produce. Furthermore, increased NaOH in brine will lead to an OER on the CER electrode. That is why a separate cell design is more fruitful in overcoming undesired issues. Moreover, the chlor-alkali process can be integrated with renewables. Na_{0.44}MnO₂, a solid-state redox mediator, shows long cyclic ability and high efficiency (Fig. 31(c)). Galvanostatic charge/discharge in 1 M NaOH/NaCl solution, respectively, at 100 mA stability produces H₂/NaOH (Step 1) and Cl₂ (Step 2) over 50 cycles by Na⁺ intercalation/deintercalation of Na_{0.44}MnO₂ (Fig. 31(d)). Identical result profiles of Na_{0.44}MnO₂ electrodes both in low concentration NaOH and high 10 M NaOH (30 wt.%), respectively, clarifying the sustainability and long-term durability of the solid-state redox mediator, which can be ideally used in practical applications. *In-situ* DEMS shows hydrogen evolution in Step 1 and Cl₂ evolution

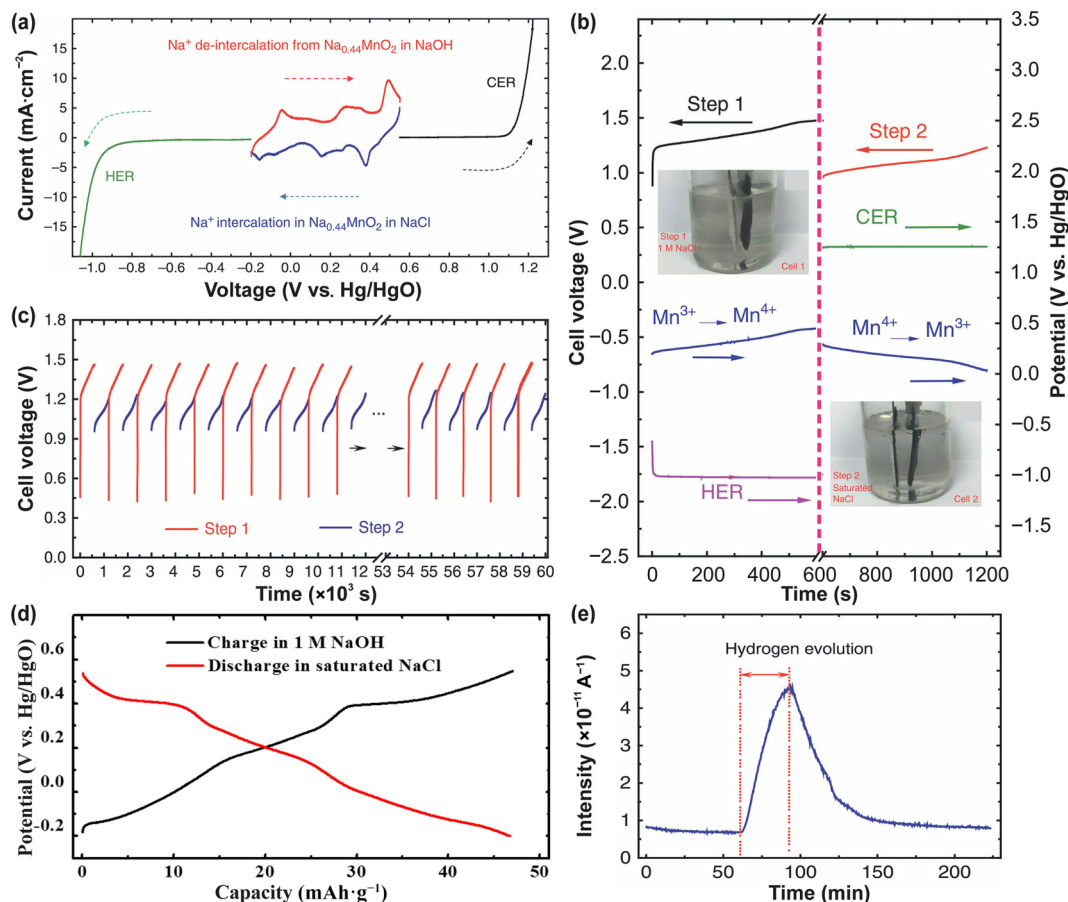


Figure 31 Solid-state redox mediator-based decoupled water splitting using Na_{0.44}MnO₂. (a) Na⁺ intercalation in Na_{0.44}MnO₂ in a saturated NaCl solution (blue) and Na⁺ de-intercalation from Na_{0.44}MnO₂ in 1 M NaOH (red) were measured using an LSV and CV; LSV data of the commercial Pt-coated (green); and RuO₂/IrO₂-coated (black) Ti-mesh electrodes. (b) Two-step chlor-alkali electrolysis (cell voltage vs. time) with a constant 100 mA applied current, showing the formation of NaOH + H₂ in cell 1 (Step 1) and Cl₂ in cell 2 (Step 2). The inset shows pictorial evidence of Steps 1 and 2. (c) Two-step chlor-alkali electrolysis cyclic profiles. Step 1 (red lines) and Step 2 (blue lines). (d) Na_{0.44}MnO₂ cycle performance at a current density of 100 mA·g⁻¹ as depicted by a charge/discharge plot. (e) Measurement of H₂ by *in-situ* DEMS of Na_{0.44}MnO₂ electrode depicting H₂ evolution with a related chronopotentiometry curve at 100 mA of applied current. Reproduced with permission from Ref. [246], © The Author(s), 2018.

in Step 2 (Fig. 31(e)). Before moving the mediator electrode to another compartment for the production of Cl_2 , adsorbed particles on the surface are rinsed away with a NaCl solution. Cl_2 generated at the anode goes to hydrolysis as $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{HCl}$. Shifting solid-state redox mediator from one compartment to another might lead to impurities, i.e., OH^- or Cl^- . That is why the author washed the mediator to minimize the impurities in another compartment. This is the disadvantage of decoupled chlor-alkali electrolysis. The H_2 and Cl_2 concentrations were measured using a drainage technique at 200 mA at 500 s, giving $\sim 100\%$ FE. The volume of Cl_2 obtained was less than that of H_2 because Cl_2 produced at the anode goes to hydrolysis ($\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{HCl}$), affecting the quantity of Cl_2 identified by iodometric titration. The average FE of Cl_2 is 90.2%. In the end, an ion-exchange membrane (Nafion film) was applied between HER and CER to check the performance of the membrane and the membrane-free chlor-alkali process, as discussed above. In this case, H_2 achieved an FE in the membrane cell of almost $\sim 100\%$. Similar to membrane-free examination, the FE of Cl_2 production was 97.4%, which is still lower than 100%, implying the presence of parasitic OER reaction. Finally, it concluded that $\text{Na}_{0.44}\text{MnO}_2$ is a robust solid-state redox mediator that can be used as a decoupling agent to produce hydrogen gas in different and efficient ways. In contrast, transferring electrodes from one compartment to another with the washing process makes the process slower and more complex, which opens new avenues for researchers to automate the process with a new industrial design [246].

Geng et al. [253, 254] designed a low-cost $\text{Na}_{0.44}\text{MnO}_2$ solid-state redox mediator to decouple the evolution of H_2 and O_2 in an alkaline electrolyte, enabling the production of high-purity H_2 without the need for a membrane through a reversible Na^+ storage reaction. Acting as an intermediate charge carrier, the system achieved energy and decoupling efficiencies of 98.7% and 97%, respectively, at a constant current of $1.3 \text{ mA}\cdot\text{cm}^{-2}$. $\text{Na}_{0.44}\text{MnO}_2$ has an orthorhombic crystal system (space group $Pbpm$). $\text{Na}_{0.44}\text{MnO}_2$ exhibits excellent electrochemical performance in decoupled systems, which can be integrated with photovoltaic cells for direct solar-to-hydrogen (STH) conversion. In this decoupled system, the water electrolysis process occurs in two steps. During the first step (hydrogen production), Na^+ is deintercalated from $\text{Na}_{0.44}\text{MnO}_2$ to form $\text{Na}_{0.44-x}\text{MnO}_2$, while H_2O is simultaneously reduced on the Pt electrode. In the second step, OH^- is oxidized on the $\text{RuO}_2/\text{IrO}_2$ electrode to generate O_2 , while Na^+ is intercalated back into $\text{Na}_{0.44-x}\text{MnO}_2$, restoring $\text{Na}_{0.44}\text{MnO}_2$. In a three-electrode system, Hg/HgO and Pt were applied as reference and counter electrodes in 1 M NaOH. CV curve of $\text{Na}_{0.44}\text{MnO}_2$ in an alkaline electrolyte (1 M NaOH) at a scan rate of $1 \text{ mV}\cdot\text{s}^{-1}$ shows four oxidation peaks at 0.1, 0.17, 0.26, and 0.4 V (vs. Hg/HgO), corresponding to the Na^+ deintercalation process from $\text{Na}_{0.44}\text{MnO}_2$. Similarly, the reduction peak during the reverse scan corresponds to the Na^+ intercalation process in the $\text{Na}_{0.44-x}\text{MnO}_2$ electrode. Multiple redox peak pairs indicate a complex mechanism during Na^+ insertion and extraction [255]. The small potential difference (0.05 V) between the main oxidation and reduction peaks reflects the high chemical reversibility of the $\text{Na}_{0.44}\text{MnO}_2$. LSV curve shows that the redox potential of the $\text{Na}_{0.44}\text{MnO}_2$ electrode lies between the onset potentials of HER and OER, confirming that $\text{Na}_{0.44}\text{MnO}_2$ can serve as a redox mediator for DWS in alkaline electrolytes. CV curves at different scan rates, ranging from 0.5 to $5 \text{ mV}\cdot\text{s}^{-1}$, tested indicate that as the scan rate increased, the current intensity also increased, indicating

good reversibility of $\text{Na}_{0.44}\text{MnO}_2$. However, this rise in current led to charge accumulation on the electrodes, resulting in the polarization phenomenon, where the oxidation and reduction peaks shifted. GC analysis shows that only H_2 was detected during Steps 1 and 2; no hydrogen was detected, confirming that $\text{Na}_{0.44}\text{MnO}_2$ effectively decouples the water electrolysis process and generates high-purity H_2 and O_2 . The FE of H_2 generation was approximately 98.7%, with an H_2/O_2 ratio of 2:1, suggesting no side reactions occurred. It is important to note that hydrogen dissolution in the aqueous solution and impedance effects can reduce efficiency. The system demonstrated high stability over more than 400 cycles.

Grader et al. [200] proposed a novel alkaline electrochemical thermally activated chemical (E-TAC) approach to DWS by dividing the water oxidation reaction into two distinct steps. The first step is an electrochemical process in which the anode is oxidized. This is followed by a spontaneous chemical step, where the anode is reduced back to its original state while oxidizing water. During this second step, the formation of the O–O bond occurs, which completes the overall water-splitting reaction. This innovative approach allows for the decoupling of the oxygen and HER, enhancing the efficiency and flexibility of the water splitting processes [256]. The standard redox potential of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ system is 190 mV higher than the reversible OER potential. The incorporation of cobalt into the $\text{Ni}(\text{OH})_2$ structure shifts the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox potential in a cathodic direction, widening the potential window between charging and overcharging. For the $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode, the steady-state water oxidation current is significantly smaller than the pseudocapacitive current. CV for both $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ and NiFe LDH anodes are shown in Fig. 32(a). The $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode displays a pseudocapacitive oxidation related to the Ni^{2+} to Ni^{3+} transition, starting at 1.3 V vs. RHE during the anodic sweep. This oxidation wave appears prior to the onset of water oxidation currents in both anodes. Unlike the NiFe LDH anode, where most of the net current originates from water oxidation (Fig. 32(b)), the $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode shows primarily pseudocapacitive behavior. The addition of cobalt enhances the performance of the anode, enabling it to reach a higher state of charge (SOC) without triggering undesirable oxygen evolution. This improvement allows for more efficient and controlled water splitting, with better utilization of the anode capacity before oxygen evolution begins.

The E-TAC cycle is safer and more efficient for hydrogen production. When the fully discharged anode was charged at a potential of 1.48 V vs. RHE, the FE was 99.7% for over 2000 s, with an accumulated charge of more significant than $50 \text{ C}\cdot\text{cm}^{-2}$. The ability of the $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode to charge at lower potentials makes it a promising candidate for grid-scale applications. Fully discharged anode at a constant potential of 1.48 V vs. RHE when charged to $55 \text{ C}\cdot\text{cm}^{-2}$, there was no detectable increase in the dissolved oxygen (DO) concentration. GC measurements show increased hydrogen concentration without a corresponding rise in oxygen concentration found in the headspace. These findings confirm that no parasitic side reactions occur during charging in E-TAC. $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode was oxidized to $\text{Ni}_{0.9}\text{Co}_{0.1}\text{OOH}$ in a 5 M KOH aqueous solution (pH = 15). $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ is charged under thermoneutral voltage (1.48 V) to minimize side reactions; otherwise, NiOOH will transform from the β -phase to the γ -phase [257–260]. FE was calculated to be $99.2\% \pm 0.1\%$. The charged anode was transferred from the cold cell to a hot ($T = 95^\circ\text{C}$; here T is temperature) electrolyte (5 M KOH) for 100 s and *vice versa* for the hydrogen

generation step. During each of the charging steps, the cell voltage and anode potential showed a consistent increase with minimal variability between cycles and no significant drift over time (Fig. 32(c)). Overall, the anode potential ranged from 1.37 to 1.45 V vs. RHE and remains well below the OER. The voltage efficiency of the E-TAC process was 98.7% across all ten cycles. 6.4 mL of hydrogen was generated at 1 atm and 25 °C during ten cycles. This process consumed 20.8 mWh of energy based on the current and cell voltage measurements (Fig. 32(d)). The E-TAC process utilized low energy consumption, requiring only 3.24 kWh·m⁻³ of hydrogen, or 39.9 kWh·kg⁻¹ of hydrogen. To scale up these laboratory tests into an operational prototype system that generates pure hydrogen and oxygen gas separately, the author proposed a multi-cell system (Fig. 32(e)). This system would have stationary anodes and cathodes in each cell, operating in a swing configuration. During hydrogen production, a low-temperature electrolyte would circulate through cell A, transporting hydrogen bubbles to the hydrogen separator. Concurrently, a hot electrolyte

would flow through cell B to regenerate the previously charged anode, producing oxygen and moving the oxygen bubbles to the oxygen separator. The entire system would operate without moving electrodes, relying solely on the movement of hot and cold electrolyte solutions (Figs. 32(f) and 32(g)). This unique multi-cell configuration, combined with the efficient E-TAC process, presents a promising pathway for scalable and sustainable hydrogen production with minimal energy input and without the complexities of moving parts or electrode degradation [200].

Previously reported decoupled mediator-based water splitting operates in acidic or alkaline solutions. During DWS, pH is versatile in controlling the overall reaction. In this strategy, Dong et al. [261] introduced a new MnO₂/Mn²⁺ solid-state redox mediator, which operates in both acidic and alkaline atmospheres simultaneously using a bipolar membrane (Fig. 33(a)). PEM and alkaline electrolyzers are mostly used for water electrolysis. Additionally, amphoteric DWS is further incorporated with an Mn-Zn battery. HER is more favorable in acidic and OER in

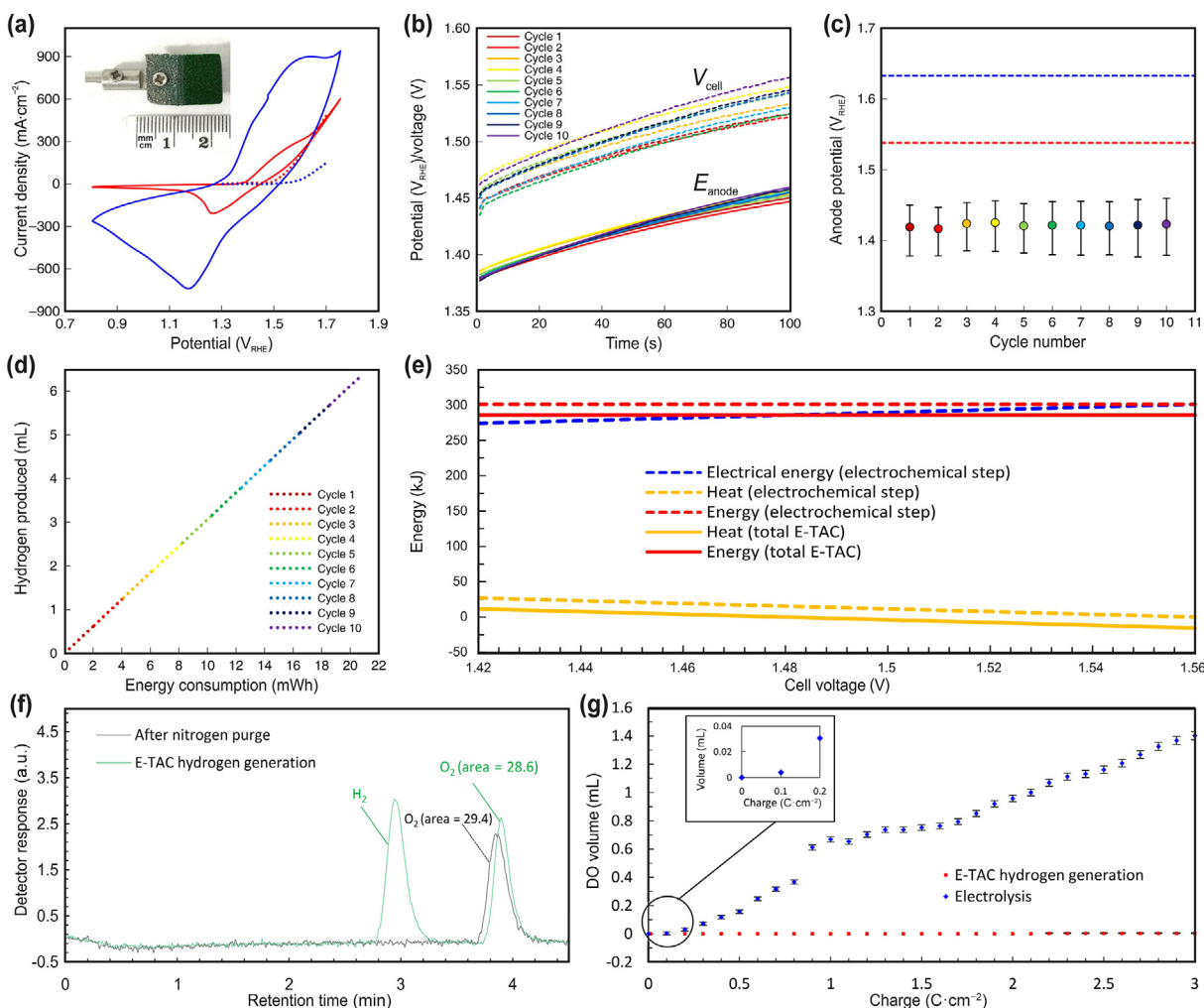


Figure 32 Solid-state redox mediator-based decoupled water splitting using $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$. (a) CV curves of $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ (blue curve) and NiFe LDH (red curve) anodes measured at a scan rate of 50 mV·s⁻¹ in 5 M KOH at ambient temperature. Inset: $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode. (b) E-TAC water splitting in alkaline solution over a current density of 50 mA·cm⁻² in 5 M KOH solution. Anode potential (E_{anode} = full lines) and cell voltage (V_{cell} = dashed lines) throughout the H_2 production phases of ten successive 100/100 s cycles. (c) Average anode potential (E_{anode} = dots) and its standard deviation (bars) throughout a single cycle. (d) Production of H_2 across several E-TAC cycles as a function of electrical energy input (at 1 atm and 25 °C). (e) Electrical, thermal, and total energy needs of the E-TAC process as a function of cell voltage. (f) E-TAC H_2 gas chromatograms were acquired by maintaining a constant current density of 50 mA·cm⁻² for 100 s in a 5 M KOH solution without heating a sample. (g) Quantification of dissolved oxygen. The amount of DO measured during the H_2 production stage of the E-TAC cycle (red-dotted line) using a regenerated $\text{Ni}_{0.9}\text{Co}_{0.1}(\text{OH})_2$ anode and the amount calculated during a control test of water electrolysis (blue line) using an uncoated nickel foam anode. Without applying any heat, readings were taken in a 0.5 M KOH solution at 100 mA (current density of 10 mA·cm⁻²). Reproduced with permission from Ref. [200], © The Author(s), 2019.

alkaline electrolytes. Pt for HER, while Ir or Ru for OER are the ideal catalysts in an acidic atmosphere with minimum overpotentials. For an alkaline atmosphere, Ni, Co, and Fe (VIII group 3d metals) are efficient catalysts for OER kinetics. HER/OER kinetics are pH dependent, so to control this, a newly emerging strategy, amphoteric decoupled water electrolysis, was introduced. As part of this approach, a BPM was partitioned into two halves, one involving HER in acidic electrolytes and the other involving OER in alkaline electrolytes. BPM has two types of voltage losses, Ohmic loss and activation loss, which are greater than those of monopolar ion-exchange membranes. Voltage loss of BPM is directly proportional to current density. Higher current densities cause degradation of BPM. Previously reported studies on amphoteric water electrolysis work on low current densities of nearly $50 \text{ mA}\cdot\text{cm}^{-2}$. To operate amphoteric DWS to produce H_2 at higher current densities, a high-performance $\text{MnO}_2/\text{Mn}^{2+}$ solid-state redox mediator was used, which operates up to $1 \text{ A}\cdot\text{cm}^{-2}$ for HER and low for OER. In addition, an Mn–Zn battery can be included in the system to store and convert energy. A three-electrode arrangement was employed to investigate DWS. HER and carbon-felt electrodes were dipped in an acidic electrolyte in one cell compartment, while the OER electrode was dipped in an alkaline electrolyte separated by a bipolar membrane. Mn^{2+} was

oxidized to MnO_2 and deposited on carbon felt to produce hydrogen at the cathode.

There is no need for a membrane between the HER and carbon felt electrodes because the deposited MnO_2 does not mix with the HER electrode. The deposited MnO_2 was converted back to Mn^{2+} and dissolved in the acidic electrolyte by evaporating oxygen at the OER electrode. CV results show the onset potential of Mn^{2+} to MnO_2 was 1.1 V vs. Ag/AgCl on carbon felt electrode in $1 \text{ M MnSO}_4 + \text{H}_2\text{SO}_4$ solution. Moreover, LSV shows 1.6 V vs. Ag/AgCl onset potential for OER was calculated in $1 \text{ M H}_2\text{SO}_4$, which was higher than the solid-state redox mediator ($\text{MnO}_2/\text{Mn}^{2+}$) (Fig. 33(b)). Furthermore, in 2 M KOH electrolyte, 0.4 V vs. Ag/AgCl OER potential was calculated, which was 0.7 V lower than redox mediator $\text{MnO}_2/\text{Mn}^{2+}$ (1.1 V). To test the viability of two-electrode, decoupled amphoteric water electrolysis, the LSV curves of both the HER and OER are monitored. It is clearly noted that LSV curves of HER require lower voltage using $1 \text{ M MnSO}_4 + \text{H}_2\text{SO}_4$ electrolyte in the presence of a redox mediator as compared to acidic or alkaline media (Figs. 33(e) and 33(f)). For DWS ($-1.37/-1.58 \text{ V}$), while for conventional water electrolysis ($-1.58/-1.84 \text{ V}$), the external input voltage is required at lower ($10 \text{ mA}\cdot\text{cm}^{-2}$) and higher ($100 \text{ mA}\cdot\text{cm}^{-2}$) current densities, respectively, to decouple HER. DEMS analysis indicates that pure

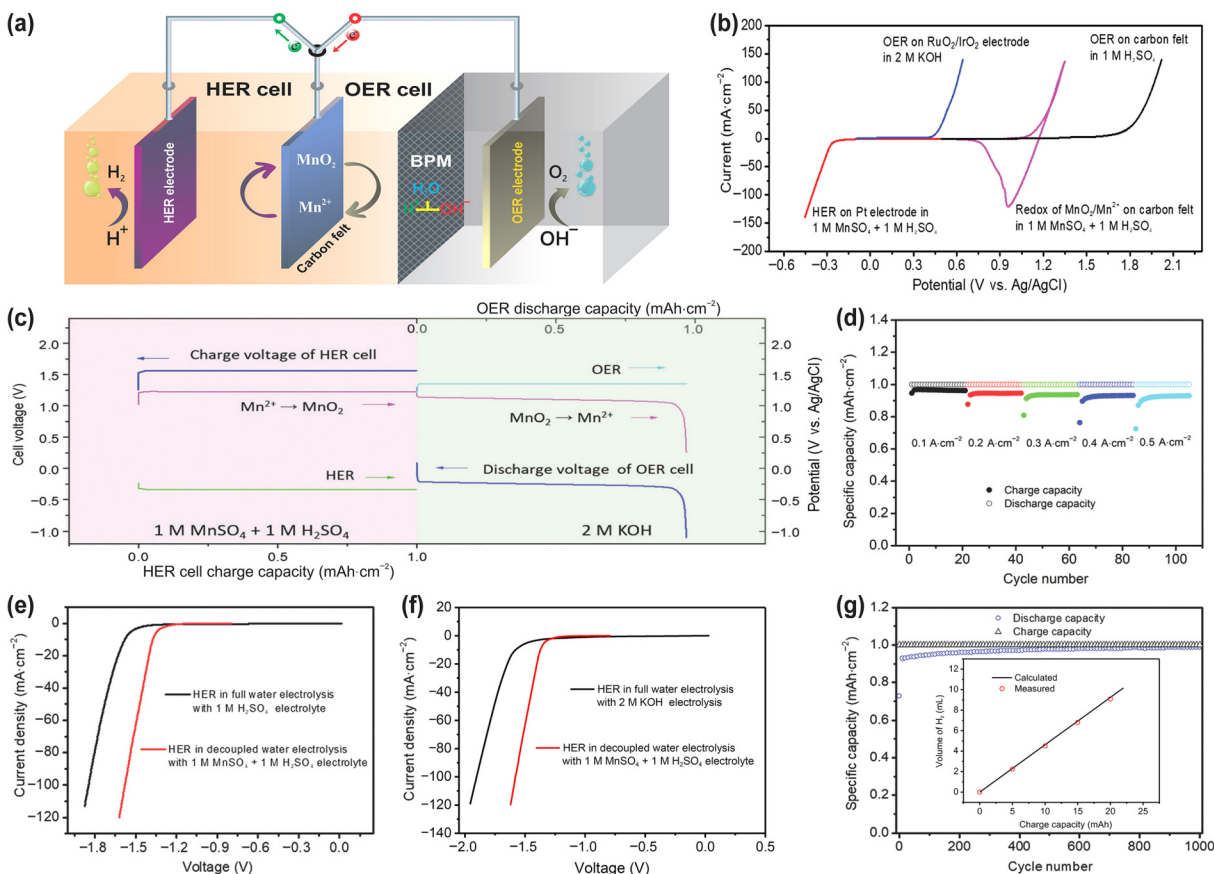
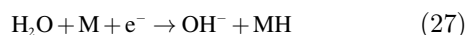


Figure 33 Solid-state redox mediator-based decoupled water splitting using $\text{MnO}_2/\text{Mn}^{2+}$. (a) Schematic diagram of amphoteric DWS. Left of the BPM: HER cell for H_2 production in acidic electrolytes (pink). Right of the BPM: OER cell for O_2 production in alkaline electrolytes (pale green). (b) CV and LSV curves of $\text{MnO}_2/\text{Mn}^{2+}$ redox mediator at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ in different electrolytes. (c) H_2 production in HER cells at $100 \text{ mA}\cdot\text{cm}^{-2}$ (left section) and O_2 generation in OER cells at $10 \text{ mA}\cdot\text{cm}^{-2}$ (right portion) are shown as potential curves. OER cells require external voltage bias due to their negative discharge platform. (d) Cyclic performance of $\text{MnO}_2/\text{Mn}^{2+}$ redox mediator. (e) LSV curves of HER electrode in 1 M sulphuric acid (black) and $1 \text{ M MnSO}_4 + 1 \text{ M H}_2\text{SO}_4$ (red) electrolytes. Conventional water electrolysis needs -1.84 V , while decoupled electrolysis needs -1.58 V to achieve $100 \text{ mA}\cdot\text{cm}^{-2}$, demonstrating a 260 mV advantage for the decoupled HER. (f) LSV curves of the HER electrode in two different electrolytes: 2 M KOH (black) and $1 \text{ M MnSO}_4 + 1 \text{ M H}_2\text{SO}_4$ (red). Conventional water electrolysis needs -1.9 V , while decoupled electrolysis needs -1.58 V to achieve $100 \text{ mA}\cdot\text{cm}^{-2}$, demonstrating a 320 mV advantage for the decoupled HER. (g) Cyclic performance of $\text{MnO}_2/\text{Mn}^{2+}$ redox mediator at $500 \text{ mA}\cdot\text{cm}^{-2}$; inset: H_2 production in HER cells at $100 \text{ mA}\cdot\text{cm}^{-2}$, a comparison of experimental and theoretical H_2 volumes. Reproduced with permission from Ref. [261], © The Royal Society of Chemistry 2021.

H₂ gas evolved during HER. Bipolar membrane shows dual behavior as a cation-exchange membrane (CEM) and an anion-exchange membrane (AEM). CEM and AEM faced acidic and alkaline electrolytes in amphoteric DWS, respectively. In OER, voltage bias increases with the increase of current density. At 10 mA·cm⁻², 1.37/0.24 V voltage bias is required for HER and OER in decoupled amphoteric water electrolysis, respectively. Combining HER and OER voltage, an overall 1.61 V bias voltage is required to initiate amphoteric DWS using BPM. While 1.58 V is needed for traditional one-step coupled acidic water electrolysis (Fig. 33(c)). Comparing conventional and amphoteric DWS (1.58/1.61) = 98.1%, a high voltage efficiency was quantified, which was higher than previously reported DWS studies. Utilizing low-power renewables like solar is feasible for OER (0.24 V at 10 mA·cm⁻²) to produce O₂, while high-power inputs, i.e., from wind, can drive HER (1.56 V at 100 mA·cm⁻²). This decoupled amphoteric system works at different current densities simultaneously with improved efficiency. MnO₂/Mn²⁺ has a low cost with a high reversibility value. The discharge capacity retention value of MnO₂/Mn²⁺ is 95.9%, demonstrating its high-performance rate. Over 1000 cycles, the MnO₂/Mn²⁺ redox mediator has maintained 98.7% CE (Figs. 33(d) and 33(g)).

The orientation of the bipolar membrane plays a better role during DWS. CEM faces acidic electrolytes, while AEM faces alkaline electrolytes of BPM, respectively. The DWS efficiency of the BPM increases when the CEM side faces the acidic electrolyte. Amphoteric DWS is not effective when the CEM side of the BPM is exposed to alkaline electrolytes, as this causes the BPM to degrade and increases the need for both acidic and alkaline electrolytes. MnO₂/Mn²⁺ redox mediator can be used in Mn–Zn batteries with integration with decoupled amphoteric water splitting by introducing Zn anode in alkaline electrolytes. Mn²⁺ was oxidized to MnO₂ during HER, while Zn²⁺ was reduced to metal zinc. Over a complete process of HER/OER, a charged voltage of 1.72 V at 10 mA·cm⁻² was obtained. This integrated system shows outstanding flexibility in producing hydrogen with the recharging capacity of the Mn–Zn battery [261].

Gibbs free energy for the dissociation of water into hydrogen and oxygen is calculated to be 237.1 kJ·mol⁻¹ H₂. Metal hydrides (MHs) were utilized in DWS due to their reversible hydrogen adsorption/desorption behaviors [262, 263]. This is a two-step process: In the first step, electrochemical hydrogenation occurs by reduction of water at the cathode with hydrogen absorption at MH, while in the second step, thermal dehydrogenation of adsorbed hydrogen at MH occurs with the release of H₂ (Fig. 34(a)). MH-mediated water splitting requires low electrical voltage as compared to traditional water splitting. This decoupling strategy is the new addition in DWS, in which H₂ and O₂ are produced at different times and spaces with a new pattern (Eqs. (27) and (28))



For this purpose, Li et al. [264] applied a Pd-coated yttrium hydride (YH_x) thin film electrode and Pd-coated LaNi_{4.5}Al_{0.5} electrode with alkaline electrolyte (KOH) for DWS to study hydrogen adsorption/desorption behavior. Cyclic voltammetry shows a reductive peak at 0.7 V of Pd–O species (Fig. 34(b)). Hydrogen adsorption on noble metals like Pt and Pd undergoes an underpotential region called underpotential deposition (UPD).

H-UPD peak is clearly shown at +0.2 V vs. RHE. Synchronized transmittance shows that H is absorbed in the YH₂-Pd electrode during the electrochemical step. Absorbed hydrogen in YH_{2+δ}-Pd electrode reversibly releases H when transmittance decreases to a certain level ~ 100 s, which can be seen in the discharge plateau at 0.2–0.3 V. An increase in optical transmittance from 0%–1.7% shows hydrogen adsorption at the YH_x-Pd electrode (Fig. 34(c)). The current density during the electrochemical hydrogenation process was maintained at 0.1 mA·cm⁻². YH_x-Pd electrode potential remains in the underpotential region from 0.29 to 0 V in ~ 1400 s, while for the Pt foil electrode, it further decreases from –0.04 to –0.07 V simultaneously. In the thermal dehydrogenation step, the hydrogenated YH_{2+δ}-Pd electrode was placed in an alkaline electrolyte with a specific temperature range, where absorbed hydrogen reversibly evolved, which can be clarified by the decrease in optical transmittance. The processes of electrochemical hydrogenation and thermal dehydrogenation that are repeated to demonstrate MH-mediated water splitting are shown in (Fig. 34(c)). Structural analysis of the YH_x-Pd electrode shows its increased stability, saving up to 25 kJ·(mol H₂)⁻¹ electrical energy by utilizing low-grade heat energy below 70 °C. Interconversion of YH₃ to YH₂ is reversible with little ΔG = 0.12 eV. YH_x-Pd electrode over 40 cycles shows high-profile stability for electrochemical hydrogenation and thermal dehydrogenation (Fig. 34(d)). Due to the addition of thermal energy during the water-splitting process, the total energy does not change despite reduced electrical energy. A DWS approach aims to reduce the need for high-quality electrical energy by replacing it with lower-quality energy produced by integrating renewable sources.

A bare yttrium electrode cannot absorb hydrogen, so a Pd coating is required to start the hydrogenation process. The 10 nm thick Pd layer sandwiched between yttrium and alkaline solution serves as a bridge to transport H from alkaline electrolytes and store it in the yttrium electrode. Furthermore, stored H at the YH_x-Pd thin film electrode is too low, which cannot be detected easily; that is why increasing the quantity of H in the powdered LaNi_{4.5}Al_{0.5}-Pd coated electrode is utilized to improve the stored H and release enough H₂ during thermal dehydrogenation. LaNi_{4.5}Al_{0.5} is the best hydrogen storage alloy widely used in Ni–MH batteries. Both hydrogen gas and oxygen gas were produced in the thermal and electrolytic stages of water splitting mediated by MH. RuO₂ acts as an anode, LaNi_{4.5}Al_{0.5}-Pd acts as a cathode, and HgO/O acts as a reference electrode. In the hydrogenation step (Step 1), hydrogen was absorbed in the LaNi_{4.5}Al_{0.5}-Pd electrode, and only O₂ was released at the anode (RuO₂) with no release of H₂. In contrast, in the thermal dehydrogenation step (Step 2), the LaNi_{4.5}Al_{0.5}H_x-Pd electrode dipped into KOH electrolyte on heating, nearly at 70 °C, released absorbed H₂ rapidly. 40–70 °C is a moderate temperature range for dehydrogenation. Increasing temperature leads to more release of hydrogen. Keeping the electrode in underpotential condition during 40 min electrolysis saved approximately 7.3 kJ·mol⁻¹ H₂ electrical energy during each cycle. Potential profiles of both the hydrogenation and dehydrogenation steps prove excellent DWS reversibility. MH-mediated water splitting has ~ 100% FE for the abovementioned electrode. Low FE has many reasons, like overcharging during electrochemical hydrogenation, dehydrogenation at ambient temperatures, low MS signal during the low release of H₂, and side reactions. At the same time, structural analysis and cyclic potential profiles suggest that the LaNi_{4.5}Al_{0.5}-Pd electrode has 100% FE (Figs. 34(e)–34(g)).

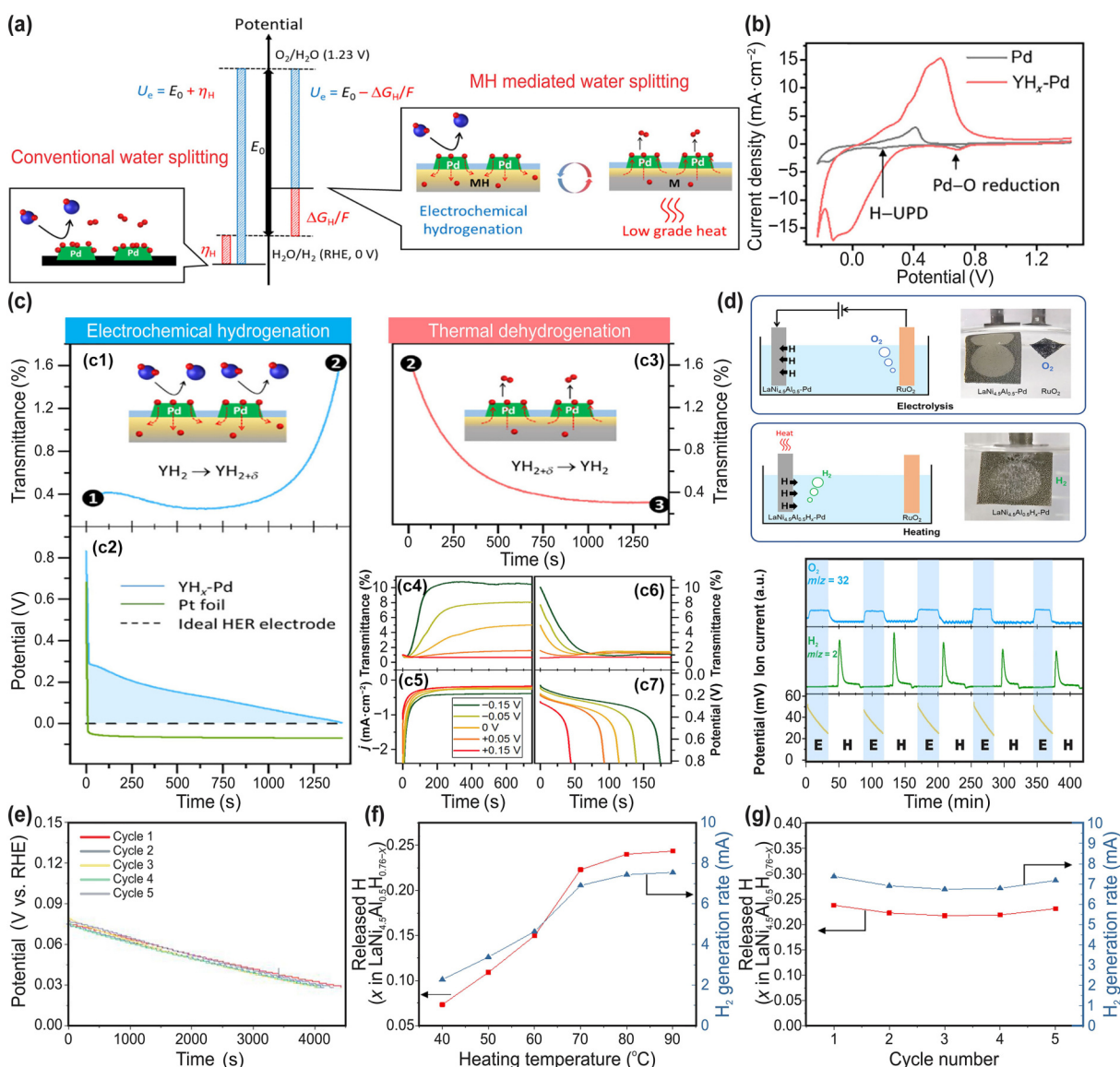


Figure 34 Solid-state redox mediator-based decoupled water splitting using metal hydride. (a) Schematic depiction of hydrogen production via conventional water splitting and MH mediated water splitting. (b) CV curves of the $\text{YH}_x\text{-Pd}$ and pure Pd electrodes at 0.05 V vs. RHE. (c) Synchronized optical transmittance and potential profiles ((c1) and (c2)) at 0.1 $\text{mA}\cdot\text{cm}^{-2}$ at 298 K of the $\text{YH}_x\text{-Pd}$ electrode during electrochemical hydrogenation. (c3) $\text{YH}_x\text{-Pd}$ electrode optical transmittance at 298 K at an open circuit potential. ((c4) and (c5)) Synchronized optical transmittance and current density profiles at a constant potential. Inset: hydrogenation potential (vs. RHE). ((c6) and (c7)) Synchronized optical transmittance and potential profiles of the hydrogenated $\text{YH}_x\text{-Pd}$ thin film electrode at 0.4 $\text{mA}\cdot\text{cm}^{-2}$ for anodic current. (d) Schematic diagram of the decoupled O_2/H_2 production by an interchanged process of the electrolysis (E) and heating (H) steps. $\text{LaNi}_{4.5}\text{Al}_{0.5}\text{-Pd}$ electrode potential (vs. RHE) and the evolved H_2/O_2 . The thermal dehydrogenation temperature is 70 °C, while the current density in the metal hydride electrolysis is 12 $\text{mA}\cdot\text{g}^{-1}$ (2.3 $\text{mA}\cdot\text{cm}^{-2}$). (e) Cyclic performance (voltage vs. time) during five cycles in 6 M KOH solution. The current is 3 mA, which is equivalent to the current density of 12 $\text{mA}\cdot\text{g}^{-1}$ or 3.8 $\text{mA}\cdot\text{cm}^{-2}$ in geometric area. Thermal dehydrogenation of the anode is carried out at 70 °C for 30 min. (f) The amount of H_2 released and the average H_2 generation rate in 30 min during the heating step at different dehydrogenation temperatures. (g) The amount of H_2 released and the average H_2 generation rate in 30 min during the heating step over 5 cycles. Reproduced with permission from Ref. [264], © Elsevier Ltd. 2021.

Previously reported DWS strategies have high theoretical electrical energy values higher than $\Delta_f G(\text{H}_2\text{O})$, where $\Delta_f G$ is formation Gibbs free energy. However, in MH-mediated water splitting, authors saved the electrical energy and H_2 and O_2 production at different times and spaces. Furthermore, MH-mediated water splitting opens new research directions for researchers. More studies on MHs can improve the performance and efficiency of DWS [264].

The necessity of DWS to generate green energy (H_2) has led to recent growth in the library of solid-state redox mediators. Yang et al. [265] made a fruitful addition to solid-state redox mediator with high-profile performance (Fig. 35(a)). In membrane-free

decoupled water electrolysis, the Prussian blue analog (PBA) (Turnbull's blue analog (TBA)) was employed as a solid-state redox mediator in an acidic electrolyte (0.5 M H_2SO_4). This mediator has excellent rate performance (42.7 $\text{mAh}\cdot\text{g}^{-1}$) at 120 $\text{A}\cdot\text{g}^{-1}$ and excellent cyclability (> 5000 cycles). TBA- $[\text{Fe}(\text{CN})_6]^{3-}$ is a defective part of PBAs that was utilized, which works on the Grotthuss proton conduction mechanism [266–270]. $\text{Cu}[\text{Fe}(\text{CN})_6]_{2/3}\cdot 3.4\text{H}_2\text{O}$ (CuFe-TBA) solid-state redox mediator shows 61% capacity retention at a current density of 1 $\text{A}\cdot\text{g}^{-1}$ over 5000 cycles. Decoupling of water occurs in two steps: In Step 1, H_2O oxidizes on the anode, and CuFe-TBA reduces at the cathode with the release of O_2 , while in Step 2, r-CuFe-TBA

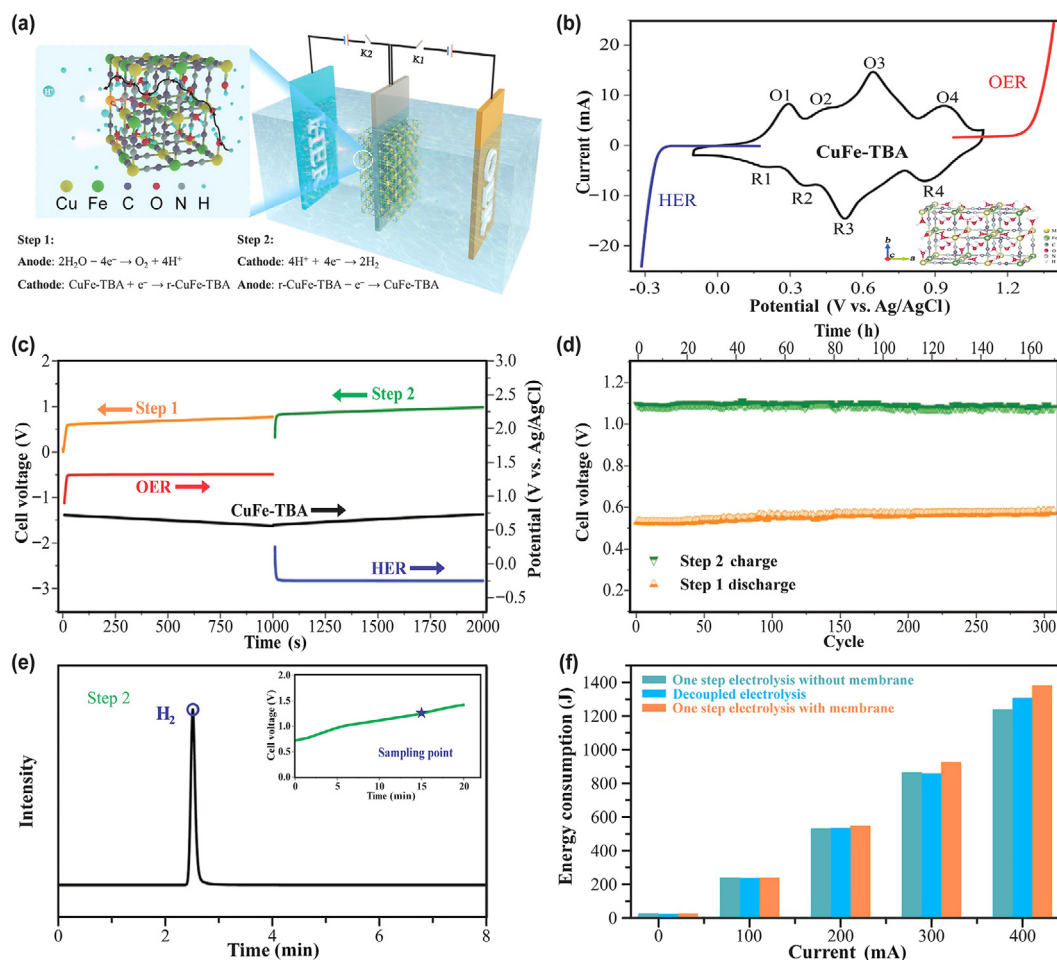
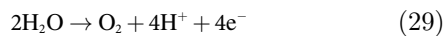


Figure 35 Solid-state redox mediator-based decoupled water splitting using TBA of Cu[Fe(CN)₆]_{2/3}·3.4H₂O (CuFe-TBA). (a) Schematic diagram. (b) CV curves at a scan rate of 10 mV·s⁻¹ in 0.5 M H₂SO₄ of the CuFe-TBA film electrode (black). The inset shows the CuFe-TBA structure. (c) The Chronopotentiometry curves of the DWS. Orange and green lines indicate O₂ (Step 1) and H₂ (Step 2) production cell voltages. OER, HER, and CuFe-TBA electrode potential are measured at 5 mA with a step time of 1000 s. (d) Stability performance at 10 mA with a step time of 1000 s. (e) Gas chromatography of HER. Inset: corresponding chronopotentiometry curve (voltage vs. time) of H₂ generation by water electrolysis, where the asterisk symbolizes the sampling time. (f) Energy usage of the three water electrolysis systems at varied currents for 20 min. Reproduced with permission from Ref. [265], © Wiley-VCH GmbH 2021.

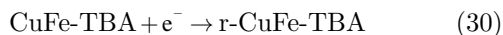
oxidizes at the anode and protons reduce at the cathode with the release of H₂ (Eqs. (29)–(32)).

Step 1:

Anode

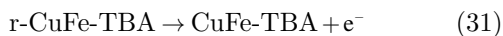


Cathode



Step 2:

Anode



Cathode



Cyclic voltammetry shows that the CuFe-TBA electrode has four reversible redox peaks at 0.29/0.22, 0.44/0.36, 0.64/0.53, and 0.93/0.86 V (vs. Ag/AgCl) over a scan rate of 10 mV·s⁻¹ (Fig. 35(b)). The first low potential peak O₁/R₁ is for the oxidation and reduction state of Cu/Cu^{II}, while the other three O₂/R₂, O₃/R₃,

and O₄/R₄ peaks, represent the oxidation and reduction state of Fe^{II}/Fe^{III}, respectively. With three different electrode configurations in an acidic electrolyte, HER was accomplished with a Pt-coated-Ti-mesh electrode, and OER was performed with a RuO₂/IrO₂-coated-Ti-mesh electrode. CuFe-TBA redox wave fits in between LSV curves of HER, and OER signifies its good reversibility and can be used in DWS. CV measurements at scan rates ranging from 1 to 30 mV·s⁻¹ reveal that the value of *b* for four anodic peaks is very close to 1.0, demonstrating its rapid kinetics. Galvanostatic charge–discharge measurements were taken in the range of –0.1 to 1.1 V (vs. Ag/AgCl) in 0.5 M H₂SO₄ electrolyte, demonstrating that CuFe-TBA has a reversible capacity over current densities of 80 mAh·g⁻¹/0.5 A·g⁻¹ and 42.7 mAh·g⁻¹/120 A·g⁻¹, respectively. Increasing the concentration of H₂SO₄ to 2 M gives an excellent reversible capacity of 46 mAh·g⁻¹ at a high current density of 400 A·g⁻¹. CuFe-TBA electrode has low charge–discharge capacity in 1 M Na₂SO₄ when replaced with H₂SO₄ electrolyte. CuFe-TBA has a large number of vacancies and abundant lattice water, which makes an H-bond network. 100% CE with 54% capacity retention was obtained when tested at 10,500 cycles at 5 A·g⁻¹, confirming its long-term cyclability. The structural stability through XRD indicates that CuFe-TBA has long-term stability during galvanostatic charge/discharge by maintaining a face-centered

cubic structure. The CuFe-TBA shows reversible lattice contraction and expansion by proton insertion/de-insertion at peak (200). The CuFe-TBA performs better than other TBA materials like MnFe-TBA, FeFe-TBA, NiFe-TBA, and CoFe-TBA. CoFe-TBA has one redox peak, while NiFe-TBA shows two redox peaks in CV curves. Due to improved redox reversibility, CoFe-TBA and NiFe-TBA give 76 and 54 mAh·g⁻¹ reversible capacity, respectively, except for two Mn/Fe-TBA materials. CoFe-TBA and NiFe-TBA can also be used as decoupling agents in acidic water electrolysis. The PEM-free water electrolysis cell used a Pt-coated-Ti-mesh cathode and a RuO₂/IrO₂-coated anode with a CoFe-TBA thin film electrode as the redox mediator. Chronopotentiometry results of a decoupled electrolytic cell over a current density of 5 mA with a step time of 1000 s show that in Step 1 (OER step), a cell voltage of ~0.68 V was acquired, which is the potential difference between the anodic potential of water oxidation by the cathodic potential of CuFe-TBA reduction. In contrast, in Step 2 (HER step), a cell voltage of ~0.90 V was acquired by a potential difference of anodic potential of CuFe-TBA oxidation by the cathodic potential of water reduction (Fig. 35(c)). Overall, a cell voltage of 1.58 V was obtained in the decoupled water electrolysis. This value is higher than the conventional membrane-free electrolyzer (RuO₂/IrO₂-Pt) of 1.57 V due to internal losses. Furthermore, CuFe-TBA electrodes show operational flexibility in DWS over higher current densities, i.e., 50, 200, and 400 mA. The cyclic profiles of DWS over 10 mA with a step time of 1000 s show that after 300 consecutive cycles of ~170 h, the cell voltage remains the same, which verifies the excellent stability of the decoupled electrolytic cell (Fig. 35(d)). Gas chromatography results indicate that during Step 1, pure O₂ was generated and detected without the evolution of H₂. In contrast, in Step 2, pure H₂ was produced and detected without the evolution of O₂ over a constant applied current of 50 mA (Fig. 35(e)). These results show that both H₂ and O₂ were decoupled and obtained at different time and space. The capacity utilization of many solid-state redox mediators at different current densities is shown in (Fig. 35(f)). Capacity utilization curves decrease dramatically over current density less than 20 A·g⁻¹ due to low electrical conductivity. CuFe-TBA shows remarkable and prominent results even at higher current densities of 100 A·g⁻¹. This unique property of CuFe-TBA speeds up the proton conduction in the electrolyte. Furthermore, this solid-state redox mediator can integrate with renewable energy resources like wind and solar for carbon-free energy utilization in decoupled electrolysis water splitting [265].

Wang et al. [271] proposed a two-component electrolyzer design to replace the conventional three-component system for DWS by using trifunctional electrocatalysts NaTi₂(PO₄)₃ (NTP) capable of OER, HER, and oxygen reduction reaction (ORR) as the gas evolution electrode (GEE). In this system, the evolution of H₂ and O₂ can be switched by reversing the current polarity. Moreover, the ORR consumes residual O₂ before the HER, ensuring high-purity hydrogen (99.9%). This design achieves a high decoupling efficiency of 97% and low HER and OER overpotentials, resulting in an energy conversion efficiency of 94.3% at a current density of 10 mA·cm⁻². Ni₃S₂/CNT foam serves as a trifunctional GEE for hydrogen and oxygen generation, with NaTi₂(PO₄)₃ or Ni(OH)₂ acting as redox mediator electrodes. A STH conversion efficiency of 10.4% is achievable using a commercial silicon PV module (14.4% efficiency) under simulated solar irradiation. Water is reduced on the GEE to produce H₂, while the Ni(OH)₂ relay electrode is oxidized to NiOOH. This occurs with the application of a specific current direction. By

reversing the current polarity, O₂ is produced on the GEE via anodic oxidation of OH⁻ ions, and the NiOOH relay is simultaneously reduced back to Ni(OH)₂. The redox reaction of Ni(OH)₂/NiOOH ensures the cyclic operation of the system. The CV curves of the Ni(OH)₂ and NTP electrode (Fig. 36(a)) show a pair of redox peaks at (0.423/0.238 V) and (0.838/0.756 V) (vs. Ag/AgCl), corresponding to the reversible Ni(OH)₂/NiOOH and Na₃Ti₂(PO₄)₃/NaTi₂(PO₄)₃ process at 1 mV·s⁻¹, respectively. The cell voltage was 0.17 V for the OER step and 1.52 V for the HER step, with the voltage difference due to the redox potential of Ni(OH)₂/NiOOH being closer to the OER than the HER potential. Furthermore, NTP, in combination with the Ni₃S₂/CNT foam, serves as a redox mediator in 1 M NaOH alkaline electrolyte. During O₂ evolution, OH⁻ ions undergo anodic oxidation on the GEE, while Na⁺ ions intercalate into the NTP electrode (NaTi₂(PO₄)₃ → Na₃Ti₂(PO₄)₃). Reversing the current polarity switches the OER to HER, while Na⁺ de-intercalates from NTP (Na₃Ti₂(PO₄)₃ → NaTi₂(PO₄)₃) occurs. The cell voltage required for the OER/HER step is 1.23/0.34 V, respectively (Fig. 36(b)).

During continuous operation at a constant current of 10 mA, the two-step water-splitting process was reversibly cycled for 16 cycles over 4.5 h without significant degradation. The HER processes also show a potential drop, indicating the occurrence of the ORR for O₂ consumption, further improving the purity of the produced H₂. Pure H₂ was obtained by adding a stir bar to the electrolyzer during ORR. After 50 min at 0.55 V, the residual O₂ gas was effectively removed, with no detectable O₂ peaks from gas chromatography. Alternatively, the residual O₂ can be removed with a vacuum pump, achieving 99.3% H₂ purity. By introducing an ORR step between OER and HER, the residual O₂ is consumed on the GEE, preventing gas evolution and ensuring the high purity of the collected H₂. For instance, after 1000 s of ORR followed by 15 min of HER, the H₂ purity reached 99.9% (Figs. 36(c) and 36(d)). GC analysis revealed that 5.13 mmol of H₂ was produced during 165 min of operation at 100 mA, achieving a near 100% FE (Fig. 36(e)). A commercial Ni(OH)₂ electrode (3 cm × 4 cm) can operate at 100 mA for 3.5 h, producing 146.3 mL of H₂ gas, corresponding to an areal capacity of 12.2 mL·cm⁻². The theoretical capacity for the NTP relay electrode is 55.5 mL·g⁻¹ (Fig. 36(e)). This design can be extended to acidic electrolytes by using appropriate multifunctional electrodes and redox mediator electrodes. This new electrolyzer design reduces water splitting system complexity and overall cost, making H₂ production more competitive.

Šutka et al. [272] reported amphoteric decoupled electrolysis using an AE pair, with H_xWO₃ and NiOOH functioning in separate acid and alkaline cells, respectively, achieving an average electrolysis efficiency of up to 71%, which is significantly higher than that observed in decoupled electrolysis where both cells are alkaline. Previous reports show that in an alkaline setup, the DWS efficiency is 58%. The electrolysis efficiency can be enhanced by a membrane-less decoupled amphoteric electrolyzer combining an acid cell in 0.5 M H₂SO₄ with a WO₃ and an alkaline cell in 1 M KOH with Ni(OH)₂ auxiliary electrodes. WO₃ nanoparticles, with a size of 30–70 nm in diameter, were synthesized by a hydrothermal method. WO₃ nanoparticles were deposited onto Ti foam, and β-Ni(OH)₂ nanoparticles were deposited onto porous Ni mesh to prepare the AEs. During the first cycle of water splitting, tungsten oxide (WO₃) is protonated to form tungsten bronze (H_xWO₃). At the same time, nickel hydroxide is oxidized to nickel oxyhydroxide (NiOOH) as WO₃ + x e⁻ + x H⁺ → H_xWO₃

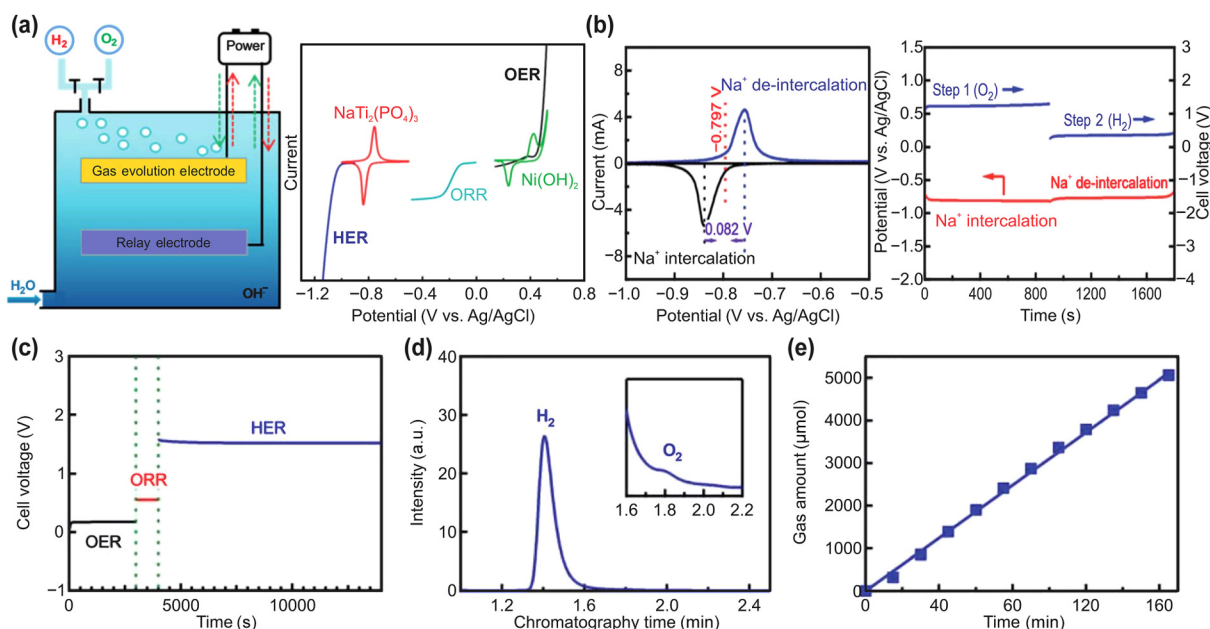


Figure 36 (a) The design, CV curves, and LSV curves of the single-cell, two-component water splitting electrolyser of the Ni(OH)₂ (green line) and NaTi₂(PO₄)₃ (red line), Ni₃S₂ foam (NSF)/CNT for the HER (blue line), the OER (black line) and the ORR (celestine line) at a scan rate of 1 mV·s⁻¹ in 1 M NaOH. (b) CV curves of the NTP, cell voltage vs. time for the H₂/O₂ production steps (blue line), chronopotentiometry curves for the NTP (red line). (c) Chronopotentiometry and (d) chromatogram curves for OER–ORR–HER steps for H₂ production. (e) The quantity of evolved H₂ was determined based on the GC analysis operated for 3 h. Reproduced with permission from Ref. [271], © The Royal Society of Chemistry 2020

and Ni(OH)₂ + OH⁻ → NiOOH + e⁻ + H₂O. This initial step is energetically costly, as the OER occurs on Pt in the acidic cell (2H₂O → O₂ + 4e⁻ + 4H⁺), and the HER occurs in the alkaline cell (2H₂O + 2e⁻ → H₂ + 2OH⁻). During electron flow from the Pt anode to the cathode, the HER (2H⁺ + 2e⁻ → H₂) takes place at the cathode in the acid cell, with H⁺ ions supplied by the H_xWO₃ AE. As H⁺ is converted to H₂ gas, H_xWO₃ reverts to WO₃. Simultaneously, the OER occurs at the anode in the alkaline cell (4OH⁻ → O₂ + 2H₂O + 4e⁻), with OH⁻ ions provided by the NiOOH AE, which is reduced to Ni(OH)₂. These processes continue until H_xWO₃ is converted to WO₃, and NiOOH is converted back to Ni(OH)₂. Since the gases are produced from ions supplied by the AEs, HER occurs in acidic media, while OER occurs in alkaline media. The deintercalation of H⁺ from H_xWO₃ (at 0.071 V) occurs at 0.3 V above the HER onset potential (at -0.235 V). The NiOOH reduction (minimum 0.226 V) is 0.57 V below the OER onset potential (0.8 V). The onset potential for H⁺ intercalation in WO₃ in the acid cell is 0 V, and saturation occurs at -0.2 V, which is 0.1 V above the HER onset potential. The maximum oxidation potential of NiOOH to Ni(OH)₂ in the alkaline cell is 0.467 V, which is 0.11 V below the onset potential for the OER. The HER on the WO₃ electrode in the acid cell and the OER on the Ni(OH)₂ electrode in the alkaline cell are closely aligned with the intercalation reaction of WO₃ and the oxidation potential of Ni(OH)₂, respectively. Gas purity from each cell was analyzed using MS. In the acidic cell, the hydrogen concentration was 99.6%, while the oxygen concentration was 0.4%. In the alkaline cell, the oxygen concentration was 99.6%, and the hydrogen concentration was 0.4%. Under different conditions, the oxygen concentration in the acid cell reached 99.7%, with hydrogen at 0.3%, while the alkaline cell showed 99.8% hydrogen and 0.2% oxygen. In the most favorable regime, the hydrogen concentration in the acid cell was 99.9%, with oxygen at 0.1%, while the alkaline cell exhibited 99.4% oxygen and 0.6% hydrogen. When operating in the opposite direction, the acid cell contained

98.8% oxygen and 1.2% hydrogen, and the alkaline cell had 99.5% hydrogen and 0.5% oxygen. The FE of the amphoteric electrolyzer, operating at 100 mA, ranged from 96%–98%, while the overall cycle energy efficiency was 67%. The efficiency reached 95% in the favorable direction but dropped to 50% in the reverse direction. Industrial alkaline electrolyzers typically achieve an efficiency of around 70% [273]. Chronopotentiometry results show that the system remained stable for 10 and 5 h in WO₃ and Ni(OH)₂ electrodes, respectively.

Yang et al. [274] developed a membrane-free alkaline decoupled water electrolysis system using GF-supported nickel-cobalt phosphate (NCP) material (GF@Ni_xCo_y-P) as a tri-functional electrode, serving as a solid-state redox mediator and a catalyst for both HER and OER, synthesized via a one-step electrodeposition process. This system demonstrated a high specific capacity of 176 mAh·g⁻¹ at 0.5 A·g⁻¹ and excellent cycle life, retaining 80% of its capacity after 3000 cycles at 5 A·g⁻¹ (Fig. 37(a)). The long-term electrochemical stability of GF@Ni₁Co₁-P at 10 mA·cm⁻², was maintained at constant potential over 48 h of continuous operation. The HER performance of GF@Ni_xCo_y-P was assessed, with GF@Ni₁Co₁-P achieving current densities of 10, 50, and 100 mA·cm⁻² at η of 247.8, 371.9, and 432.3 mV, respectively. While these results are notable, they are less efficient compared to a commercial Pt-coated Ti-mesh electrode (Ti@Pt) in 1 M KOH electrolyte at a scan rate of 5 mV·s⁻¹ (Fig. 37(b)). In contrast, the GF@Ni-P sample exhibited significantly higher overpotentials and a larger Tafel slope. To further assess the electrochemical stability of GF@Ni₁Co₁-P, long-term HER stability tests were conducted at 10 mA·cm⁻² over a continuous 48 h period. The redox potential of GF@Ni₁Co₁-P was found to be located between the onset potentials of HER and OER (Fig. 37(c)). This tri-functional capability is a crucial feature of the membrane-free decoupled electrolysis system, where GF@Ni₁Co₁-P serves as the redox mediator, HER, and OER electrode. Oxygen generation was achieved by coupling OER at the anode and the reduction of

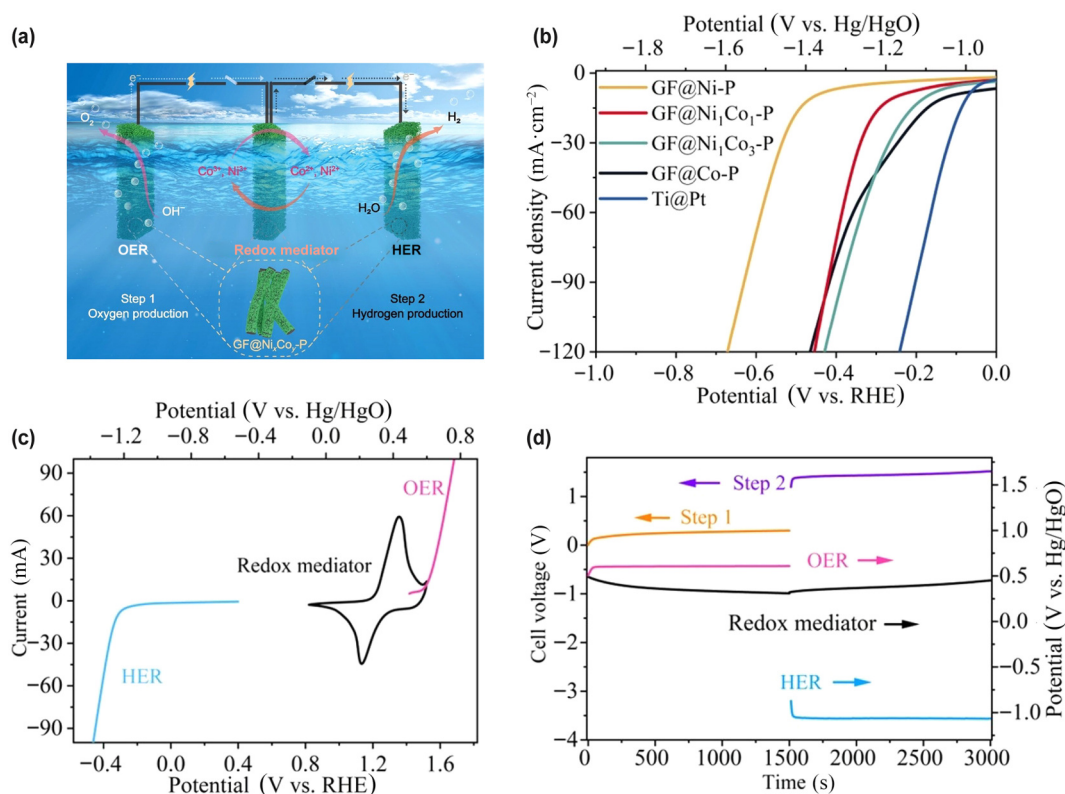


Figure 37 (a) Schematic illustration of decoupled water electrolysis system based on the tri-functional GF@NiCo₂-P solid-state redox mediator. (b) LSV curves of different electrodes in 1 M KOH at a scan rate of 5 mV·s⁻¹ for HER. (c) CV and LSV curves of the GF@NiCo₂-P electrode. (d) The cell voltage of O₂ production (Step 1, orange) and H₂ production (Step 2, purple). Chronopotentiometry curves of the OER electrode (red), the HER electrode (blue), and the redox mediator (black) at 5 mA. Reproduced with permission from Ref. [274], © Wiley-VCH GmbH 2023.

GF@NiCo₂-P at the cathode (GF@NiCo₂-P → r-GF@NiCo₂-P). Similarly, hydrogen production can be achieved by coupling the cathodic HER with the anodic oxidation of r-GF@NiCo₂-P. As a result, the tri-functional GF@NiCo₂-P electrode facilitates HER and OER and acts as a solid-state redox mediator, enabling decoupled water electrolysis. Chronopotentiometry measurements of the decoupled system at a current of 5 mA reveal that during oxygen production (Step 1), the anode potential is 0.60 V vs. Hg/HgO. In contrast, the cathode potential is 0.35 V vs. Hg/HgO, resulting in a cell voltage of 0.25 V. For hydrogen production (Step 2), the cell voltage is 1.43 V, derived from an anode potential of 0.37 V vs. Hg/HgO (r-GF@NiCo₂-P) and a cathode potential of -1.06 V vs. Hg/HgO (water) (Fig. 37(d)). Therefore, the total voltage for the decoupled water electrolysis process using GF@NiCo₂-P as a tri-functional electrode is 1.68 V at 5 mA. Chronopotentiometry data at higher currents (10, 50, and 100 mA) demonstrate that this system operates effectively across a wide current range. The total voltage of 1.60 V at 5 mA in this setup is slightly lower than that of a decoupled cell using GF@NiCo₂-P as the tri-functional electrode, which is attributed to the superior HER performance of the Pt catalyst compared to GF@NiCo₂-P.

Researchers have developed various innovative designs for DWS in separate tanks, which remains a desirable approach. Wu et al. [275] introduce a novel, continuous roll-to-roll process that enables fully decoupled HER/OER reactions in two electrolyte tanks. The system employs specially designed “cable-car” electrodes (CCE) that alternate between the HER/OER tanks, achieving continuous hydrogen production with a purity exceeding 99.9% and a CE of 98% over extended periods. This membrane-free water splitting system significantly reduces the

cost of constructing electrolyzers by eliminating the need for expensive membranes. The roll-to-roll transfer of Ni(OH)₂-based CCEs facilitates this process, leveraging the Ni(II)/Ni(III) redox cycle to avoid direct oxygen production. The CCEs are designed for continuous operation, minimizing the need for costly membranes. The hydrogen production device consists of several modules: a stainless-steel conveyor that transports the CCEs, a hydrogen production and collection module, and an electrode recovery module (Figs. 38(a) and 38(b)). In 1 M KOH, a voltage of 1.4 V was used to drive hydrogen production, while a voltage below 0.9 V was applied for oxygen generation. The system allows for simultaneous hydrogen and oxygen production through the nickel hydroxide-coated electrode, facilitating a Ni(II) to Ni(III) transition during hydrogen evolution. The electrodes are then transferred to the second tank via a conveyor belt, where they are reduced from Ni(III) to Ni(II) to facilitate oxygen production. This design leverages the nickel hydroxide electrode as an auxiliary electrode, effectively transferring hydrogen or oxygen atoms between the tanks without traditional membrane or diaphragm separations. The electrodes were submerged in each tank for 10 min to simulate real operating conditions. Over 100 cycles (with each cycle consisting of 10 min of charging and 10 min of discharging), HER/OER processes occurred independently in the two tanks. The results showed a stable oxidized potential of approximately 0.50 V vs. Hg/HgO for hydrogen production and a reduced potential of about 0.35 V vs. Hg/HgO for oxygen production. The potential fluctuated by roughly 0.10 V during each charging and discharging cycle, while the overpotential remained consistently low. In the first tank, at 50 mA, a cell voltage of approximately 1.6 V is required for hydrogen production. This design requires a constant voltage below 1.6 V to drive the HER process.

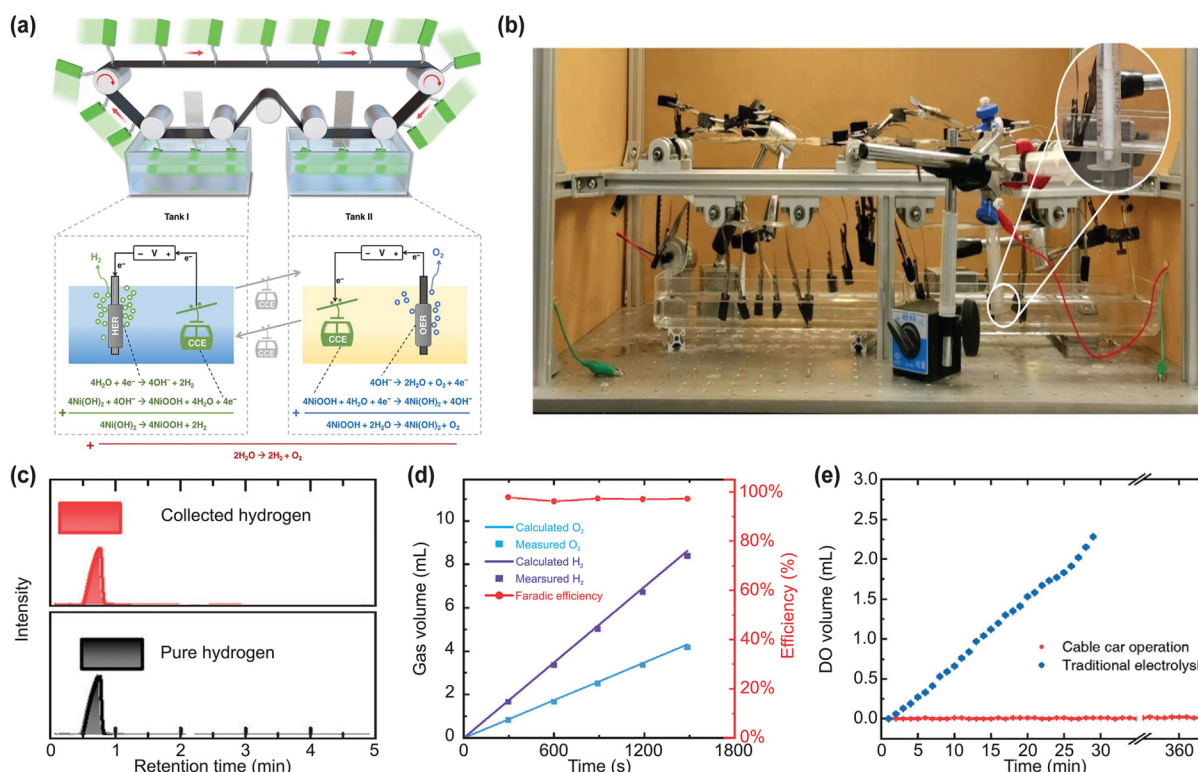


Figure 38 (a) The schematic illustration of the CCE system with (b) a digital photograph of the reaction design. (c) GC results for the collected and pure hydrogen samples. (d) The volume and efficiency of gas production. The measured volume of produced H_2 and O_2 . (e) Dissolved oxygen measurement in the HER tank (red). When traditional electrolysis (H_2 and O_2 evolve from the same tank) is applied, the dissolved oxygen keeps rising in the tank. Reproduced with permission from Ref. [275], © The Author(s), 2023.

Separating the hydrogen and oxygen production processes minimizes the risk of forming a gaseous product mixture or other undesirable byproducts, even when the operating voltage fluctuates. A constant current of 50 mA in the second tank corresponded to a cell voltage of approximately 0.75 V. A constant voltage of 0.80 V was applied to the prototype, allowing the reaction to proceed with a voltage of less than 1.0 V. This design opens up possibilities for future large-scale applications using electricity from low-quality or intermittent renewable sources. For industrial-scale implementations, collection modules equipped with gas pumps or tubes could be used. GC analysis confirmed the collected hydrogen purity to be 99.93%, and the absence of oxygen in the collected gas ensures the safety and practicality of the system (Fig. 38(c)). The operating voltage can fluctuate due to mechanical movement or varying distances between the CCEs and counter electrodes. Nevertheless, the FE of hydrogen production approached 100%, as measured by the volume of hydrogen generated (Fig. 38(d)). Furthermore, dissolved oxygen tests indicated that the dissolved oxygen concentration in the first tank did not significantly increase, even as the CCEs were continuously immersed and lifted during operation (Fig. 38(e)). Additionally, the dissolved oxygen tests confirmed that despite the mechanical transfer of the electrodes, no significant increase in dissolved oxygen was observed in the hydrogen production tank.

The all-pH functional capacitive decoupled water electrolyzer (all-pH-CDWE), developed by Chen et al. [276], is a single-cell, bifunctional HER/OER electrocatalysts-based two-electrode system that separates and produces high-purity H_2 and O_2 simply by reversing the current polarity at electrodes. This design (Fig. 39(a)) shows great promise for large-scale and cost-effective H_2 production. The designed all-pH-CDWE electrolyzer is

capable of near-complete electrolyte usage throughout 800 continuous cycles of round-trip water electrolysis. The all-pH-CDWE scales up to 720 C at a high current of 1 A per cycle with a stable HER average voltage of 0.99 V, achieving energy efficiencies of 94% (in acidic) and 97% (in alkaline) electrolytes at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$. H_2 and O_2 generation depends on the reaction kinetics of the cathode, and anode comprises cathodic H^+ or H_2O reduction and adsorption of anodic anions (SO_4^{2-} in an acidic electrolyte, OH^- in an alkaline electrolyte, or $H_2PO_4^-/HPO_4^{2-}$ in a neutral electrolyte) and anodic H_2O oxidation reaction and the cathodic anion desorption process. Pt-coated Ti-mesh and activated carbon (AC)-coated carbon paper electrodes in the Swagelok cell were used to measure DWS (Fig. 39(b)). The acidic-CDWE have average voltages of 0.84/1.13, 0.84/1.21, 0.83/1.25, and 0.84/1.29 V at current densities of 5, 10, 15, and 20 $\text{mA}\cdot\text{cm}^{-2}$, respectively, during the H_2/O_2 generation process, indicating a negligible change in the HER. In addition, at a high current density of 20 $\text{mA}\cdot\text{cm}^{-2}$, the acidic-average CDWE voltage during the H_2 production process is significantly lower at 0.84 V compared to the acidic-average CWE voltage of 1.98 V (Fig. 39(c)). The energy efficiency of acidic-CDWE with a total driving voltage of 1.97 V is about 94% as compared to acidic-CWE with an electrolytic voltage of 1.85 V at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$. The energy efficiency of the acidic-CDWE drops from 94% to 93% when the current density is raised from 10 to 20 $\text{mA}\cdot\text{cm}^{-2}$, which can be attributable to the outstanding rate performance of the AC electrode. AC not only saves energy but also has a very long cycle life. H_2/O_2 cyclic performance was studied over a period of 360 s at 10 $\text{mA}\cdot\text{cm}^{-2}$ (Fig. 39(d)).

Cyclic performance of acidic-CDWE as compared to acidic-CWE over 800 cycles (~160 h) shows high stability of HER/OER

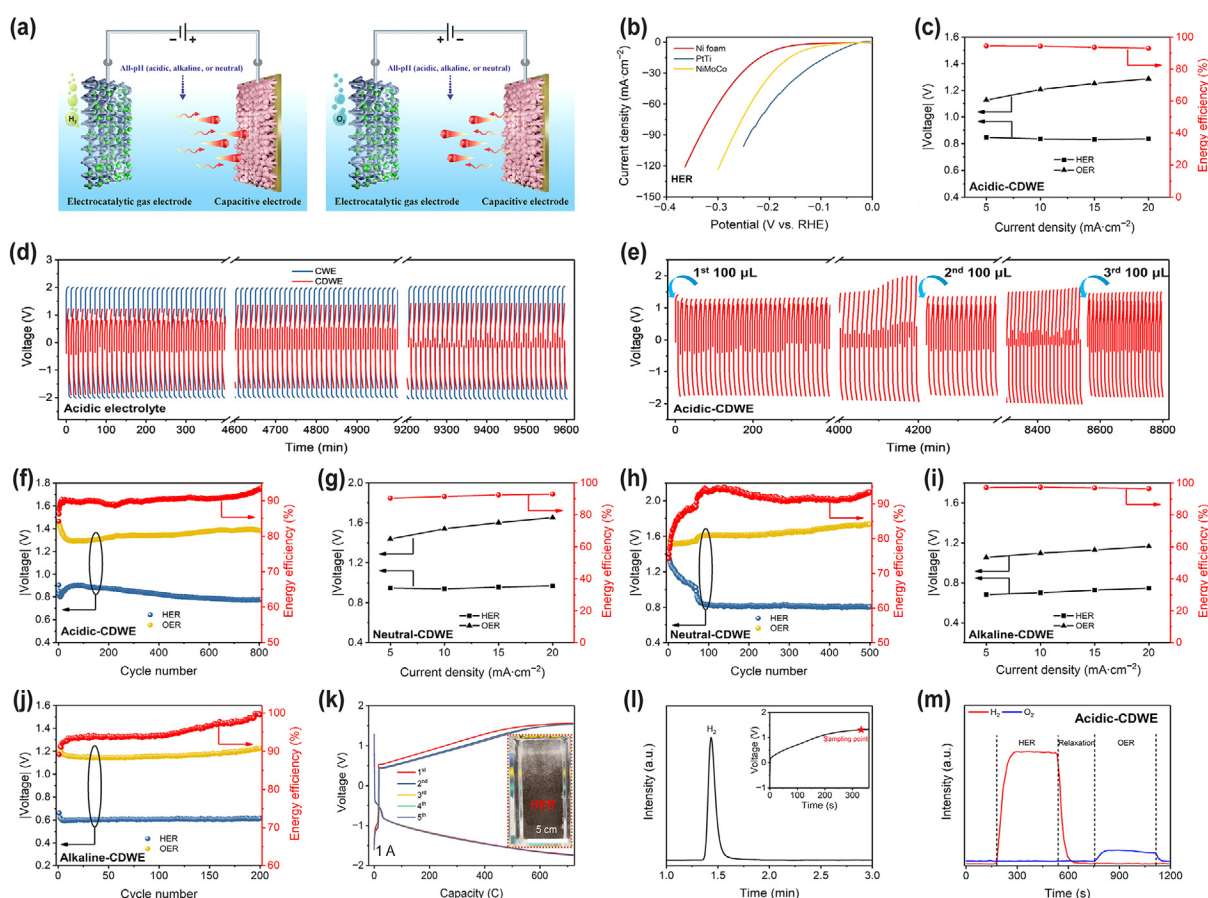


Figure 39 (a) Schematic illustration of all-pH-CDWE decoupled water electrolyzer with a single-cell configuration. (b) HER performance of different catalysts. (c) HER/OER voltage vs. current density efficiency curves in acidic-CDWE using a Swagelok cell. (d) Voltage–current waveform comparisons between acidic-CDWE and acidic-CWE while cycling over $10 \text{ mA}\cdot\text{cm}^{-2}$ and 360 s of operation. (e) Cyclic efficiency of H_2/O_2 production by using and adding $100 \mu\text{L}$ electrolyte to the acidic-CDWE. (f) Average voltage and energy efficiency in acidic-CDWE with cycle number-dependent HER/OER. (g) HER/OER voltage vs. current density efficiency curves in neutral-CDWE using a Swagelok cell. (h) Cycle number dependent HER/OER average voltage and energy efficiency over $10 \text{ mA}\cdot\text{cm}^{-2}$ with an operative time of 216 s in neutral-CDWE. (i) HER/OER voltage vs. current density efficiency curves in alkaline-CDWE using a Swagelok cell. (j) Alkaline-CDWE operation time of 216 s at an average voltage and energy efficiency of over $10 \text{ mA}\cdot\text{cm}^{-2}$ (depending on cycle number). (k) H_2/O_2 formation cycle voltage curves in alkaline-CDWE at 1 A current and 720 s cycle duration. The inset shows H_2 generation at 1 A. (l) GC analysis for HER. H_2 production by water electrolysis voltage curve is shown in the insets. The asterisk indicates the sample point. (m) *In-situ* DEMS curves for the acidic-CDWE for H_2 (red) and O_2 (blue) generation in whole water electrolysis at $10 \text{ mA}\cdot\text{cm}^{-2}$ for 360 s. Reproduced with permission from Ref. [276], © The Author(s), 2023.

for H_2/O_2 production with a restricted electrolyte of 300 L (Fig. 39(e)). The minor voltage fluctuations observed during cycling in H_2/O_2 production arise from variations in the catalytic HER and OER activity of the Pt electrode. Highly stable energy efficiencies can be seen over 800 cycles (Fig. 39(f)). During the initial cycles linked to the activation of the AC electrode, the energy efficiency increases. After 350 cycles ($\sim 70 \text{ h}$) with a continuous current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, the acidic-CDWE evaluated at a restricted electrolyte capacity of 100 L maintained average voltages of 2 V. This indicates that the electrolytic cell is making almost full use of the water solution. With an additional 100 L of electrolyte, the cell voltage can return to its initial level and cycle for over 350 cycles. By continually introducing 100 L of the electrolyte into the cell, acidic-CDWE can cycle with a high electrolyte consumption ratio of over 100%, proving that it generates steady H_2 and O_2 and utilizes the water solution extremely effectively. The AC electrode's outstanding stability in the acidic-CDWE is confirmed by the lack of noticeable change in energy dispersive X-ray spectroscopy (EDS), XPS, and micromorphology after 800 cycles. Compared to the neutral-CWE, the neutral-CDWE has lower average HER/OER voltages. For a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$, the HER voltage of neutral-

CDWE is 0.95 V. Its energy efficiency is 90% (Fig. 39(g)). Analyses of the neutral-CDWE at 10, 15, and $20 \text{ mA}\cdot\text{cm}^{-2}$ show the electrolyzer's adaptability to a variety of operating conditions (Fig. 39(h)). Over 500 cycles ($\sim 216 \text{ s}$) of H_2/O_2 production at an applied current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, the HER average voltage tends to settle at 0.8 V with an energy efficiency of 90%, demonstrating remarkable stability. With a cell average voltage of 1.74 V and HER average voltage of 0.68 V at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$, the alkaline-CDWE has a high energy efficiency of 97% (Fig. 39(i)). The average voltage of the HER can be maintained at 0.7, 0.73, and 0.75 V even when the current density is raised to 10, 15, and $20 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 39(j)). As a conclusion, the two-electrode design technique could decouple pH-universal water electrolysis with outstanding activity and stability, demonstrating the operational flexibility of this all-pH-CDWE and its potential for widespread application in the water electrolysis business. NiMoCo, a bifunctional HER/OER electrocatalyst in alkaline electrolytes, was presented by Chen et al. based on the studies mentioned above for industrial-scale applications.

Regarding water splitting, NiMoCo outperforms Ni foam and noble metal PtTi catalysts, with 108 mV (HER)/330 mV (OER)

overpotentials at $20 \text{ mA}\cdot\text{cm}^{-2}$. More than 100 h of steady $50 \text{ mA}\cdot\text{cm}^{-2}$ current toward HER and OER demonstrated the NiMoCo catalyst stability. Alkaline 2 M KOH electrolyte was poured into the poly(methyl methacrylate) (PMMA) container, along with the electrode plates. Multiple consecutive cycles of H_2/O_2 production were achieved via the water electrolytic process using an alkaline-CDWE with an applied current of 1 A and an operational time of 720 s (Fig. 39(k)). Over many complete cycles, exceptionally stable average HER/OER voltages of 0.99/1.35 V were measured. The AC electrode shows extraordinary durability in industrial-scale water electrolysis, as evidenced by its unchanged micromorphology and XPS spectra. Compared to the alkaline CWE, the energy efficiency of the scaled-up alkaline-CDWE using a NiMoCo-coated nickel foam gas electrode is 80%. It has been discovered that using optimized AC electrodes can improve energy efficiency even more. The picture profile of large H_2 bubbles at 1 A current in the enlarged alkaline-CDWE is shown in the inset (Fig. 39(k)). Without a membrane, this may convert sunlight into green hydrogen. In photovoltaic-powered water electrolysis using natural sunshine, the working voltage of HER is around 1.47 V. The detection of just H_2 shows that no O_2 was generated throughout the HER process. After the charging procedure was finished, a 20 min rest period was performed to purge the system of the newly-formed H_2 (Fig. 39(l)). GC analysis shows that O_2 was discovered during the subsequent discharging operation with no H_2 formation (Fig. 37(m)). The results revealed the feasibility of capacitive decoupling water electrolysis for generating high-purity H_2 and O_2 . The aforementioned *ex-situ* GC and *in-situ* DEMS findings proved the efficiency and durability of the developed capacitive decoupled water electrolyzers as a cutting-edge H_2/O_2 production and separation technology. Overall, the author effectively constructed and proved that the all-pH-CDWE, when operated at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$, exhibited excellent energy efficiency of 94% in the acidic-CDWE and 97.5% in the alkaline-CDWE relative to the driving voltage of CWE. Chen et al. [277] developed a single-atom Co-doped Co-Ru@RuO₂ OER catalyst via ultrafast pulse-heating, which showed 400 h stability at $10 \text{ mA}\cdot\text{cm}^{-2}$ in acidic media. The same group also developed a PtRuNi/C catalyst for hydrogen oxidation reaction (HOR)/HER in acidic and alkaline media for hydrogen gas batteries [278]. They further synthesized a RuFe@CF catalyst via Joule heating, which exhibited 250 h of stability during water splitting at $200 \text{ mA}\cdot\text{cm}^{-2}$ in acidic media [279]. Additionally, they fabricated a multifunctional NCP bifunctional catalyst via electrodeposition in 1 M KOH, which maintained stability for 10 h during water splitting at $10 \text{ mA}\cdot\text{cm}^{-2}$ [280].

The current densities and stabilities of redox mediators are typically low, limiting their practical applications. To address this, Wang et al. [281] propose the use of supercapacitors Na_{0.5}MnO₂ (a pseudocapacitor) and activated carbon (a double-layer capacitor) as solid-state redox mediators for DWS. These supercapacitors exhibited significantly higher current densities ($1 \text{ A}\cdot\text{cm}^{-2}$) and much longer cycle lives (8000 cycles) compared to commonly studied battery-based mediators like NiOOH/Ni(OH)₂. Supercapacitors can serve as effective redox relays with high current densities and stability, providing new insights into the design of DWS systems. Supercapacitors, such as electric double-layer capacitors and pseudocapacitors, have been extensively studied, and their applications are well established [282–284]. In the context of DWS, the primary function of the redox mediator is to efficiently “decouple” the HER/OER through robust and rapid redox reactions. Supercapacitors, with their high and adjustable

power rates (specific power ranging from 500 to $10,000 \text{ W}\cdot\text{kg}^{-1}$), fast charge/discharge times (seconds to minutes), high CE (85%–98%), and extended cycle life (over 500,000 cycles), may therefore be better suited as solid-state redox mediators than battery-based relays like NiOOH. In Step 1, the HER process is coupled with the charging of the supercapacitor, and in Step 2, reversing the current enables the OER process to be coupled with the discharging of the supercapacitor. Na_{0.5}MnO₂ was chosen due to its favorable redox properties, low cost, high specific capacitance, and long cycle life. Both activated carbon and Na_{0.5}MnO₂ showed rapid gas evolution rates due to the fast charging/discharging of the supercapacitors. These electrodes also exhibited high CE, with the tunable decoupling efficiency directly related to the gas evolution rate. Furthermore, both electrodes demonstrated remarkable durability, completing 8000 cycles in 223 h, underscoring their potential for long-term use in DWS systems. These supercapacitor-based relay mediators demonstrate significantly better performance than traditional battery-based electrodes. This research introduces new perspectives on selecting redox mediators for DWS.

Unlike conventional battery electrodes, supercapacitors enable rapid charge/discharge cycles with high current flow, thanks to their capacitive ion storage mechanism. Supercapacitors facilitate faster hydrogen production under high current conditions in the DWS process when used as relays. AC is the relay electrode at a current density of $1 \text{ A}\cdot\text{cm}^{-2}$, and the HER/OER requires a potential of 2.54/2.43 V, respectively. The system also demonstrates stable performance across varying current densities (500 and 800 mA), indicating that supercapacitors can function effectively as relays for DWS even with unstable power supplies. In this setup, decoupling is achievable under different current conditions: For instance, low current density (1 A) in the first step (with AC electrode discharge) is used to produce oxygen, followed by a larger current (10 A) in the second step to generate large quantities of high-purity hydrogen rapidly. This approach could enable the swift production of high-purity hydrogen. The calculated FE for hydrogen production was nearly 100%. GC analysis shows that at a current of 100 mA, with an operating time of 90 min, 2.79 mmol of hydrogen gas was produced, resulting in an FE of approximately 100%. The selection of appropriate redox mediators is critical for successful decoupled electrolysis. Traditional battery-based solid-state redox mediators, such as NiOOH/Ni(OH)₂, often struggle with long-term stability and sufficient current density, limiting their practicality. In contrast, supercapacitors offer superior charge/discharge rates, specific power, CE, and cycle stability, making them more suitable for intermittent renewable energy sources, such as solar and wind power.

Dutta et al. [285] reported a hybrid membrane-free cell for decoupled hydrogen production in acidic and alkaline media, utilizing earth-abundant materials (Fig. 40(a)). This innovative design integrates electrocatalytic reactions with a capacitive storage mechanism. The system achieved an energy efficiency of 69% at $10 \text{ mA}\cdot\text{cm}^{-2}$ with CoFeP as a bifunctional catalyst and reached an FE of 99% at $100 \text{ mA}\cdot\text{cm}^{-2}$. Importantly, the cell maintained stable operation for over 20 h in an alkaline medium without electrode degradation. This membrane-free design offers significant flexibility and robustness for hydrogen production applications, building upon the concept of supercapacitive electrolyzers (SCEs). CoFeP bifunctional catalyst energy consumption was measured at $48 \text{ kWh}\cdot\text{kg}^{-1}$ in alkaline conditions, which could be further reduced by replacing activated CC (ACC). The process is divided

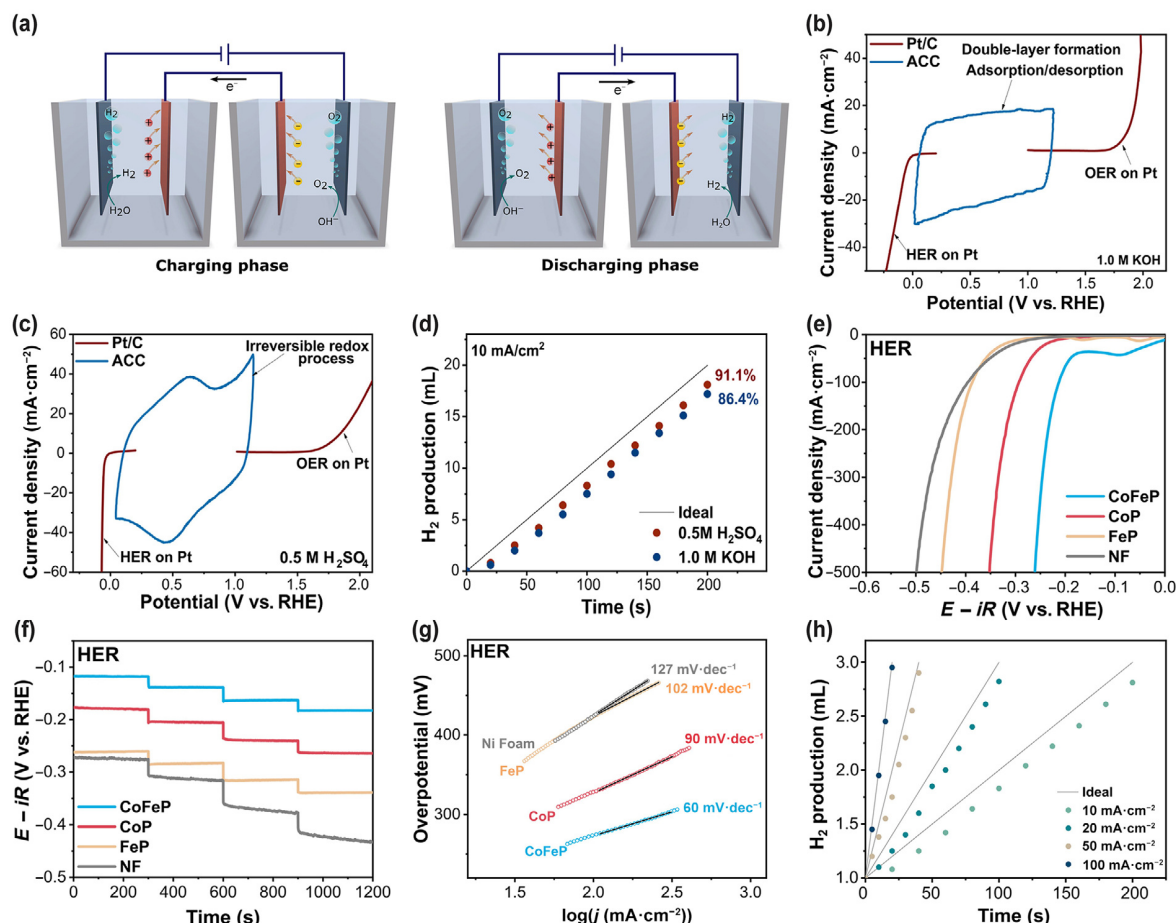


Figure 40 (a) Proposed mechanism for supercapacitive electrolyzer during the charging and discharging step. (b) and (c) CV and LSV curves of activated carbon cloth and Pt/C in 1.0 M KOH and 0.5 M H_2SO_4 , at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. (d) H_2 production in both acidic and alkaline media. (e) LSV curves of different catalysts at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. (f) Chronopotentiometry at different current densities. (g) Tafel plot in 1.0 M KOH. (h) Performance of supercapacitive electrolyzer in a decoupled system. Hydrogen gas production at different current densities. Reproduced with permission from Ref. [285], © The Author(s), some rights reserved; exclusive licensee American Association for the Advancement of Science 2024.

into two key steps: charging and discharging. During the charging phase, the HER produces hydrogen from the cathodic chamber. Concurrently, in the anodic cell, the bifunctional electrode facilitates the OER, generating oxygen from the anodic chamber. In alkaline conditions, OH^- ions are adsorbed at the capacitive electrode in the cathodic cell. In contrast, potassium ions (K^+) are adsorbed in the anodic cell when KOH is used as the electrolyte. The LSV results show that Pt/C exhibits excellent HER activity, with low overpotentials of 55 mV in acidic media and 77 mV in alkaline media at $10 \text{ mA}\cdot\text{cm}^{-2}$ (Figs. 40(b) and 40(c)). However, Pt/C showed poor OER activity, though faster OER kinetics were observed in alkaline media at higher current densities. The overpotentials required to achieve a $10 \text{ mA}\cdot\text{cm}^{-2}$ current density were 643 mV in alkaline and 616 mV in acidic media. These overpotentials indicate the energy required for the electrocatalytic reactions to occur.

In alkaline media, the capacitive storage properties of ACC were demonstrated through the quasi-rectangular shape of the cyclic voltammogram, indicating efficient charge storage. In acidic media, a reversible redox pair was observed at 0.5 V vs. RHE, corresponding to the reversible oxidation of ACC-oxygenated groups. The FE for hydrogen production was slightly higher in acidic conditions (91.1%) compared to alkaline conditions (86.4%) (Fig. 40(d)). However, after the initial losses during the first 10 s, both media reached an FE of 99% for hydrogen production. The

high cell voltage required for this system, especially with Pt/C as the catalyst for OER. The electrochemical activity of the CoFeP catalyst was evaluated via LSV in 1.0 M KOH (Fig. 40(e)). Nickel foam exhibited poor performance for HER with a high onset potential. In contrast, CoFeP achieved overpotentials of 205, 251, and 273 mV at current densities of 10, 50, and $100 \text{ mA}\cdot\text{cm}^{-2}$, respectively. Comparatively, CoP and FeP required higher overpotentials, with 329 and 423 mV needed to reach $100 \text{ mA}\cdot\text{cm}^{-2}$. The dynamic performance of CoFeP was further assessed by chronopotentiometry, where the current density was ramped up from 10 to $100 \text{ mA}\cdot\text{cm}^{-2}$. The CoFeP electrode reached a steady potential within 5 to 10 s, demonstrating its rapid response to applied power, comparable to control samples. The CoFeP catalyst showed a significant performance improvement, with a Tafel slope of $60 \text{ mV}\cdot\text{dec}^{-1}$. In contrast, FeP and CoP had Tafel slopes of 102 and $90 \text{ mV}\cdot\text{dec}^{-1}$, respectively. At the same time, nickel foam exhibited a Tafel slope of $126 \text{ mV}\cdot\text{dec}^{-1}$ (Figs. 40(f) and 40(g)). This performance highlights the potential of CoFeP as a highly efficient bifunctional catalyst for decoupled electrolysis.

The supercapacitive electrolyzer was constructed using CoFeP-coated nickel foam as a bifunctional electrocatalyst alongside an activated carbon cloth as an auxiliary electrode with a loading mass of $10 \text{ mg}\cdot\text{cm}^{-2}$. During the transition between the charging and discharging steps, an Ohmic drop of 100 mV was observed, indicating some resistance within the system. The hydrogen

production during the charging step at varying current densities was measured using the Archimedes method (Fig. 40(h)). A steady increase in dissolved hydrogen concentration was detected over several cycles. In contrast, the oxygen concentration remained stable, confirming effective gas separation. The FE of hydrogen production was 91% at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, likely due to surface polarization. However, when the current density was increased to $100 \text{ mA}\cdot\text{cm}^{-2}$, the FE improved to 99%, indicating efficient gas separation and reduced losses at higher current densities. Energy consumption for hydrogen production was $48 \text{ kWh}\cdot\text{kg}^{-1}$ at $10 \text{ mA}\cdot\text{cm}^{-2}$, corresponding to 69% energy efficiency based on the lower heating value. A significant contribution to the system energy losses came from Ohmic resistance, with a resistivity of $3.55 \Omega\cdot\text{cm}^{-2}$, as shown in the Nyquist plot. This suggests that improvements in electrode conductivity and contact resistances could further reduce energy losses. The stability of the electrochemical cell was evaluated over 20 h (100 cycles) at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ in 5.0 M KOH. The voltage profile demonstrated the reversibility of the cycles, with no appreciable increase in final voltage during either charging or discharging. This indicates that the bifunctional catalyst maintained its activity without degradation, and no significant remnant potential built up on the auxiliary electrode. These results affirm the stability and efficiency of the supercapacitive electrolyzer design for decoupled hydrogen production.

Sutka et al. [286] introduced a non-traditional DWS through an ultra-small anatase TiO_2 nanoparticles (size of 4.5 nm diameter) as a pseudocapacitive material that stores H^+ ions generated from OER in a pseudocapacitive material, which are later released to drive HER. These particles exhibit a high electrochemical surface area (ECSA) with a capacitance of $375 \text{ F}\cdot\text{g}^{-1}$, achieving overall energy efficiency of 52.4% during water splitting, with excellent stability maintained over 3000 cycles (Fig. 41(a)). There are two

primary strategies to decoupled water electrolysis: (1) electron-coupled proton buffers, which store and release H^+ or OH^- ions; (2) pseudocapacitive electrodes, which accumulate these ions during one reaction (e.g., OER) and release them during the other (e.g., HER) [28, 172, 174, 178, 200, 272]. $\text{Ni}(\text{OH})_2$ -based pseudocapacitors for alkaline media and WO_3 -based systems for acidic conditions, both Ni and W present challenges due to stability concerns, environmental risks, and supply issues [106, 187, 287, 288]. TiO_2 , one of the most abundant and stable oxides globally, provides a promising alternative for H^+ intercalation. The ultra-small TiO_2 nanoparticles not only provide excellent stability but also deliver efficient electrolysis. CV analysis of the Aeroxide P25 TiO_2 electrode ($\approx 25 \text{ nm}$) has electrochemical double-layer capacitance between -0.3 and 0.4 V vs. saturated calomel electrode (SCE). Below -0.3 V vs. SCE, a sharp increase in cathodic current occurs, indicating hydrogen gas bubble formation. The voltage cycle is limited to -0.5 V to prevent excessive HER. The behavior of the TiO_2 particles in this context is linked to their surface area to volume ratio, which scales inversely with particle size. Due to the relatively large size of P25 TiO_2 particles, H^+ intercalation into the TiO_2 structure is minimal. In contrast, ultra-small TiO_2 particles (4.5 nm) exhibit a much higher surface area to volume ratio, enabling significant H^+ intercalation, leading to the enhanced performance in redox reactions for the same mass of material.

To fully understand the differences in CV profiles between P25, ultra-small TiO_2 particles with surfactant, and ultra-small TiO_2 particles without surfactant, it is essential to consider how H^+ intercalation occurs (Fig. 41(b)). Since H^+ intercalation takes place at the particle surface, a higher surface area to volume ratio in smaller particles increases intercalation efficiency. Removing the surfactant in ultra-small TiO_2 samples maximizes the exposed surface area, leading to optimal H^+ intercalation and more prominent redox peaks. The study found that ultra-small TiO_2

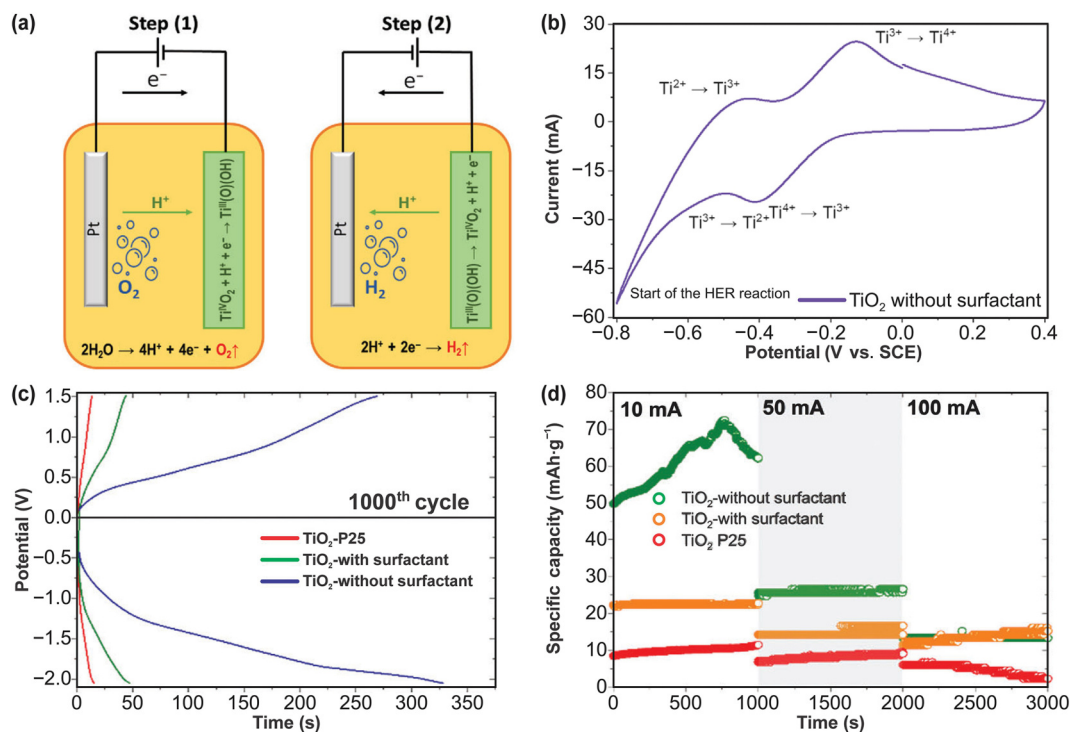


Figure 41 (a) Schematic illustration of decoupled water splitting using a TiO_2 auxiliary electrode. (b) CV curves of TiO_2 auxiliary electrode without surfactant nanoparticle in $0.5 \text{ M H}_2\text{SO}_4$ at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. (c) Chronopotentiometry measurements at the 1000th cycle. (d) Long-term stability test at different current densities. Reproduced with permission from Ref. [286], © The Author(s), 2024.

nanoparticles without surfactant demonstrated the strongest redox features, as they facilitated the dominating redox reaction. These particles exhibited significant storage capacity, with the first H^+ intercalation cycle taking 262 s, while deintercalation occurred in 260 s. In contrast, for ultra-small TiO_2 with a surfactant, the intercalation and deintercalation times were much shorter, at 47 and 43 s, respectively. For P25 TiO_2 particles, these times were even shorter, at 11.2 and 10.5 s. Over 1000 cycles, both P25 TiO_2 and ultra-small TiO_2 without surfactant showed increased cycle duration, likely due to spontaneous deintercalation processes over longer cycles. Interestingly, the ultra-small TiO_2 with surfactant sample maintained nearly 100% stability over 1000 cycles, attributed to the surfactant role in preventing particle aggregation or disintegration during the reaction process, thus preserving the particle structure and performance throughout the cycling. This analysis highlights the critical role of particle size, surface exposure, and the presence of surfactants in determining the intercalation kinetics and cycling stability of TiO_2 -based pseudocapacitive materials used in decoupled water electrolysis systems. Chronopotentiometry tests at higher current densities (50 and 100 mA), the TiO_2 -without surfactant sample exhibited the best performance at 50 mA. However, at 100 mA, the performance of the TiO_2 -with surfactant sample became equivalent, highlighting how the surfactant affects the rate capabilities of the system. The drop in capacity observed in the TiO_2 electrodes at higher currents can be attributed to the larger voltage drop across the film, which reduces the active material participation in the H^+ intercalation reaction. This voltage drop is significantly larger in the TiO_2 -without surfactant sample than in the TiO_2 -with surfactant sample due to a higher resistance value.

The surfactant stabilizes the ultra-small TiO_2 particles, thus improving their rate performance, particularly at higher currents. SEM analysis shows that TiO_2 electrodes before and after electrochemical cycling revealed no significant morphological changes, suggesting that the electrodes maintained their structural integrity. At lower current densities ($= 100 \text{ mA}\cdot\text{g}^{-1}$), the bare TiO_2 (without surfactant) exhibited superior performance, whereas the surfactant-coated TiO_2 demonstrated equivalent performance at commercially relevant current densities ($\sim 1 \text{ A}\cdot\text{g}^{-1}$) with enhanced stability. The overall efficiency of the decoupled water splitting process reached 52.4%, approaching the efficiencies of commercial membrane electrolyzers, which operate at 80°C in highly alkaline conditions. The H^+ intercalation and deintercalation cycle times for the 1000th cycle of the TiO_2 without surfactant were 328 s for intercalation and 269 s for deintercalation. For the TiO_2 with surfactant, the cycle times were much shorter, 47 and 44 s, respectively. The P25 TiO_2 sample showed even faster times of 15.2 and 13.3 s (Fig. 41(c)). The use of *in-situ* H_2 sensors, linked to a gas chromatograph, confirmed selective H_2 evolution during Step 2 of the decoupled process, further validating the proposed mechanism. This work demonstrates the viability of decoupled electrolysis by leveraging charge storage and H^+ intercalation at pseudocapacitive TiO_2 electrodes (Fig. 41(d)). The small TiO_2 particles deposited on carbon cloth exhibited a high pseudocapacitive response (up to $375 \text{ F}\cdot\text{g}^{-1}$), facilitating highly effective H^+ intercalation and deintercalation during the DWS process. The surfactant-stabilized TiO_2 electrodes prove promising for future applications, showing both high stability and efficiency.

Using membranes and diaphragms in water electrolysis can prevent gas mixing but often reduces efficiency and increases hydrogen production costs. Šutka et al. [288] introduced a novel concept of DWS, where hydrogen and oxygen evolution are

spatially and temporally separated using a WO_3 -based charge storage electrode as a redox mediator in an acidic environment. This electrolysis process involves two steps: First, the OER takes place, and the H^+ intercalates into the WO_3 material. In the second step, the deintercalation of H^+ from the WO_3 is followed by its reduction into hydrogen gas (H_2) at the opposing electrode. This approach yields H_2 and O_2 gases with a purity exceeding 99.9%, and the overall efficiency of the electrolyzer is approximately 65%. Pt and pseudocapacitive WO_3 -based auxiliary electrodes were utilized. The efficiency of the HER cycle is significantly higher (341%) due to the favorable acidic conditions and the energy released from WO_3 discharge. The overall efficiency of the electrolyzer reaches 65%. During the first 20 cycles, the auxiliary electrode activates but remains stable afterwards. After performing 100 cycles at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$, followed by 100 cycles at $500 \text{ mA}\cdot\text{g}^{-1}$ and another 100 cycles at $1000 \text{ mA}\cdot\text{g}^{-1}$, the cycle time variation was less than 1% at the higher current densities, indicating stable electrolysis performance throughout the process. Chronopotentiometry tests at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$ after completing tests at $1000 \text{ mA}\cdot\text{g}^{-1}$ demonstrate the high stability of the WO_3 auxiliary electrode in enabling decoupled electrolysis for hydrogen production. SEM results revealed good adhesion of WO_3 particles to the carbon cloth. No hydrogen is produced during the intercalation cycle. Oxygen concentration increased by 99.4%, while hydrogen concentration increased by only 0.6%, confirming the production of high-purity oxygen gas during the intercalation cycle. No oxygen was produced during the deintercalation cycle. In the deintercalation cycle, the hydrogen gas produced reached a high purity of 99.9%, indicating successful production of high-purity H_2 . The volumetric displacement method was used to measure the volume of the gases over time. Non-Faradaic processes include spontaneous deintercalation, transient polarization currents, leakage currents, and adsorbed charge currents on the electrode surface [289]. However, focusing solely on the HER cycle, where hydrogen is released, and the WO_3 electrode de-intercalates, the efficiency reached an impressive 341%. This high efficiency is attributed to the energy contribution from the intercalated WO_3 nanoparticle, which provides a built-in potential that lowers the standard required for water electrolysis. Long-term stability tests at various current densities showed excellent durability of the WO_3 electrode. Furthermore, it is notable that no membranes or diaphragms were required for this electrolysis process, which reduces the cost of the system.

Šutka et al. [288, 290] further improved the performance of WO_3 as an effective redox mediator electrode in DWS with an acid electrolyte. The performance of WO_3 was evaluated based on the effects of lyophilization and annealing on its capacity, showing that WO_3 can intercalate and deintercalate H^+ ions during electrolysis. The lyophilized WO_3 exhibited more than double the capacity of the air-dried samples, with values of 495.55 and $201.41 \text{ F}\cdot\text{g}^{-1}$, respectively. Additionally, an impressive capacity of $837.43 \text{ F}\cdot\text{g}^{-1}$ was achieved when WO_3 was annealed under an inert atmosphere. FE for all prepared samples was high, in the range of 98–99%, and the energy efficiency varied between 34% and 58%. This approach builds on recent advancements in two-step acidic DWS using WO_3 as a pseudocapacitive electrode, a promising method for hydrogen production [288]. High-specific-capacity electrodes like WO_3 can extend the duration of the H_2/O_2 evaluation step and reduce the required driving voltages. Introducing oxygen vacancies and W^{5+} defects through annealing in an inert atmosphere enhanced the WO_3 nanoparticle capacity by up to 50%, making the material more conducive to H^+

intercalation. These point defects alter the surface electronic structure, facilitating the intercalation of OER products, particularly H^+ ions. CV in an aqueous 0.5 M H_2SO_4 solution revealed two distinctive cathodic peaks for annealed samples, at approximately -0.05 and -0.3 V, corresponding to the stepwise reduction of W^{6+} to W^{5+} and subsequently to W^{4+} . These reduction steps are key to the intercalation of protons into the WO_3 lattice. The annealed WO_3 electrode exhibited a more distinct, mass transfer-limited process, as evident from the wider peaks. In contrast, unannealed samples displayed nonrectangular CV shapes, indicating greater contributions from double-layer capacitance and pseudocapacitance.

Thus, the annealing in an inert atmosphere significantly improves WO_3 electrode performance, making it a highly effective material for decoupled acid water electrolysis. The air-annealed WO_3 sample displays clear oxidation transitions for W^{4+} to W^{5+} and a broad transition peak for W^{5+} to W^{6+} in the anodic direction [291]. When annealed in nitrogen, these peaks become more distinct, indicating a higher presence of W^{4+} and better-defined redox behavior. This suggests that the nitrogen-annealed sample has a greater capacity for H^+ intercalation, as confirmed by its longer cycle times during electrochemical testing. Indeed, the capacity of WO_3 increased by approximately 40% when annealed in an inert nitrogen atmosphere compared to the air-annealed and as-prepared samples. The inert atmosphere annealing leads to a higher presence of W^{5+} species and oxygen vacancies, as observed through XPS analysis. These defects act as “self-doping”, which enhances the material’s pseudocapacitive performance, raising the specific capacity from $664.14 \text{ F}\cdot\text{g}^{-1}$ in air annealed samples to $837.43 \text{ F}\cdot\text{g}^{-1}$ for the nitrogen-annealed WO_3 . Lyophilization was employed to prevent particle agglomeration and significantly increase the specific surface area of the WO_3 nanoparticles, from $50.704 \text{ m}^2\cdot\text{g}^{-1}$ for the unannealed sample to a substantial increase in specific capacity (from 201.41 to $495.55 \text{ F}\cdot\text{g}^{-1}$). Although annealing reduced the specific surface area slightly, the capacity still rose to $664.14 \text{ F}\cdot\text{g}^{-1}$ due to the formation of monoclinic WO_3 from the dehydration of tungstite. Long-term chronopotentiometry experiments at different current densities confirmed the durability of the lyophilized WO_3 samples, which exhibited FE values of 98%–99%. The overall electrolysis efficiency ranged from 34% to 58%, with an H_2 cycle efficiency between 307 and $371 \text{ mAh}\cdot\text{g}^{-1}$. These findings underscore the importance of optimizing surface morphology and annealing conditions to maximize the performance of WO_3 as an effective pseudocapacitive material for H^+ intercalation.

Chen et al. [292] utilized $\text{K}_{0.5}\text{MnO}_2\text{-Ti}$ (KMO-Ti) synthesized via a simple sol-gel method as a solid-state redox mediator to effectively decouple the H_2 and O_2 evolution processes in alkaline water electrolysis, thereby enabling a membrane-free method for H_2 production. The $\text{K}_{0.5}\text{MnO}_2\text{-Ti}$, serving as a charge storage mediator electrode, demonstrated a stable $100 \text{ mAh}\cdot\text{g}^{-1}$ capacity at a current density of $0.1 \text{ A}\cdot\text{g}^{-1}$, attributed to the reversible K^+ insertion/extraction mechanism. The decoupled electrolysis device achieved step voltages of 1.02 and 0.57 V for H_2 and O_2 production, respectively, at a current of 5 mA with a nearly 100% FE. The H_2 production step involves the reduction of H_2O at the cathode and K^+ extraction from KMO-Ti. The subsequent O_2 production step involves K^+ insertion into KMO-Ti and the oxidation of H_2O at the anode. The valence state transitions between Mn^{3+} and Mn^{4+} accompany this process. The electrochemical performance of KMO-Ti and KMO was evaluated in a 1 M KOH alkaline electrolyte using a three-electrode system.

KMO and KMO-Ti CV curves were recorded at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. The redox peaks at $-0.16/0.24$ and $-0.1/0.19 \text{ V}$ (vs. Hg/HgO) indicate high electrochemical reversibility. Notably, KMO-Ti displayed a smaller peak-to-peak separation than KMO, suggesting higher redox reversibility and faster reaction kinetics with reduced polarization during the process. The redox potential windows for both KMO and KMO-Ti were positioned between the onset potentials of HER and OER as compared to commercial Pt and $\text{RuO}_2/\text{IrO}_2$ electrodes.

Further kinetic analysis of the KMO-Ti electrode via CV at scan rates from 1 to $30 \text{ mV}\cdot\text{s}^{-1}$ showed that the peak current (i_p) and scan rate (v) followed the power law relationship ($i_p = av^b$, where a and b are parameters). The b values for anodic and cathodic peaks were 0.72 and 0.73 , respectively, confirming the rapid kinetics of KMO-Ti. The performance of the decoupled system was further assessed by chronopotentiometry in 1 M KOH , with applied currents ranging from 2 to 200 mA . During Step 1 (HER process), the cell voltage was 1.02 V , which resulted from the potential difference between the cathodic reduction of H_2O to H_2 and the anodic oxidation of $\text{K}_{0.5}\text{MnO}_2\text{-Ti}$ ($\text{K}_{0.5}\text{MnO}_2\text{-Ti} \rightarrow \text{K}_{0.5-x}\text{MnO}_2\text{-Ti}$). In Step 2 (OER process), the cell voltage was 0.57 V , arising from the potential difference between the anodic oxidation of H_2O ($\text{OH}^- \rightarrow \text{O}_2$) and the cathodic reduction of $\text{K}_{0.5-x}\text{MnO}_2\text{-Ti}$ ($\text{K}_{0.5-x}\text{MnO}_2\text{-Ti} \rightarrow \text{K}_{0.5}\text{MnO}_2\text{-Ti}$). These steps combined to give an overall voltage of 1.59 V for the DWS, which is comparable to the conventional membrane-free Pt- $\text{RuO}_2/\text{IrO}_2$ electrolyzer voltage of 1.54 V . For comparison, a similar test using KMO as the redox mediator showed slightly higher voltages in both steps, consistent with the CV results. GC analysis shows that hydrogen was detected during Step 1, and after a purification step to remove residual H_2 , oxygen was detected during Step 2. This demonstrates that the decoupled water electrolyzer with $\text{K}_{0.5}\text{MnO}_2\text{-Ti}$ as the redox mediator can produce high-purity H_2 and O_2 without needing a membrane, facilitating accessible collection and utilization. The FE for H_2 and O_2 production were 99.1% and 99.5%, respectively. This work shows that integrating hydrogen production with potassium-ion battery technology offers a promising approach for renewable energy conversion and storage.

Recently, the Yamada group explored the fast proton (de)intercalation in $\alpha\text{-MoO}_3$, which was used as a cathode in aqueous $\text{MoO}_3\text{-Zn}$ battery [293]. $\alpha\text{-MoO}_3$ is known for its ultrafast proton transfer properties and can be used as a redox mediator for rapid hydrogen production in acidic electrolytes. The fast proton transfer is attributed to a dense hydrogen bond network within the lattice oxygen arrays of H_xMoO_3 . $\alpha\text{-MoO}_3$ demonstrates a large capacity of $204 \text{ mAh}\cdot\text{g}^{-1}$ and rapid hydrogen production at a current density of $10 \text{ A}\cdot\text{cm}^{-2}$ ($\sim 153 \text{ A}\cdot\text{g}^{-1}$), surpassing many previously reported solid-state redox mediators. Its bilayered structure, along with the multivalent redox centers (Mo^{6+} , Mo^{5+} , Mo^{4+} , and Mo^{3+}), has made $\alpha\text{-MoO}_3$ a promising material for fast kinetics and large-capacity battery applications [266, 294, 295]. Yamada et al. [296] investigated $\alpha\text{-MoO}_3$ as a high-rate, large-capacity redox mediator for DWS, enabling the production of pure hydrogen in a membrane-free system (Fig. 42(a)). $\alpha\text{-MoO}_3$ facilitated rapid hydrogen production at a current density of up to $10 \text{ A}\cdot\text{cm}^{-2}$. IrO_x/Ti felt, Pt mesh, and a carbon cloth-supported $\alpha\text{-MoO}_3$ mediator ($\sim 10 \text{ mg}\cdot\text{cm}^{-2}$) were utilized. In Step 1, O_2 evolution occurred at the IrO_x/Ti felt electrode, while proton interaction with $\alpha\text{-MoO}_3$ resulted in the formation of $\text{H}_{2.5}\text{MoO}_3$ ($\text{MoO}_3 \rightarrow \text{H}_{2.5}\text{MoO}_3$). In Step 2, hydrogen was produced at the Pt electrode, while proton deintercalation in $\text{H}_{2.5}\text{MoO}_3$ returned it to MoO_3 ($\text{H}_{2.5}\text{MoO}_3 \rightarrow \text{MoO}_3$). CV was

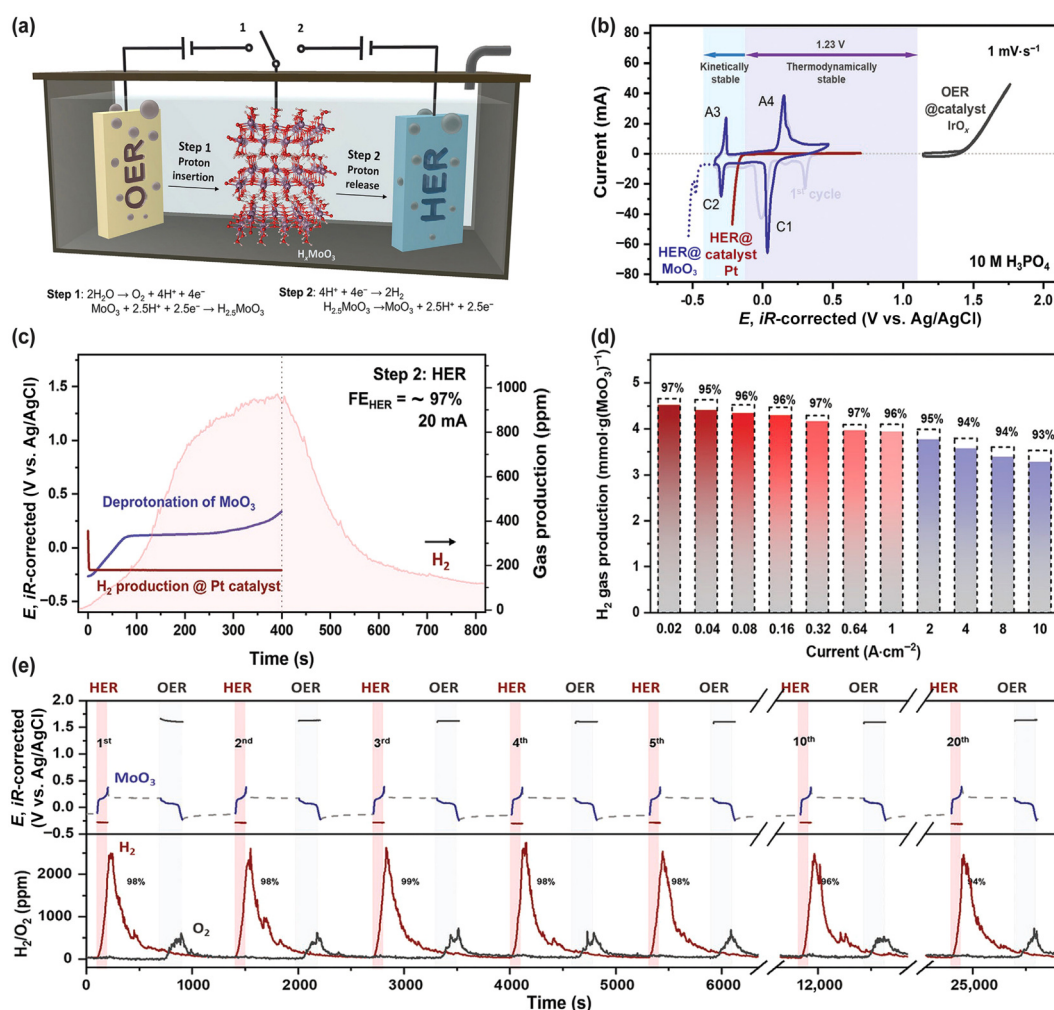


Figure 42 (a) Schematic illustration of the DWS using α - MoO_3 as solid-state redox mediator. (b) CV and LSV curves of α - MoO_3 , Pt, and IrO_x catalyst. (c) Chronopotentiometry curves of HER step at a current rate of 20 mA with a step duration of 400 s. (d) Hydrogen gas is produced based on the capacity acquired, and detected gas based on the MS signal with a mass loading level of 10 $\text{mg}\cdot\text{cm}^{-2}$ (red bars)–65 $\text{mg}\cdot\text{cm}^{-2}$ (blue bars), along with FE. (e) Twenty consecutive OER/HER cycles. Reproduced with permission from Ref. [296], © The Author(s), 2023.

measured for α - MoO_3 at a scan rate of 1 $\text{mV}\cdot\text{s}^{-1}$ in an aqueous 10 M H_3PO_4 having a cutoff potential set between -0.30 and 0.45 V vs. Ag/AgCl. CV curve of the first cycle shows four cathodic and two anodic peaks (Fig. 42(b)). After that, curves became symmetric, showing two pairs of redox peaks at ~ -0.3 and 0.2 V vs. Ag/AgCl. The difference between the first and subsequent cycles is due to proton trapping in the α - MoO_3 structure during the initial protonation, where approximately one proton per MoO_3 was trapped due to the absence of fast diffusion channels. About 1.5 protons per MoO_3 were reversibly involved in successive cycles, allowing for rapid cycling ($\text{H}_1\text{MoO}_3 \leftrightarrow \text{H}_{2.5}\text{MoO}_3$). The remaining 1.0 H^+ in α - MoO_3 can be extracted by applying a constant voltage at the end of deprotonation for 3 h. The redox peaks in subsequent cycles correspond to proton (de)intercalation between $\text{H}_1\text{MoO}_3/\text{H}_x\text{MoO}_3$ and $\text{H}_x\text{MoO}_3/\text{H}_{2.5}\text{MoO}_3$ ($0 < x < 1.5$). The potential of the HER catalyst electrode (Pt) was held constant at approximately -0.21 V vs. Ag/AgCl, while the potential of α - MoO_3 increased from -0.18 to 0.33 V upon deprotonation.

The total hydrogen gas measured by mass spectrometry was estimated at 40.2 μmol , approximately double the amount of oxygen produced in the first step, with a FE of 97% (Fig. 42(c)). No HOR occurred on the α - MoO_3 electrode, even in a pure

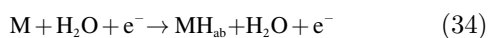
hydrogen atmosphere. When released, protons trapped in the H_1MoO_3 produce approximately 50% additional hydrogen gas on the HER electrode when a constant potential of 0.5 V vs. Ag/AgCl was applied to the α - MoO_3 electrode. This demonstrated that α - MoO_3 is an effective proton host, decoupling OER/HER into two steps. The average voltages for these steps were 1.58 and 0.32 V, respectively, which are lower than the 1.78 V typically required in a coupled case. The incremental overpotential was as low as 0.12 V, indicating high efficiency. The system achieved significant current rates of up to 1 $\text{A}\cdot\text{cm}^{-2}$ with a high FE for hydrogen production of 96%. Across all current rates examined, the FEs remained above 95%, indicating both high rate and efficient hydrogen production in the prototype system (Fig. 42(d)). Gas production during 20 consecutive OER and HER cycles when the current was increased to 80 mA for the fast HER steps and maintained at 40 mA for the slower OER steps, with a 500 s pause between each HER/OER step to distinguish the gas products. The potentials of the OER and HER electrodes remained constant at around 1.6 and -0.3 V vs. Ag/AgCl, respectively, in each cycle, while the potential of α - MoO_3 oscillated between -0.3 and 0.4 V during repeated (de)protonation cycles. Hydrogen production increased sharply during the HER step, followed by a decrease once the current stopped, with FEs ranging from 94% to 99%

(Fig. 42(e)). The α - MoO_3 on high mass loading 10 to 65 $\text{mg}\cdot\text{cm}^{-2}$ also gives better and more stable results. The hydrogen produced with α - MoO_3 (~ 4 mmol H_2 per g of MoO_3 at 100 $\text{A}\cdot\text{g}^{-1}$) was more than three times higher than that with CuFe-TBA.

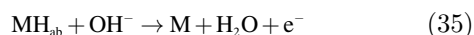
The hybrid water electrolysis process offers a green and sustainable route for producing fine chemicals while generating hydrogen, driven by advances in anodic electrocatalysts. Xu et al. [297] reported the preparation of a nickel-cobalt-layered double hydroxide (Ni-Co LDH) modified nickel foam synthesized at room temperature through a simple soaking method. This Ni-Co LDH electrode effectively catalyzes the dehydrogenation oxidation of primary amines, producing aromatic and aliphatic nitriles in high yields. Furthermore, the Ni-Co LDH electrode serves as an electron reservoir, enabling DWS with 100% CE in a membrane-free electrolytic cell. Nitrile compounds are essential in the synthesis of numerous industrial chemicals [298, 299]. Integrating primary amine electrooxidation with HER provides a mild, oxidant-free approach for generating nitriles. Different types of catalysts, such as NiSe, NiP, vacancy-rich $\text{Ni}(\text{OH})_2$, Mn-doped $\text{Ni}(\text{OH})_2$, and bimetallic or trimetallic metal-organic frameworks (MOFs), accelerate the selective oxidation of primary amines [300–306]. Ni-Co LDH exhibits superior electrocatalytic activity compared to Co LDH. Furthermore, the Ni-Co LDH electrode was used as an electron reservoir to decouple traditional water electrolysis into separate hydrogen and oxygen evolution steps, producing pure hydrogen in a single-compartment electrolytic cell. For this purpose, a platinum plate cathode, a commercial carbon rod anode, and the Ni-Co LDH electrode achieved a cell voltage of 1.57 V for hydrogen production and 0.66 V for oxygen evolution. Both processes were carried out at an applied current of 30 mA for 300 s, resulting in 100% CE. Moreover, the cell maintained stable voltages during 10 consecutive cycles, confirming the durability of the Ni-Co LDH electrode. Findings highlight the potential of Ni-Co LDH electrodes, particularly their charge storage capability and role as redox mediators in decoupling water electrolysis.

Zhang et al. [307] proposed a novel approach integrating a nickel-metal hydride battery as a redox mediator with cost-effective NiFe layered double hydroxides (LDHs)-NiFe alloy gradient hybrid bifunctional catalysts as gas evolution electrodes to decouple HER/OER. The HER/OER cell utilizing a hydrogen storage alloy, nickel hydroxide, and catalytic electrode, respectively, requires only 0.28 V for HER and 0.25 V for OER to reach a 100 $\text{mA}\cdot\text{cm}^{-2}$ current density. Furthermore, a NiOOH -Zn cell was introduced to replace OER with a reaction involving Zn. A nickel-hydrogen cell, composed of a hydrogen storage alloy and $\text{Ni}(\text{OH})_2$, served as the redox mediator. At the same time, the synthesized NiFe-based bifunctional catalyst was employed as the gas production electrode for HER and OER. The operational steps for this process are as follows (Eqs. (33)–(38)):

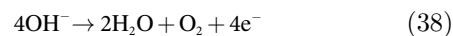
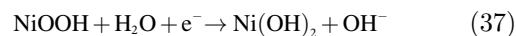
Step 1: Ni-MH batteries are charged



Step 2: HER



Step 3: OER



$\text{Ni}(\text{OH})_2$ undergoes oxidation during charging, losing electrons and hydrogen ions, while during discharge, it is reduced, regaining electrons and hydrogen ions [308]. The bifunctional NiFe-based catalyst consists primarily of NiFe alloy and NiFe-LDH. LSV curves for the NiFe-based bifunctional catalyst show low overpotentials of 163 mV (HER) and 193 mV (OER) at a 100 $\text{mA}\cdot\text{cm}^{-2}$ current density. Remarkably, the catalytic performance of this catalyst for HER is comparable to that of the commercial Pt/C catalyst. In addition, the as-prepared NiFe-based bifunctional catalyst demonstrates outstanding performance in OER. The double-layer capacitance (C_{dl}) values were measured as 29.51 $\text{mF}\cdot\text{cm}^{-2}$ for HER and 18.97 $\text{mF}\cdot\text{cm}^{-2}$ for OER, indicating excellent electrochemical activity. The TOF for HER at an overpotential of 190 mV was 0.246 s^{-1} , while for OER at an overpotential of 270 mV, the TOF was 0.085 s^{-1} . The exchange current density (j_0) is HER/5.01 $\text{mA}\cdot\text{cm}^{-2}$ and OER/0.007 $\text{mA}\cdot\text{cm}^{-2}$. The Tafel slope for HER/OER was 120/55 $\text{mV}\cdot\text{dec}^{-1}$, respectively. Step 1 was operated at 100 $\text{mA}\cdot\text{cm}^{-2}$ for 200 s, while Steps 2 and 3 ran for the same time and current density, resulting in a CE of 100%. The NiFe-based bifunctional catalyst achieved a total voltage of 1.96 V for Steps 1, 2, and 3, corresponding to an overall electrolysis efficiency of 92.8%. GC analysis indicates that no oxygen was detected during hydrogen generation, demonstrating the system's excellent performance for decoupled HER and OER. To assess the cycling stability, a current of 20 mA was applied to Step 1 for 30 min, and 100 mA was applied to Steps 2 and 3. Each step was operated for 6 min. The FE remained 100% after 35 cycles, indicating stable H_2/O_2 separation. The CV curves of Zn/Zn^{2+} indicate that the primary NiOOH -Zn cell achieved a discharge voltage of 1.65 V. In Step 3, the OER was replaced by Zn oxidation ($\text{Zn} \rightarrow \text{Zn}(\text{OH})_4^{2-}$), with no significant impact on hydrogen production in Step 2. After charging for 200 s in Step 1, Step 3 could discharge at the same current density for an equivalent time, ensuring 100% CE and effective charge utilization. To test battery stability, Step 1 was charged with 250 mA for 20 min, followed by applying 25 mA to Steps 2 and 3; both steps operated for 200 min, maintaining 100% CE with no degradation after 4200 min, confirming the system stability. The discharge voltage of 1.65 V in Step 3 was sufficient to power Step 1 (1.3 V) or multiple repetitions of Step 2 (0.28 V). Additionally, Zn^{2+} produced in alkaline solutions during Step 3 can be recovered when sufficient energy allows for continuous hydrogen production while minimizing Zn consumption.

Zhao et al. [309] reported a novel approach utilizing doping and heterostructure engineering to develop an advanced charge buffer electrode, $\text{I-Ni}(\text{OH})_2/\text{Co}(\text{OH})_2$ @nickel foam, for efficient HER and OER. The HER process at the cathodic electrode demonstrated continuous hydrogen generation over a 1500 s cycle at 0.1 A, showcasing impressive performance. During this process, the $\text{I-Ni}(\text{OH})_2/\text{Co}(\text{OH})_2$ @NF electrode underwent oxidation, reaching a working voltage of 1.572 V. This was followed by the OER, where the charge mediator was regenerated, leading to oxygen generation at 0.33 V, maintaining gas production in both stages. Moreover, integrating an oxidizing mediator with a Zn sheet effectively replaced the second OER stage, forming a battery-like system. This membrane-free alternating H_2/O_2 evolution

strategy demonstrates a cost-effective approach for hydrogen production. CV curve of the I-Ni(OH)₂/Co(OH)₂@NF electrode reveals clear redox signals at 0.642/0.267 V vs. Hg/HgO, corresponding to the Ni/Co hydroxide redox reactions (M(OH)₂ to MOOH). LSV comparisons with benchmark electrodes Pt-Ti and RuO₂/IrO₂-coated titanium mesh (Ru/Ir-Ti) highlight the performance of the I-Ni(OH)₂/Co(OH)₂@NF electrode. The redox potential of this electrode lies between the onset potentials for HER and OER, demonstrating its charge storage capability and enabling DWS. The coupling strategy in the I-Ni(OH)₂/Co(OH)₂ heterojunction significantly enhances charge storage, as reflected in the increased CV area compared to Ni(OH)₂ and I-Ni(OH)₂ alone. This suggests that electron transfer within the heterojunction effectively suppresses O₂ generation at higher oxidation potentials. The oxidized mediator undergoes reduction, facilitating the reformation of the charge storage medium for subsequent hydrogen production. Step 1 involves hydrogen evolution at the cathode, where the potential is recorded as -1.05 V vs. Hg/HgO, enabling continuous H₂ production. Concurrently, the anode undergoes an oxidation process, transitioning the Ni(OH)₂-Co(OH)₂ phase to NiOOH-CoOOH at 0.52 V vs. Hg/HgO. The voltage difference between these reactions is 1.57 V at 0.1 A, sustaining hydrogen evolution for 1500 s. In Step 2, oxygen evolution occurs at an operating voltage of 0.77 V vs. Hg/HgO. Simultaneously, a reduction occurs at the cathode, converting NiOOH-CoOOH back to Ni(OH)₂-Co(OH)₂ at 0.44 V vs. Hg/HgO, resulting in a cell potential of 0.33 V during oxygen evolution. Chronopotentiometry experiments at varying currents (0.05, 0.15, and 0.2 A) showed that the duration of hydrogen generation can be modulated by adjusting the current. The voltage differences between Steps 1 and 2 indicate the potential for integration with intermittent renewable energy sources, such as wind and solar power. A significant distinction in Step 2 involves the discharge of the MOOH-Zn battery (MOOH → M(OH)₂ and Zn → ZnO₂²⁻), facilitating the reduction of MOOH back to M(OH)₂, a key advantage over the traditional O₂-generation process. This discharge mechanism enhances the charge storage capacity. It supports the regeneration of the electrode materials, as shown in the charging and discharging behavior of I-Ni(OH)₂/Co(OH)₂@NF under different current densities (100–180 mA). The results demonstrate excellent areal capacitance and robust charge storage, highlighting the potential of this membrane-free system for efficient, scalable hydrogen production powered by renewable energy sources [261].

Gan et al. [163] revealed a novel ACS-OER process involving the electrochemical oxidation and subsequent reduction of nickel hydroxides to NiOO⁻ active species. The final release of O₂ occurs through a distinct reductive step, driven by weakened Ni-O covalency in the NiOO⁻ species [256]. This process enables significantly lower overpotentials than conventional anodic oxygen evolution. For example, thermochemically driven OER has been previously reported, where H₂ evolves at the cathode while Ni(OH)₂ is oxidized to NiOOH at the anode, which then spontaneously releases O₂ through a chemical reduction by water. However, achieving an efficient reaction rate for this chemical step requires elevated temperatures (95–120 °C), which adds complexity to the system [105, 200, 310]. In this study, Gan and coworkers reported the discovery of a fast-kinetic ACS-OER process through the electrochemical Ni(OH)₂/NiOOH redox reaction. Transition metals, such as Fe, influence the ACS-OER process. CV was performed in Fe-free KOH solution to isolate the effect of Fe substitution. The Ni(OH)₂/C catalyst exhibited

significantly higher Ni(OH)₂/NiOOH redox peaks and OER activity compared to the Ni(OH)₂/C-120 catalyst. Both catalysts demonstrated a similar β-Ni(OH)₂-like phase after OER testing [311, 312]. The strong correlation between the formation of NiOO⁻ and the amount of cathodically evolved O₂ suggests that NiOO⁻ is generated through the oxidation of Ni(OH)₂. Therefore, this OER is defined as an ACS-OER process. This implies that both conventional anodic OER and ACS-OER share the same RDS, the decomposition of NiOO⁻ to release O₂. However, they proceed differently to overcome this bottleneck [158].

The findings revealed a sequential O₂ release pathway, where the ACS-OER follows the same initial steps as conventional anodic OER to form the active oxygen species (OO⁻). However, in ACS-OER, a subsequent reduction of NiOO⁻ weakens the Ni-O bond, promoting O₂ release. This reduction-driven OER operates at much lower overpotentials. During charging, Ni(OH)₂ at the positive (anodic) electrode is oxidized to NiOOH. It is important to note that only a portion of NiOOH can undergo further deprotonation and O-O coupling to form NiOO⁻. This is because NiOO⁻, generated by O-O coupling between μ₁-O and μ₂-O forms predominantly at edge sites, while in-plane sites remain as NiOOH. Additionally, even at edge sites, only a fraction of NiOOH can deprotonate due to its specific pK_a value [256]. During discharging, the NiOOH/NiOO⁻ species at the positive (cathodic) electrode is reduced back to Ni(OH)₂, releasing O₂. In this process, the Ni oxyhydroxide positive electrode accepts fewer electrons from the external circuit during discharging than it releases during charging due to internal electron transfer between high-valent Ni and the negatively charged OO⁻ species. Simultaneously, a portion of the generated H₂ or other fuels (e.g., waste pollutants) is oxidized at the negative (anodic) electrode, producing electrical energy. This charging-discharging cycle enables time decoupled H₂/O₂ evolution, completing the water electrolysis process at much lower overpotentials (< 200 mV). The CE of this cycle is inherently less than 100%, as some of the charge input is used for water splitting. Furthermore, the CE largely depends on the amount of NiOO⁻ formed; larger amounts of NiOO⁻ lead to lower CE. To prevent anodic OER, the cutoff voltage was set to 1.5 V. The specific capacity and CE during the first cycle were calculated to be approximately 299 mAh·g⁻¹ and 85%, respectively, indicating that 15% of the total charge input is utilized for water splitting. Over 100 charging-discharging cycles, the specific capacity gradually decreased to 186 mAh·g⁻¹, while the CE increased from 85% to 96%, indicating reduced performance in DWS. This decline in performance is likely linked to decreased ACS-OER activity of the Ni(OH)₂/C catalyst. This process contrasts with the conventional four-electron anodic OER. This work not only provides insights into the alkaline OER mechanism but also offers a promising approach for energetically efficient DWS and energy storage.

4.2 Organic solid-state redox mediators

In the abovementioned DWS, insoluble inorganic solid-state redox mediators were utilized. In light of this tactic, a new alternative approach to decoupled water was launched using insoluble organic solid-state redox mediators. For DWS in an acidic electrolyte, an organic polytriphenylamine (PTPAn) battery electrode was introduced as an insoluble solid-state redox mediator (Fig. 43(a)). The reaction mechanism of this mediator is different from ECPBs, having an anion adsorption/desorption mechanism. This has an advantage over molecular redox mediators because it is membrane-free, as reported by Xia et al.

[199]. Further extending this approach, two solar-driven water electrolysis PEC cells and hybrid system (combining PV and electrolysis system) were experimentally evaluated. Molecular redox mediators have some drawbacks, such as (1) the use of expensive membranes, (2) the internal resistance of the membranes lowers the performance, and (3) OER overpotential affects the reaction rate. Chemical oxidative polymerization of triphenylamine (TPAn) yields PTPAn. In an acidic electrolyte, a Pt plate was utilized as the counter electrode, and Ag/AgCl was employed as the reference electrode in 0.5 M H_2SO_4 . CV and LSV curves of PTPAn were investigated at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$ of Pt- and $\text{RuO}_2/\text{IrO}_2$ Ti-coated electrodes for HER and OER, respectively. Two pairs of reversible redox waves located at 0.5/0.48 and 0.6/0.58 V (vs. Ag/AgCl) were obtained, giving confirmation of two kinds of isomers of PTPAn (Fig. 43(b)). A positive and negative peak scan difference of 0.02 V confirms its electrochemical reversibility.

The charging mechanism of PTPAn is based on the adsorption/desorption of anions coupled with the loss and gain of electrons, which differs from previously reported ECPBs. Organic materials have low electronic conductivities, which can be increased by additives. Galvanostatic charge/discharge experiments were performed from 0 to 0.7 V (vs. Ag/AgCl) to evaluate PTPAn's capacity to store the charge. It was found that $77 \text{ mAh}\cdot\text{g}^{-1}$ of reversible discharge capacity could be achieved at a current density of $0.2 \text{ A}\cdot\text{g}^{-1}$ (Fig. 43(c)). PTPAn has a greater

charge storage capacity as compared to soluble molecular redox mediator, i.e., silicotungstic acid (theoretical capacity = $\sim 18.6 \text{ mAh}\cdot\text{g}^{-1}$) value. The performance of DWS was studied using chronopotentiometry results with the applied current in the range of 2–100 mA (Figs. 43(d) and 43(e)). Cyclic performance is shown in (Fig. 43(f)). Decoupling can be done by using two smaller inputs, one for HER and the second for OER, in two steps. In the first step, 0.7 V is required for H_2 evolution over PTPAn oxidation to PTPAn^+ and H_2O reduction at the cathode ($\text{H}^+ \rightarrow \text{H}_2$). In the second step, 0.95 V is required for O_2 evolution over water oxidation ($\text{H}_2\text{O} \rightarrow \text{O}_2$) at the anode and PTPAn^+ reduction to PTPAn at the cathode (Fig. 43(g)). PTPAn shows 100% CE for both HER and OER. The investigation was done at different currents to validate the operational flexibility. Cell voltages of 1.0 V for HER (Step 1) and 1.22 V for OER (Step 2) are needed to initiate DWS at a higher current (100 mA at 100 s). Two-step DWS requires higher current than conventional PEM-based water electrolysis (Fig. 43(h)). 100% CE based on cyclic performance over 120 cycles shows the device stability for hydrogen and oxygen production. 97.8% FE for H_2 was obtained. The authors also applied this solar-to-hydrogen conversion strategy directly using a photovoltaic module without any membrane or diaphragm. Solar energy to hydrogen efficiency obtained using a silicon photovoltaic module was 5.4%. Finally, PTPAn, an organic battery electrode, was utilized as an insoluble solid-state redox mediator for DWS in acid media in conjunction with PV-based water

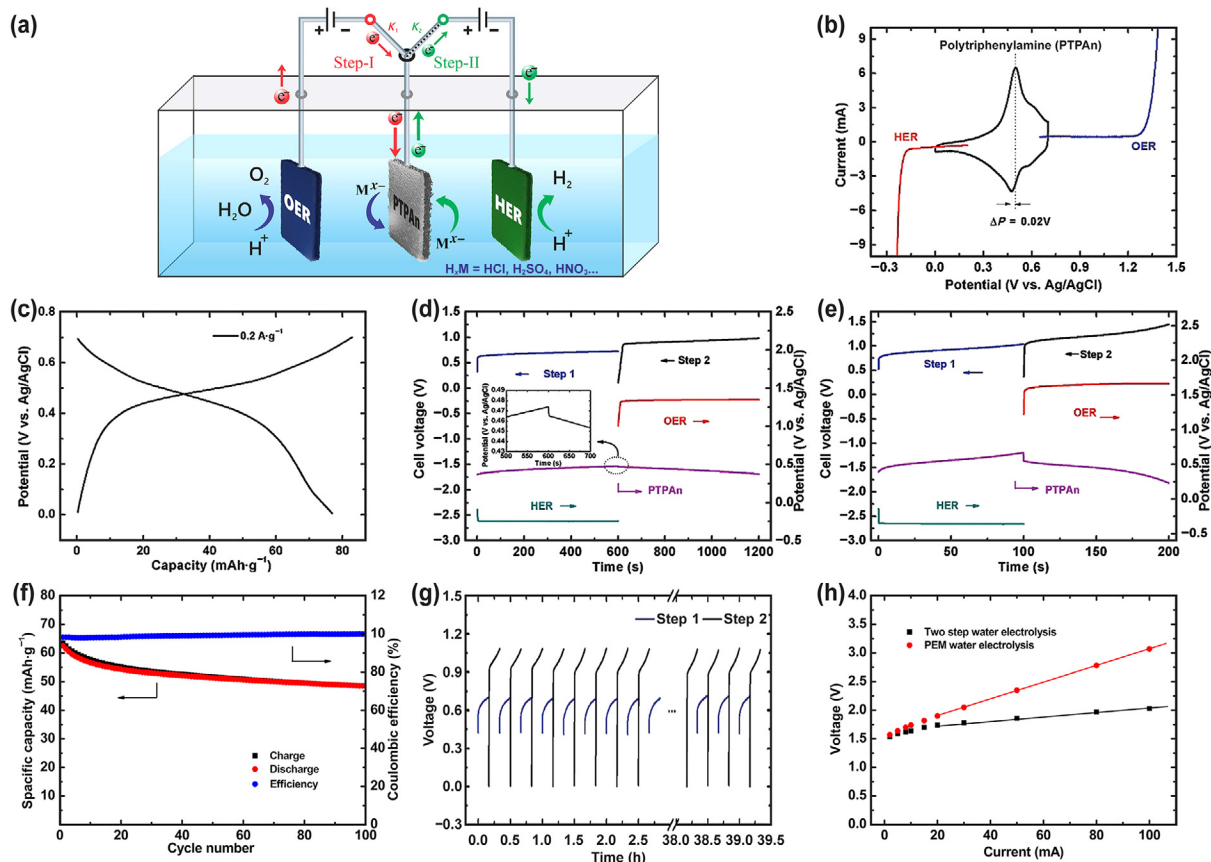


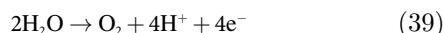
Figure 43 Solid-state redox mediator-based decoupled water-splitting using polytriphenylamine. (a) Water electrolysis H_2/O_2 decoupling diagram. (b) CV and LSV curves of the PTPAn electrode (black) in 0.5 M H_2SO_4 . (c) Charging/discharging curves of PTPAn at a current density of $0.2 \text{ A}\cdot\text{g}^{-1}$ in 0.5 M H_2SO_4 . ((d) and (e)) Chronopotentiometry curves (voltage vs. time) of the cell at a current of 5 and 100 mA. (f) CE (100%) and capacity retention (76.5%) of PTPAn electrode over 100 cycles at the current density of $1 \text{ A}\cdot\text{g}^{-1}$ in 0.5 M H_2SO_4 . (g) Chronopotentiometry curves of the H_2/O_2 generation cycle with an applied current of 5 mA and step time of 600 s. (h) PEM versus two-step water electrolysis voltage comparison. Reproduced with permission from Ref. [199], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

electrolysis. 6.2 mL of hydrogen was produced within 100 s in the HER step, approaching the theoretical value of 6.34 mL with 97.8% FE.

In acidic electrochemical water electrolysis, pyrene-4,5,9,10-tetraone (PTO) was outlined as a decoupling agent by Wang and colleagues [313]. PTO is a membrane-free organic proton buffer, an insoluble solid-state redox mediator. O₂ and H₂ may be theoretically separated with little effort by inserting an electron-coupled proton buffer electrode between the anode and cathode. The kinetics of reactions as a whole can be stated as follows (Eqs. (39)–(42)):

OER (Step 1):

Anode



Cathode



HER (Step 2):

Anode



Cathode



SEM and TEM of PTO show its rod-like morphology, having a

diameter of ~ 400 nm. Three different electrode designs were used in an acidic electrolyte (0.5 M H₂SO₄): a Pt-coated Ti-mesh electrode for HER, a commercial RuO₂/IrO₂-coated Ti-mesh electrode for OER, and a PTO film electrode. The CV curve of PTO electrode at a scan rate of 5 mV·s⁻¹ with an LSV reveals two pairs of reversible redox peaks, 0.34/0.2 and 0.46/0.32 V (vs. Ag/AgCl). According to these calculations, the PTO electrode redox potential is between the HER and OER onset potentials (Fig. 44(a)). CV responses at different scan rates of the PTO electrode were summarized by the $i_p = av^b$ equation. The b value of the PTO electrode is 0.77 (greater than 0.5), which shows that the diffusion process cannot control the fast kinetics of the mediator. Moreover, the kinetics of PTO were verified by electrochemical impedance spectroscopy. Galvanostatic charge–discharge investigations within the range of 0–0.7 V (vs. Ag/AgCl) were carried out to check the PTO electrode proton/electron storage capacity. At a current density of 0.2 A·g⁻¹, the PTO electrode shows a reversible capacity of 156 mAh·g⁻¹, a superior theoretical storage capacity than the previously reported ECPB soluble molecular redox mediators. An increase in current density leads to a decrease in the specific storage capacity of PTO. A reversible capacity of 107 mAh·g⁻¹ is achieved at a high current density of 20 A·g⁻¹. Over 200 cycles, the PTO electrode retains 80% of its original capacity at 1 A·g⁻¹. A varying applied current within a range of 5 to 1000 mA was applied to check the performance of the DWS of the PTO electrode.

Chronopotentiometry results show an average cell voltage of 1.1/0.56 V, which was achieved for OER (Step 1) and HER (Step

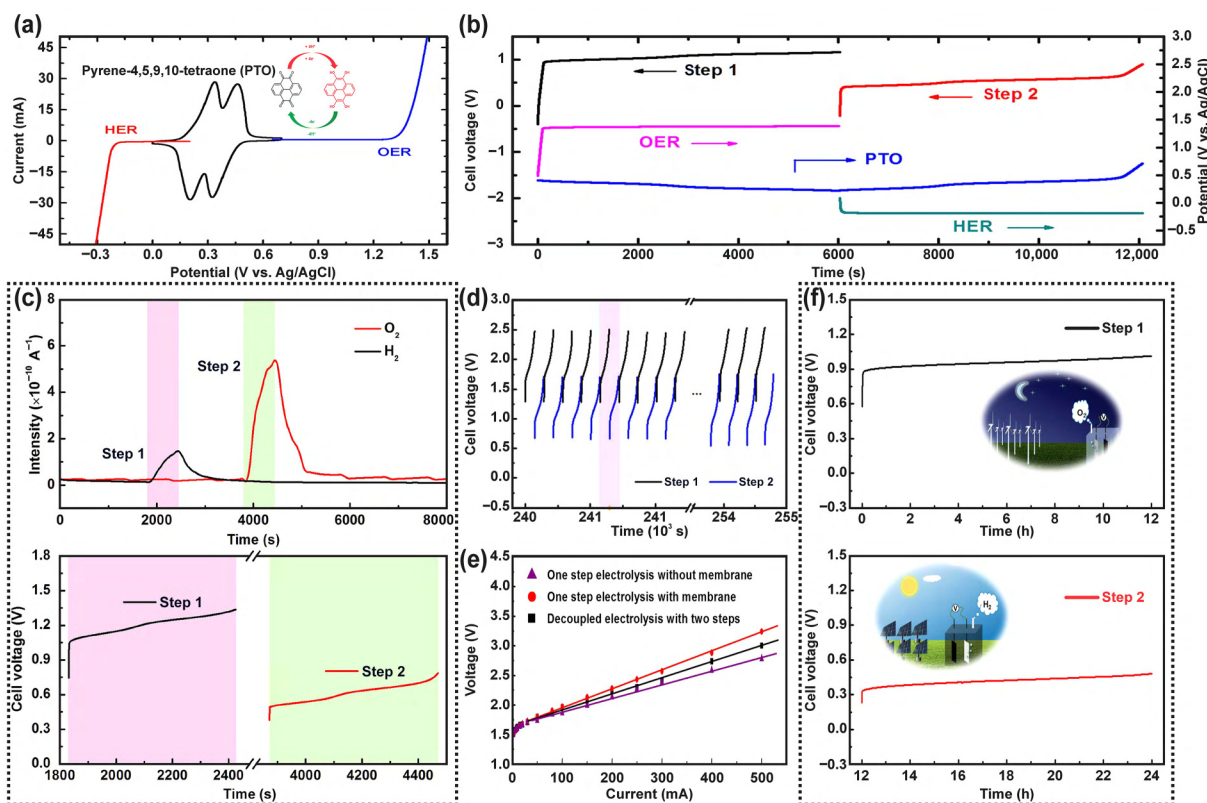


Figure 44 Solid-state redox mediator-based decoupled water splitting using pyrene-4,5,9,10-tetraone. (a) CV curves of the PTO electrode (black) at a scan rate of 5 mV·s⁻¹ in 0.5 M H₂SO₄, while LSV curves of the HER (red) and OER (blue) electrodes. Inset: reaction mechanism of PTO electrode. (b) Chronopotentiometry curves (voltage vs. time) of the decoupled cell at a current of 5 mA, with a step time of 6000 s. The voltages for O₂/H₂ production (Steps 1 and 2) are labeled as black and red lines. (c) *In-situ* DEMS analysis and the corresponding chronopotentiometry curves (voltage vs. time) at an applied current of 50 mA of the electrolytic cell produce high-purity H₂/O₂. (d) Cyclic performance of the PTO electrode from the 201–300 cycle of the decoupled electrolysis process over an applied current of 500 mA and a step time of 72 s. (e) Cell voltages comparison of three systems. (f) Chronopotentiometry measurement data clarifies flexible renewables use in the daytime and at night with a current of 1 mA. Reproduced with permission from Ref. [313], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.

2), respectively, when a current of 5 mA was applied (Fig. 44(b)). It is clearly seen that the cell voltage increases sharply in Step 2 at 6000 s because PTO-4H has been oxidized to PTO with the release of proton. Time equality between Steps 1 and 2 gives 100% CE (Figs. 44(c) and 44(d)). At higher currents, i.e., 50 and 500 mA, the cell voltages for Steps 1 and 2 are 1.27/1.84 and 0.6/1.15 V at 600 and 72 s, respectively. Cyclic performance over 300 consecutive cycles at different applied currents (5, 50, and 500 mA) shows the high stability of alternate production of hydrogen and oxygen. The *in-situ* DEMS results show that during DWS, no hydrogen was detected during Step 1-OER, and in the same way, no oxygen was detected in Step 2-HER, which clarifies the purity of hydrogen and oxygen during the whole process (Fig. 44(e)). The acquired FE of H_2 was 98.7%. It should be noted that mass loading of PTO is an important factor in determining each step duration during the cyclic process. Therefore, it is possible to produce hydrogen from solar energy during the day and oxygen from wind power at night (Fig. 44(f)). Additionally, PTO-based DWS can utilize non-precious OER/HER electrodes.

For DWS in acidic conditions, Chen et al. [314] proposed PANI, a cheap, insoluble, organic solid-state redox mediator. Given its low molecular weight and favorable redox potentials, PANI demonstrates a workable discharge capacity of $125 \text{ mAh}\cdot\text{g}^{-1}$ over a current density of $0.2 \text{ A}\cdot\text{g}^{-1}$. Cell voltages as low as 0.80 V are sufficient to power HER and OER. Larger molecular weight compounds like $H_3Mo_{12}PO_{40}$ (weight-average molecular weight (M_w) > $1800 \text{ g}\cdot\text{mol}^{-1}$) and $H_4SiW_{12}O_{40}$ (M_w > $2800 \text{ g}\cdot\text{mol}^{-1}$) have a lower charge storage capability than the previously mentioned redox mediators. Small organic compounds have charge storage capacity and water solubility that are both excellent, but CE is reduced due to side reactions at the membrane or diaphragm. In this regard, conducting polymers are promising redox mediators for DWS because of their proper redox potentials, high charge storage capacity, and reversible redox cycle [315]. The synthesized PANI powder is dark green and has a poor crystalline structure. The powdered PANI coated on Ti mesh was used as a solid-state redox mediator electrode. In conventional water splitting, a practical voltage of $\geq 1.6 \text{ V}$ is required as compared to theoretical voltage (1.23 V), along with > 300 mV overpotential (Fig. 45(a)). The effectiveness of PANI as an electrochemical material was studied in a 0.5 M H_2SO_4 solution. CV curve of PANI shows two redox couples of leucoemeraldine/emeraldine at 0.39 V and emeraldine/pernigraniline at 0.85 V by losing and gaining of electrons (Fig. 45(b)). The redox peaks located between HER and OER onsets show the capability of a mediator that can be used to decouple water. LSV curve shows $-0.08/0.56 \text{ V}$ cell voltage was required to produce H_2 at Pt electrode by reduction of protons and reduction of PANI electrode, respectively (Fig. 45(c)). In contrast, 0.75/1.65 V cell voltage was required to oxidize PANI and water oxidation to produce O_2 at RuO_2/IrO_2 electrode to reach a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$. For our simplicity, 1.09 V is required for OER with a combination of (RuO_2/IrO_2)-PANI electrode to produce O_2 by oxidation of water, while 0.83 V is required for HER with a combination of PANI-Pt electrode to produce H_2 at a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$. It requires an overall voltage of 1.92 V for the two-step decoupled water splitting.

PANI shows better charge-discharged storage capacity ($125 \text{ mAh}\cdot\text{g}^{-1}$) in 0.5 M H_2SO_4 at $0.2 \text{ A}\cdot\text{g}^{-1}$ current density (Fig. 45(d)), which is higher than previously reported redox mediators, i.e., polytriphenylamine ($77 \text{ mAh}\cdot\text{g}^{-1}$), phosphomolybdic acid ($27.6 \text{ mAh}\cdot\text{g}^{-1}$), and silicotungstic acid ($18.6 \text{ mAh}\cdot\text{g}^{-1}$) [28, 172]. The high storage capacity of PANI is due to its low molecular weight, simple structure, multiple redox peaks, and

broad redox potential. PANI shows 100% CE with 92% capacity retention over 40 cycles (Fig. 45(e)). The equilibrium potential of PANI plays an important role in smooth DWS. At 0.7 V, an equilibrium potential of PANI HER and OER operates on the same potential, nearly 0.75 V. Balanced voltage has an advantage because there will be no need for an additional power supply. For HER, 0.55 V at PANI-Pt electrode, and for OER, 1.32 V at RuO_2/IrO_2 -PANI electrode cell voltage of over 0.4 V PANI equilibrium potential is required at a current density of 5 mA (Figs. 45(f) and 45(g)). Chronopotentiometry result shows the DWS performance of the PANI electrode at equilibrium potentials (Fig. 45(h)). When the PANI equilibrium potential is raised from 0.4 to 0.7 V, the cell voltage needed to supply the same current for HER and OER is raised to 0.8 V. Finally, a 0.8 V power supply is required to start the DWS, which cannot be achieved earlier. PANI shows excellent performance over solar irradiations using Si solar cells having $\sim 1.0 \text{ V}$ (Fig. 45(i)).

Zhao et al. [316] developed a strategy for the *in-situ* growth of ultrathin nanosheet arrays of two-dimensional MOFs (2D-MOFs) on various supports using a simple one-step chemical bath deposition method. The organic ligand, 2,6-naphthalenedicarboxylic acid dipotassium, was added into an aqueous solution of metal salts (iron nitrate and nickel acetate) in the presence of a substrate (Fig. 46(a)). The resulting integrated MOF electrodes exhibit unexpectedly superior performance for the HER and OER for overall water splitting. The crystal structure of the MOF consists of alternating organic hydrocarbon (2,6-naphthalenedicarboxylate groups) and inorganic metal-oxygen layers (MO_6 units, where $M = \text{Cu, Fe, or Ni}$). The metal ions are octahedrally coordinated, each bonded to two trans-monodentate carboxylates and four equatorial water molecules, while each naphthalene dicarboxylate bridges two metal atoms. The NiFe-MOF also demonstrates high activity towards the HER in water splitting. The electrocatalytic performance of NiFe-MOF for HER in 0.1 M KOH at $10 \text{ mA}\cdot\text{cm}^{-2}$ exhibits a low overpotential of 134 mV, better than that of calcined NiFe-MOF (255 mV), bulk NiFe-MOF (196 mV), and Ni-MOF (177 mV) (Fig. 46(b)). The TOF of NiFe-MOF for HER at an overpotential of 400 mV is 2.8 s^{-1} . This performance is comparable to that of state-of-the-art non-precious metal-based HER catalysts. Additionally, a prolonged chronoamperometric (CA) test at -0.2 V vs. RHE (Fig. 46(c)), for 2000 s, showed a stable current response, with identical LSV curves before and after the test, indicating excellent durability of the NiFe-MOF for HER. At an applied cell voltage of 1.6 V, a significant amount of H_2 gas is generated at the cathode and O_2 gas at the anode, as confirmed by GC analysis. At a voltage of 1.55 V, the electrolytic cell demonstrates excellent catalytic activity, achieving a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ (Fig. 46(d)), which is 70 mV lower than Pt/C and IrO_2 . Additionally, the Tafel slope for the NiFe-MOF ($256 \text{ mV}\cdot\text{dec}^{-1}$) is lower than that of the Pt/C and IrO_2 system ($267 \text{ mV}\cdot\text{dec}^{-1}$). LSVs further bolster the robustness of water electrolysis (Fig. 46(e)). The cell also shows excellent stability in a prolonged CA test at 1.5 V for 20 h (Fig. 46(e), inset). Partial reduction of NiO_6 within the MOF led to the formation of a Ni/NiO₆ interface at the cathode. At this interface, OH^- generated from water splitting preferentially attaches to the NiO_6 site due to strong electrostatic attraction to the positively charged Ni^{2+} species, while a nearby Ni site facilitates hydrogen adsorption and the Volmer step, enhancing HER catalytic activity [317]. Summary of recent studies on insoluble solid-state redox mediators for decoupled water splitting can be seen in Table 4.

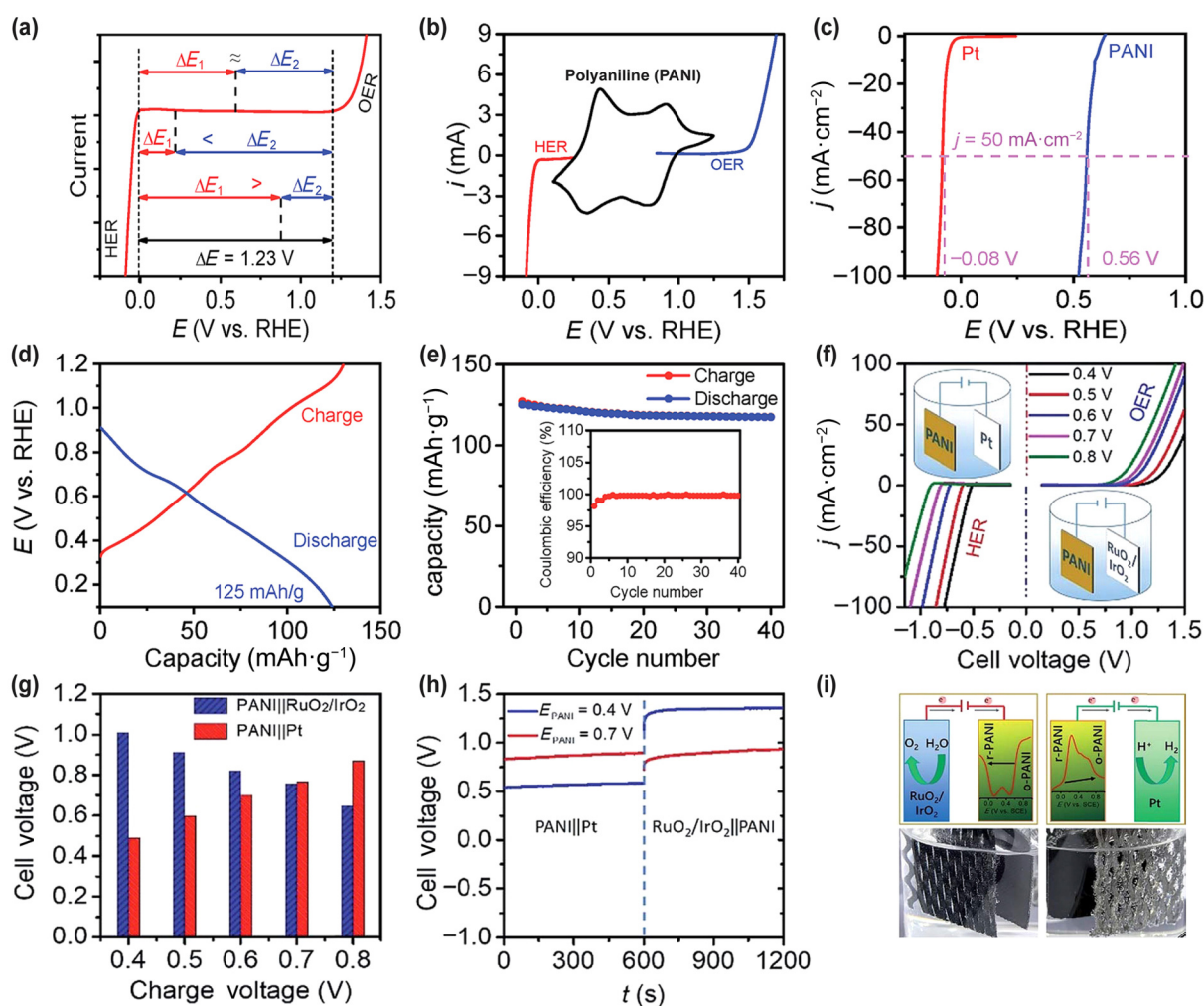


Figure 45 Solid-state redox mediator-based decoupled water splitting using polyaniline. (a) The necessary voltage for water splitting using redox mediators. (b) CV and LSV curves of the PANI film electrode, RuO₂/IrO₂, and Pt electrode at a scan rate of 10 mV·s⁻¹. (c) LSVs of PANI and Pt electrode to produce H₂. (d) Galvanostatic charge/discharge. (e) PANI electrode cyclic stability at 0.2 A·g⁻¹. (f) PANI||Pt LSVs for the HER and RuO₂/IrO₂||PANI LSVs for the OER that can be used in the DWS process. (g) Decoupled HER/OER onset cell voltages. (h) Decoupled HER/OER chronopotentiometry curves at 5 mA (0.025 A·g⁻¹) across the PANI electrode at 0.4 and 0.7 V equilibrium potentials. (i) Commercial Si solar cell-driven decoupled OER and HER. Reproduced with permission from Ref. [314], © The Royal Society of Chemistry 2019.

5 Hybrid water splitting

Liu et al. [333] introduced a novel electrolysis approach to produce hydrogen from low temperature conversions of natural feedstocks, including cellulose, lignin, and even wood and grass powders. At the anode, electrons are transferred from raw biomass to POM molecules through heat or light, with aqueous polyoxometalate serving as a catalyst. Hydrogen is produced when protons released by biomass diffuse to the cathode. Electrical energy consumption for water electrolysis at 0.2 A·cm⁻² is as low as 0.69 kWh·m⁻³ of H₂, just 16.7% of the total energy consumption. Hydrogen has the highest energy density of any fuel (143 kJ·kg⁻¹); 1 kg of hydrogen is equivalent to 2.63 kg of gasoline [334]. The electrolysis method is a quick and easy method to yield hydrogen fuel (Fig. 8(c)). Biomass electrolysis, which generates hydrogen by exchanging the oxygen reduction reaction with the oxidation of biomass-derived fuels at the anode, can drastically decrease the amount of electric energy required for hydrogen creation compared to water electrolysis. For H₂ synthesis directly from native biomass, a new chemical electrolysis conversion (CEC) technique was used, where polyoxometalates acted as both a catalyst and an electron-proton carrier in this process. Electrodes made of graphite felt served as the anode, while Pt/C electrodes

were utilized for the cathode. When phosphomolybdic acid (H₃PMo₁₂O₄₀) was added to the biomass before electrolysis, the color of the mixture changed from yellow to dark blue when exposed to sunlight or direct heating, indicating POM reduction and biomass oxidation (Fig. 47(a)). When the reduced POM blue turned completely yellow on the anode side, the chemical electrolysis conversion cycle was complete. Hydrogen can be produced by irradiating or heating the biomass-POM solution as it circulates in the electrolyzer. CV curves of pure PMo₁₂ and SiW₁₂ solutions (pure PMo₁₂/SiW₁₂ = 1 mmol·L⁻¹, glucose-PMo₁₂/SiW₁₂ = 2 mol·L⁻¹, 1 mmol·L⁻¹) at a scan rate of 10 mV·s⁻¹ on graphite electrode (0.157 cm²), respectively, show the rate of reaction reversibility (Figs. 47(b) and 47(c)). The stability of the H₂ evolution was tested by continuous experiments with the biomass-POM electrolysis device at current densities of 50, 100, and 200 mA·cm⁻² while subjected to both heating (through feeding with glucose-PMo₁₂ solution) and UV-irradiation (by feeding with glucose-SiW₁₂ solution). Simultaneously, the amount of generated H₂ gas was measured, with the potential remaining stable throughout the process, yielding a total of 24 mL of H₂ (Figs. 47(d)–47(g)).

POM's consistent performance is dependent on stable electron

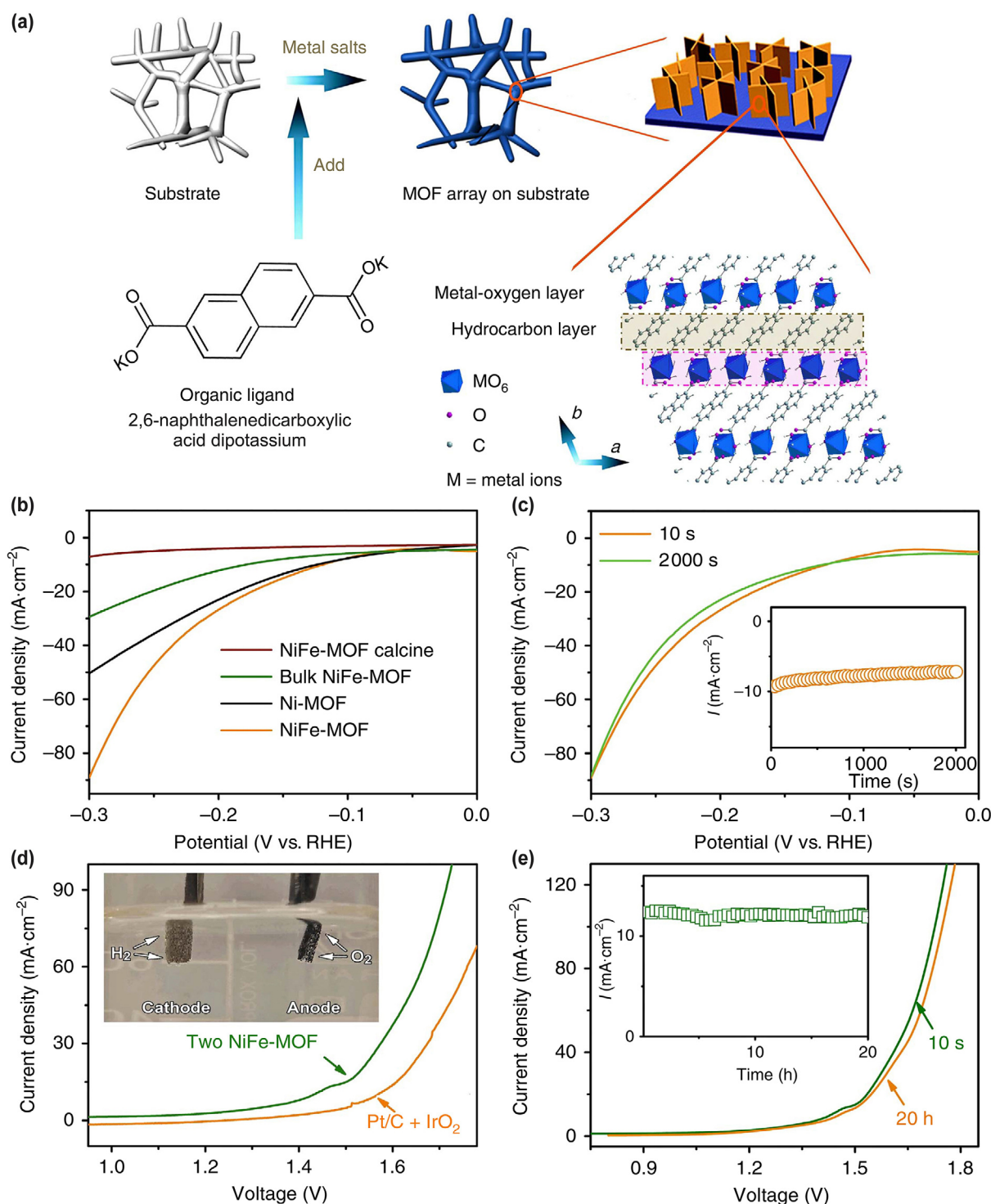


Figure 46 (a) Synthetic technique of metal-organic framework nanosheet array. NiFe-MOF and other MOF samples have electrocatalytic properties for HER and water splitting. (b) LSV at 10 mV·s⁻¹ in 0.1 M KOH. (c) LSV curves of NiFe-MOF before and after chronoamperometric testing for 2000 s at -0.2 V (vs. RHE) in 0.1 M KOH; the inset shows corresponding CA profile. (d) LSV plots of a full electrolytic cell using two NiFe-MOF electrodes obtained at 10 mV·s⁻¹ in 0.1 M KOH; the inset shows H₂ and O₂ gas bubbles at the NiFe-MOF electrodes at an applied cell voltage of 1.6 V. (e) LSV plots of the two-electrode electrolytic cell obtained before and after 20 h chronoamperometric analysis at a voltage of 1.5 V; the inset shows a consistent chronoamperometric plot. Reproduced with permission from Ref. [316], © The Author(s), 2017.

capture from biomass. Results reveal that the reaction rates are sufficient for continuous hydrogen generation despite the biomass-POM reaction rate being highly dependent on various factors. A theoretical estimate of hydrogen gas production by electrolysis at a constant current was derived based on Faraday's principles, yielding an average FE of 96.74%. This high FE indicates efficient

electron transfer throughout the process from biomass to H₂. Understanding the amount of hydrogen extractable from biomass and identifying the system's ultimate products would be valuable, as the results depend on biomass composition, reaction temperature, and duration, as well as the type and concentration of polyoxometalates used. The native biomass with the highest

Table 4 Summary of recent studies on insoluble solid-state redox mediators for decoupled water splitting

Insoluble solid-state redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		$E_{1/2}$ (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
Ni(OH) ₂		Pt-Ti mesh	RuO ₂ /IrO ₂ -Ti-mesh	1 M KOH	14	1.6	0.4	0.46 vs. RHE	100	100	20	20 cycles	[179]
Mo-NiCoP		Ni(OH) ₂	Mo-NiCoP/NF	1 M KOH	—	-1.1	0.64	0.5, 0.6 vs. RHE	—	—	10	10 cycles	[318]
Co-Ni(OH) ₂		Pt-Ti	RuO ₂ /IrO ₂ -Ti	1 M KOH	—	-1.05	0.63	0.266 and 0.564 Hg/HgO	—	—	~ 8.3	28 cycles	[319]
NiOOH/Ni(OH) ₂		Platinised Ni-coated stainless-steel	Ni _{0.9} Co _{0.1} (OH)	5 M KOH	14	—	—	1.31–1.41 vs. RHE	100	100	10–200	100 cycles, each 100 s	[200]
NiOOH/Ni(OH) ₂		Pt	Ni	1 M NaOH	14	—	—	0.55 vs. SHE and 2.0	100	100	5	100 cycles and 125 h	[180]
Ni(OH) ₂ /NiOOH		Pt coated Ti-Mesh	Hematite (α-Fe ₂ O ₃) photoanodes	1 M NaOH	14	—	—	—	96	96	—	~ 125 h	[197]
Ni(OH) ₂ /NiOOH	Ni(OH) ₂ ↔ NiOOH	Pt	Ni/Ni(OH) ₂	—	14	—	—	—	100	100	113	60 cycles/3200 s	[245]
Ni(OH) ₂ /NiOOH and WO ₃ /H ₂ WO ₃		Pt	Ni(OH) ₂ /NiOOH and WO ₃	0.5 M H ₂ SO ₄ and 1 M KOH	—	0, -0.2, and 0.3	0.57	0.467	96–98	96–98	100	100 cycles and 10 and 5 h	[272]
Ni(OH) ₂ /NiOOH		Ni(OH) ₂	Ni(OH) ₂	1 M KOH	14	1.4	0.9	—	~ 100	~ 100	50	100 cycles and 10 h	[275]
Ni-MH and Ni(OH) ₂		NiFe LDHs–NiFe alloy gradient	NiFe LDHs–NiFe alloy gradient	6 M KOH	—	0.28	0.25	1.65	100	100	100	35 cycles and 100 h	[307]
l-Ni(OH) ₂ /Co(OH) ₂ @NF		Pt-Ti	RuO ₂ /IrO ₂ -coated titanium mesh	1 M KOH	—	-1.05 and 0.52 vs. Hg/HgO	0.77 vs. Hg/HgO, 0.642, 0.267	1.57	93	93	100–180	27 cycles	[309]
Ni(OH) ₂ /NiOOH		Pt/C, Ni(OH) ₂ /C, and Fe- and Ni(OH) ₂ /C	Pt/C, Ni(OH) ₂ /C, and Fe-Ni(OH) ₂ /C	0.1 KOH	—	—	1.56	—	96	96	5	100 cycles	[163]
Na _{0.44} MnO ₂		Pt	RuO ₂ /IrO ₂	1 M NaOH	—	1.06	0.59	-0.25–0.4 vs. RHE	98.7	97	~ 1.33	400 cycles	[253]
Na _{0.44} MnO ₂		Pt-Ti mesh	RuO ₂ /IrO ₂ -Ti mesh for CER	1 M NaOH for HER and saturated NaCl for CER	13.7	1.3	1.07 V for CER and no OER	-0.04, 0.08, 0.28, 0.34, and 0.49 V vs. Hg/HgO	100	FE of Cl ₂ 97.4	100	50 cycles	[246]
Na _{0.5} MnO ₂ and pseudocapacitor	(De)intercalation of ions (e.g., H ⁺ , K ⁺ , Na ⁺ , and S ²⁻)	NiFe-LDH@Pt	NiFe-LDH@Pt	1 M NaOH	—	1.15	0.514	-0.2–0.4 vs. Ag/AgCl	100	100	1000	8000 cycles and 223 h	[281]
K _{0.5} MnO ₂ -Ti		Pt	RuO ₂ /IrO ₂	1 M KOH	—	1.02	0.57	0.045 vs. RHE	100	100	5	100 cycles	[292]
NaTi ₂ (PO ₄) ₃		Ni ₃ S ₂ foam on CNTs	Graphitic carbon	1 M NaOH	14	0.34	1.23	+0.423 and +0.238 vs. Ag/AgCl	100	100	10	16 cycles	[271]
WO ₃		Pt and WO ₃	FTO and WO ₃	0.5 M H ₂ SO ₄	—	0.22	0.33	-0.3, -0.2, 0.21, and 0.3 vs.	90.2	90.2	100	100 cycles and ~ 130 h	[288]

(Continued)

Insoluble solid-state redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		$E_{1/2}$ (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
WO ₃		Carbon felt/WO ₃ , Pt wire	Carbon felt/WO ₃ , Pt wire	0.5 M H ₂ SO ₄	—	-0.05 and -0.3	—	—	98–99	98–99	10	500 cycles	[290]
Cu[Fe(CN) ₆] ^{1/3,3,4} H ₂ O (CuFe-TBA)		Pt	RuO ₂ /IrO ₂	0.5 M H ₂ SO ₄	0.3	0.66	0.68	0.25, 0.40, 0.58, 0.89 vs. Ag/AgCl	100	—	~ 1.67	300 cycles and 170 h	[265]
α-MoO ₃		Ti	Zn	10 M H ₃ PO ₄ and 32 M ZnCl ₂ + 1 M P ₂ O ₅	—	0.32	1.58	—	99.65	99.65	2 A g ⁻¹	1000 cycles	[293]
α-MoO ₃		Pt and MoO ₃	IrO ₂ /Ti	10 M H ₃ PO ₄	0.2–0.5	-0.25	1.25	-0.3 and 1.6 vs. Ag/AgCl	> 95	~ 95	1000	20 cycles	[295]
Polysulfides (S _{x+1} ²⁻ /S _x ²⁻)		CoNi@NGs	CoNi@NGs	1 M NaOH	—	1.61	0.15	0.4 and 0.8 vs. Ag/AgCl	—	—	10	15 cycles	[320]
MnO ₂ /Mn ²⁺	M(OH) ₂ ↔ MOOH, M = Ni and Mn	Pt	RuO ₂ /IrO ₂	2 M KOH and 1 M H ₂ SO ₄	0	1.37	0.24	1.2 vs. Ag/AgCl	98.7	—	10	1000 cycles	[261]
MnO ₂ /MnOOH		LaNi ₅	Ni(OH) ₂	6 M KOH	14	-0.828	0.402	0.15 vs. SHE	~ 100	—	10	10 cycles and 20 h	[321]
Mn ²⁺ /MnO ₂	Mn, MnO ₂ ↔ MnOOH and MnO ₂ ↔ Mn ²⁺	Pt-Ti mesh	Carbon felt for Mn ²⁺	0.5 M H ₂ SO ₄ and 1 M MnSO ₄	—	1.5	—	1.2 vs. Ag/AgCl	—	—	45	10,000 cycles	[322]
Co-Ni-Mn	↔ Mn ²⁺	Pt-Ti	Co-Ni-Mn	1 M KOH	—	-1.10	0.64	0.264 and 0.637 vs. RHE	—	—	~ 8.3	30 cycles	[323]
Co ₂ P/CoP	Co ²⁺ ↔ Co ³⁺ ↔ Co ⁴⁺	Carbon rod	Co ₂ P/CoP	1 M KOH	—	0.25	1.45	0.5–1.6 vs. Ag/AgCl	—	—	10	2000 cycles	[324]
FeO _x	Fe ⁰ ↔ Fe ²⁺ ↔ Fe ³⁺	Pt	Ni-Fe	1 M KOH	14	-0.6	0.3	-1.2–-0.6	> 90	> 90	20	50 cycles	[325]
FeO _x /AC		Pt	TiO ₂ /Co-phosphate	3 M H ₂ SO ₄ for HER and 6 M KOH for OER	14	0	~ 1.2	+0.8–+1.5 vs. SHE	> 90	> 90	10	5000 cycles	[325]
Metal hydride (YH _x -Pd)	—	LaNi _{4.5} Al _{0.5} -Pd	RuO ₂	6 M KOH	—	-0.15 vs. RHE	—	—	100	100	2.3	8 h	[264]
Ni-Mn-P		Carbon rod	Ni-Mn-P/NF	1 M KOH	14	-0.13	1.52	1.1 and 1.6 vs. Ag/AgCl	> 93	> 93	35.2	2000 cycles and > 5.5 h	[326]
Active carbon		Pt wire	Pt wire	0.5 M KOH	—	-0.913	1.166	-2.9 and 1.0 vs. SHE	—	—	20	300 cycles	[327]
All-pH-CDWE	Pseudo-capacitance	Pt-coated Ti-mesh and NiMoCo	AC-coated carbon paper and NiMoCo	0.5 M H ₂ SO ₄ , 2 M KOH, and 1 M KH ₂ PO ₄ /K ₂ HPO ₄	0–14	0.84	1.13	1.97 (acidic) and 1.74 (alkaline)	94 in acidic and 97 in alkaline	94 in acidic and 97 in alkaline	5	Acidic (800 cycles and 160 h) and alkaline (200 cycles)	[276]
CoFeP/NiF		Pt/C and CoFeP/NiF cloth	Activated carbon and CoFeP/NiF	0.5 M H ₂ SO ₄ , 1 M KOH, and 5 M KOH	—	—	—	1.85	99	99	100	100 cycles and 20 h	[285]
TiO ₂ nanoparticles		Pt, TiO ₂ /carbon felt and TiO ₂	Pt and TiO ₂	0.5 M H ₂ SO ₄	—	—	—	1.5–2.0	93.4	93.4	100	3000 cycles	[286]

(Continued)

Insoluble solid-state redox mediators													
Mediator	Decoupling mechanism	Catalyst		Electrolyte	pH for redox potential	Voltage inputs (V)		$E_{1/2}$ (V)	Best reported Faradaic efficiency (%)		Current density (mA·cm ⁻²)	Stability (cycle or h)	References
		HER	OER			HER	OER		HER	OER			
GF@Ni _x Co _y -P	—	GF@Ni _x Co _y -P	GF@Ni _x Co _y -P	1 M KOH	—	0.35 vs. Hg/HgO and 0.37 – (-1.06) = 1.43	0.60 vs. Hg/HgO and 0.6 – 0.35 = 0.25	0.25 + 1.43 = 1.68	100	100	5, 10, 50, and 100	400 cycles and 100 h	[274]
Ni-Co LDH/NiF	—	Pt	C	1 M KOH	—	1.57	0.66	2.23	100	100	30	10 cycles and 6 h	[297]
CoO	—	Pt	Ni	—	14	—	—	+0.750–+0.850 vs. SHE	100	—	200–400	—	[328, 329]
Fe ³⁺ /Fe ²⁺	—	Pt	Carbon paper	—	2.5	—	—	+0.770 vs. SHE	100	71	—	—	[330]
Fe ^{3+/2+}	—	—	—	—	2.6	—	—	0.92 vs. SHE	—	—	—	—	[331]
PANI	(De)doping of ions (e.g., SO ₄ ²⁻ and H ⁺)	Pt/Ti	RuO ₂ /IrO ₂ /Ti	0.5 M H ₂ SO ₄	0.3	0.83	1.09	0.39 and 0.85 vs. RHE	100	100	50	40 cycles	[314]
PTPAn	—	Pt/Ti mesh	RuO ₂ /IrO ₂ /Ti mesh	0.5 M H ₂ SO ₄	0.3	-0.25	1.35	0.49 and 0.59 vs. Ag/AgCl	97.8	97.8	100	120 cycles and 600 s	[199]
PTO	Keto-enol tautomerism	Pt-Ti mesh	RuO ₂ /IrO ₂ -Ti-mesh	0.5 M H ₂ SO ₄	0.3	0.6	1.27	+0.46 and +0.589 vs. SHE	98.7	98.7	0.2–20 A·g ⁻¹	300 cycles and 6000 s	[313]
Diquinoxalino[2,3-a:2',3'-c]phenazine (HATN)	—C=N- ↔ -CH-NH-	Pt	RuO ₂ /IrO ₂	0.5 M H ₂ SO ₄	—	0.38	1.39	0.02, 0.11, and 0.30 vs. Ag/AgCl	92.2	—	~ 6.67	500 cycles	[332]
NiFe-MOF	—	Pt/C and NiFe-MOF	RuO ₂ and NiFe-MOF	0.1 M KOH	—	—	—	1.6	95 ± 2.5	95 ± 2.5	10	~ 6 h	[316]

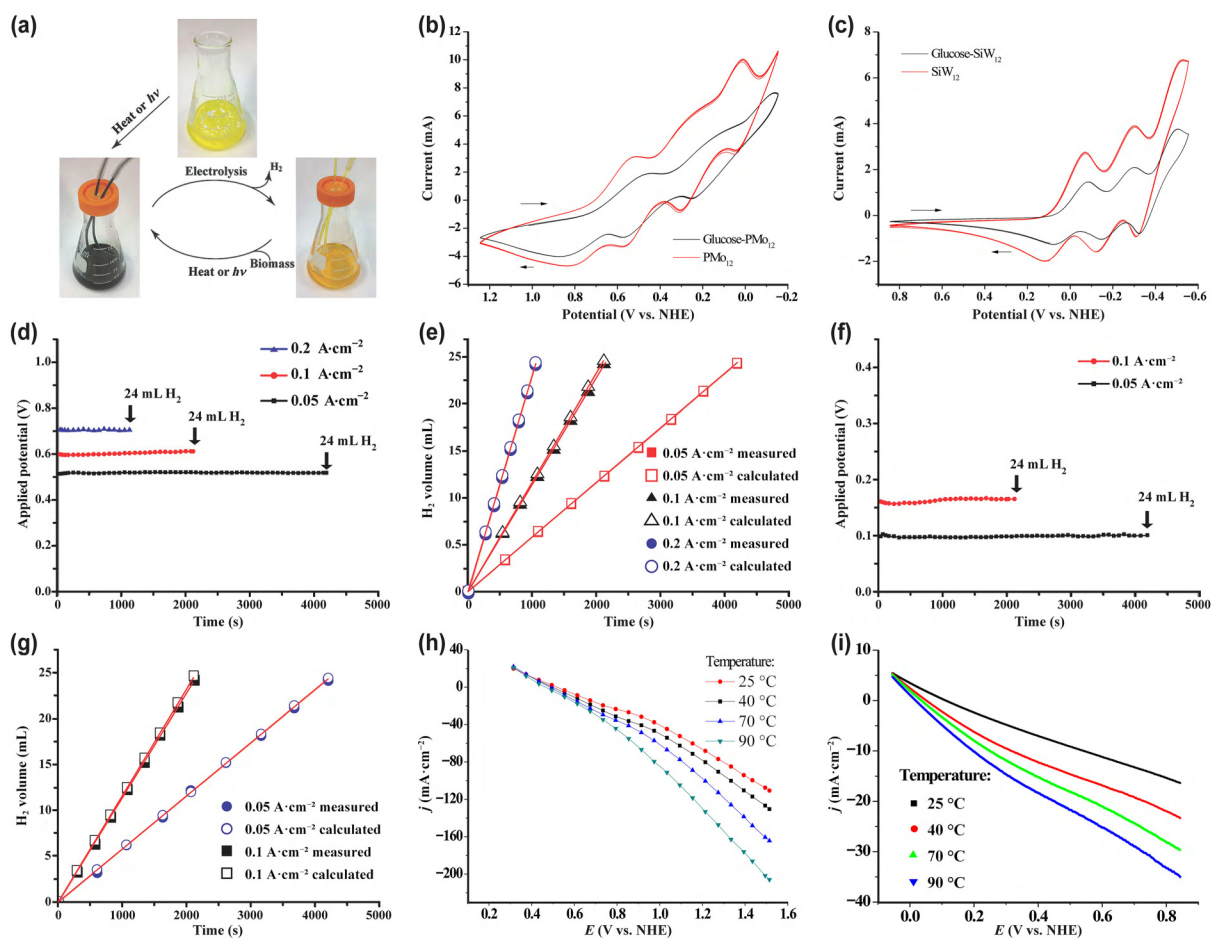


Figure 47 (a) The chemical electrical conversion process of biomass is shown schematically, along with before and after electrolysis, to produce hydrogen. ((b) and (c)) CV curves of pure PMo_{12} and SiW_{12} solutions at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ on graphite electrode. (d) Changes in applied potential as a function of time, simultaneous heating and electrolysis of an $\text{H}_4\text{PMo}_{12}\text{O}_{40}$ (PMo_{12})-glucose solution at three different current densities (0.05 , 0.1 , and $0.2 \text{ A}\cdot\text{cm}^{-2}$). (e) Quantifying the amount of hydrogen gas produced by electrolysis of PMo_{12} -glucose at a constant current density using Faraday's law. (f) Changes in applied potential as a function of time over simultaneous UV-irradiation electrolysis of an $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiW_{12})-glucose solution at constant current densities (0.05 and $0.1 \text{ A}\cdot\text{cm}^{-2}$). (g) H_2 volume acquired during SiW_{12} -glucose constant current density electrolysis and Faradaic efficiency calculation. ((h) and (i)) Linear potential sweep curves of PMo_{12} -glucose and SiW_{12} -glucose solutions at different temperatures. Reproduced with permission from Ref. [333], © The Royal Society of Chemistry 2016

molecular weight was depolymerized first, yielding the low molecular weight derivatives. Acetic acid (HAc), formic acid, and glycolic acid are the primary oxidation residues of starch, glucose, and cellulose. Linear potential sweep curves of PMo_{12} -glucose and SiW_{12} -glucose solution at different temperatures (Figs. 47(h) and 47(i)). GC experiments show that the solution reactions produced only carbon dioxide gas. Total organic carbon analysis showed that after repeated 20 cycles of oxidation and electrolysis, 80% of the original glucose was transformed to CO_2 when glucose was utilized as the feeding raw material. The use of lignin led to the detection of CO_2 in the exhaust gas, along with aromatic compounds, such as vanillin and methyl vanillate, in the solution. If light irradiation, rather than heat, were used to trigger the biomass-POM interactions, the vanillin and methyl vanillate would be transformed into carbon dioxide. In conclusion, a novel strategy for efficient biomass to H_2 CEC has been presented. If biomass could be fully decomposed into carbon dioxide, CO_2 would become the only byproduct introduced into the system, enabling complete recycling of polyoxometalates. This research holds promise for hydrogen generation, given its low electric energy requirements, direct use of raw biomass, and the absence of a noble-metal catalyst at the anode.

Sun et al. [181] reported an innovative strategy to decouple H_2

and O_2 . In this strategy, new types of changes were made to the anode side of the electrolytic cell. O_2 is not an important byproduct of DWS at the anode. Therefore, organic species were used to replace oxygen in order to generate value-added products via H_2 gas release at the cathode side of the electrochemical cell. An electrode composed of $\text{Ni}_3\text{S}_2/\text{NF}$ bifunctional catalyst (used for both anode and cathode applications) was utilized. Instead of using oxygen, the anode hosted organic chemicals, including ethanol, benzyl alcohol (BA), furfural (FF), furfuryl alcohol (FFA), and HMF, to produce higher-value compounds along with LSV curves of $\text{Ni}_3\text{S}_2/\text{NF}$ at a scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$ in 1.0 M KOH with and without 10 mM organic substrates and corresponding oxidation of selected organics to value-added compounds (Figs. 48(a)–48(e)). These liquid value-added products are generated at significantly lower overpotentials compared to OER. The author just discussed HMF conversion to FDCA, a value-added product for ease of awareness. This type of strategy is more beneficial because high-value products were obtained at both electrodes with low input voltages. Previously reported ECPB strategies for DWS were undoubtedly excellent, but the cost of the overall configuration of the cell increases. Moreover, it also requires high overpotentials to drive OER, which produces O_2 that has no important value. To achieve these targets, applied organic

products have some properties to replace O_2 . (1) Organic products can easily be dissolved in aqueous solutions. (2) The obtained value-added product should be in liquid form. (3) The oxidation potential of an organic product should be lower than the OER potential. (4) Non-precious electrocatalysts can be employed. A bifunctional electrocatalyst Ni_3S_2/NF , Ag/AgCl, and carbon rod were employed as working, reference, and counter electrode, respectively, in between anion exchange membrane with two compartment configurations in an alkaline electrolyte. Researchers explored the fact that metalloenzymes comprised of earth-abundant metals, i.e., Co, Ni, Fe, and Mn, show robust efficiency during oxidation at the anode [335–346]. In biorefinery technology, biomass is converted into fuels and chemicals [347–350]. The porous structure of Ni_3S_2/NF enhances its electrochemical activity. In the absence of organic species on the anodic side, bifunctional electrocatalyst Ni_3S_2/NF shows ~ 1.50 V electrode potential vs. RHE for OER, while introducing 10 mM biomass in the anodic side shifts the onset potential from 1.50 to 1.35 V with the rapid increase in current density within 1.40 V vs. RHE, resulting in efficient conversion to value-added products (Fig. 48(f)). The overpotential of biomass oxidation reactions is at least 160 mV less than OER.

Chronoamperometry results show that all five organic species were converted to high-value-added products, carried out at 1.423 V with approximate unity of FE (Fig. 48(g)). The author further takes HMF to get detailed information during its conversion to FDCA. FDCA follows two pathways: It transforms to 2,5-

dimethylfuran (DFF) or HMFCFA and then forms FFCA to finally make FDCA. Conversion of HMF to FDCA yields 100% FE with a 98% production of FDCA. HMFCFA pathway is more favorable than DFF. 96% to 98% FE of FDCA over 5 cycles exhibits robust stability of the Ni_3S_2/NF bifunctional catalyst for HMF oxidation. Post-HMF Ni_3S_2/NF results show no major electrocatalyst changes were seen. Some organic species may be transferred to the cathode side through an anion exchange membrane. To check the compatibility of HER with HMF oxidation using Ni_3S_2/NF electrode, the author supposed that all HMF was present on the cathode side to get some exciting information. Overlapped polarization curves with and without 10 mM HMF and Tafel slope slightly raised from 128 to 136 mV $\cdot$ dec $^{-1}$ indicate that there is no significant impact of HMF on the HER side (Figs. 48(h)–48(j)). Chronopotentiometry results from over 18 h show that the required potential increased by < 40 mV over a current density of -10 mA $\cdot$ cm $^{-2}$. The formation and release of H_2 bubbles were clearly seen on the surface of the Ni_3S_2/NF electrode. This non-precious electrode Ni_3S_2/NF requires -116 mV overpotential to reach 10 mA $\cdot$ cm $^{-2}$ which is lower than previously reported bifunctional HER electrocatalysts, i.e., Ni_3S_2 nanosheet arrays (-223 mV) [351], NiFe LDH/NF (-200 mV) [352], and MoC_x/C (-151 mV) [353]. Without HMF, ~ 1.55 V cell voltage is required for overall water splitting. If we study separately at current densities of 10, 20, 50, and 100 mA $\cdot$ cm $^{-2}$, the cell voltages of 1.58, 1.66, 1.76, and 1.84 V were required, respectively, in the absence of HMF for overall water splitting. These values lowered rapidly

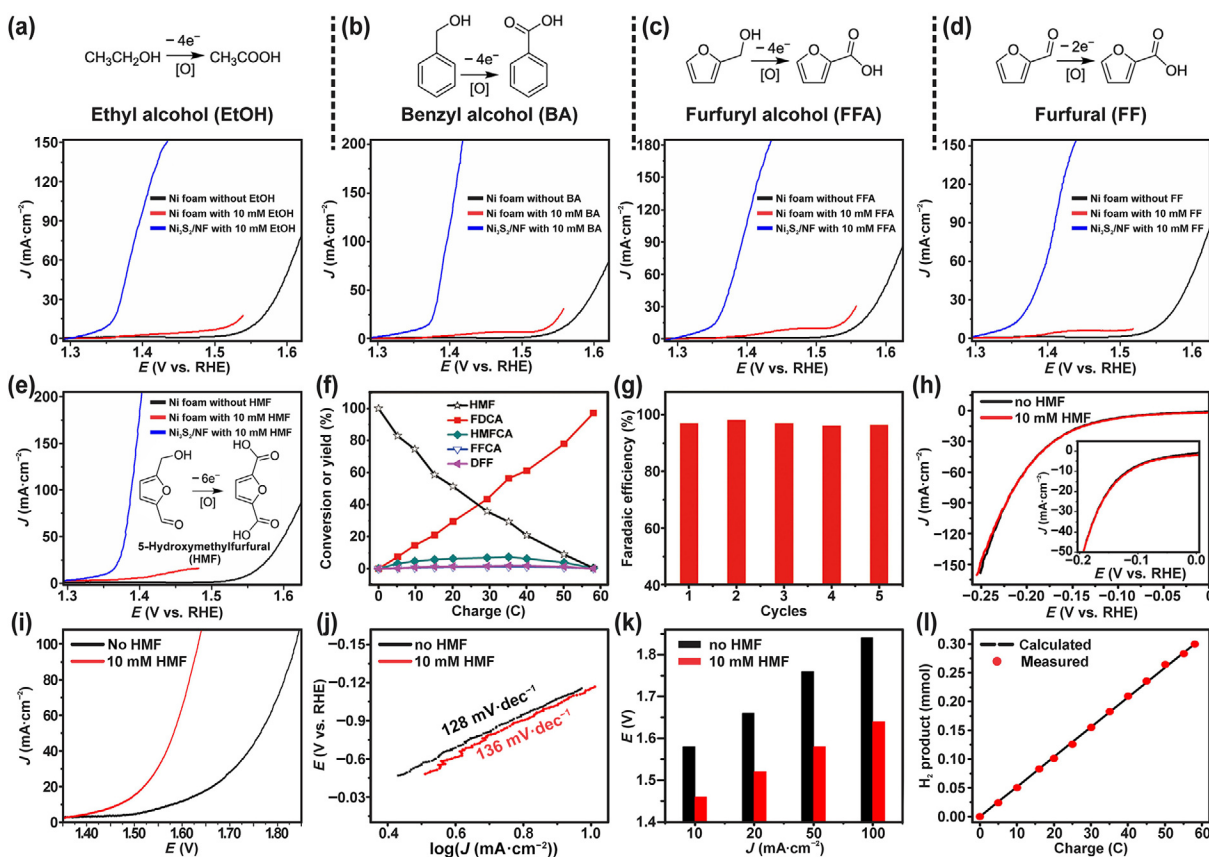


Figure 48 ((a)–(e)) Oxidation of selected organics to value-added compounds and corresponding LSV curves of Ni_3S_2/NF at a scan rate of 2 mV $\cdot$ s $^{-1}$ in 1.0 M KOH with and without 10 mM organic substrates. (f) HMF electrochemical oxidation conversion and yield changes. (g) Faradaic efficiencies of Ni_3S_2/NF bifunctional electrocatalyst for FDCA generation under five successive cycles. ((h)–(j)) Scanned at 2 mV $\cdot$ s $^{-1}$, the LSV curves and associated Tafel plots for hydrogen evolution in 1.0 M KOH with and without 10 mM HMF on a Ni_3S_2/NF bifunctional electrocatalyst. (k) Overpotentials comparison of Ni_3S_2/NF with and without 10 mM HMF in 1.0 M KOH. (l) GC analysis measured hydrogen quantity versus theoretically estimated H_2 quantity assuming 100% FE for H_2 evolution. Reproduced with permission from Ref. [181], © American Chemical Society 2016.

when 10 mM HMF was added to the electrolytic cell by ~ 1.40 V. The current densities of 10, 20, 50, and 100 $\text{mA}\cdot\text{cm}^{-2}$ require cell voltages of 1.46, 1.52, 1.58, and 1.64 V, respectively, and were obtained in the presence of HMF for overall water splitting (Fig. 48(k)). These values are smaller than those bifunctional electrocatalysts reported previously, like Co-P (1.64 V for 10 $\text{mA}\cdot\text{cm}^{-2}$), $\text{Ni}_3\text{P}_4/\text{NF}$ (1.70 V for 10 $\text{mA}\cdot\text{cm}^{-2}$), $\text{NiFe-LDH}/\text{NF}$ (1.70 V for 10 $\text{mA}\cdot\text{cm}^{-2}$), and CoO_x/CN (1.90 V for 50 $\text{mA}\cdot\text{cm}^{-2}$) for overall water splitting [181]. GC results show that H_2 generated experimentally was matched by theoretical value with 98% FE of FDCA production (Fig. 48(l)).

The innovative hybrid energy decoupled alkaline water splitting system proposed by Xia et al. [354] introduces a novel electrolysis technique for hydrogen generation. This approach combines the electrochemical reduction of water with the electrochemical oxidation of liquid fuels, such as methanol, ethanol, isopropanol, formate, or hypophosphite solutions. Nickel hydroxide is utilized as a solid-state redox mediator in the process. This technique leverages principles commonly employed in fuel cells, where the anodic ethanol oxidation reaction (EOR) in alkaline media is widely used. By integrating fuel oxidation with water electrolysis, this method offers an alternative, potentially more efficient route for hydrogen production, with $\text{Ni}(\text{OH})_2$ acting as a key mediator to facilitate the decoupling of the reactions (Fig. 49(a)). This setup could reduce energy requirements and improve the overall efficiency of hydrogen generation in alkaline media [355–358]. In this setup, the HER and EOR were implemented in a system separated by an anion exchange membrane. The setup utilized a Pt plate as the cathode and a PdNiP alloy as the anode, with the solid-state redox mediator incorporated via a $\text{Ni}(\text{OH})_2$ /multi-

walled carbon nanotubes (MWNTs) electrode. Both the Pt-plate and $\text{Ni}(\text{OH})_2/\text{MWNTs}$ electrodes were immersed in a 1 M KOH electrolyte, whereas the PdNiP electrode was placed in a mixed solution of 1 M KOH and 1 M ethanol ($\text{C}_2\text{H}_5\text{OH}$). The PdNiP alloy nanoparticle networks, known for their high electrocatalytic activity and stability, were used for EOR in the alkaline solution. CV and LSV curves of the $\text{Ni}(\text{OH})_2/\text{MWNTs}$ electrode showed two redox peaks within a potential window of 0.35 to 0.5 V vs. Hg/HgO (black curve), with onset potentials of approximately -0.9 V for HER (red curve) and -0.55 V for EOR (blue curve) vs. Hg/HgO (Fig. 49(b)). To produce hydrogen in an electrolysis cell without involving the OER, a cell voltage of approximately 1.5 V is required. In Step 1 of the process, hydrogen production occurs with a cell voltage of around 1.5 V, which is derived from the potential difference between the anodic oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH at 0.5 V (vs. Hg/HgO) and the cathodic reduction of H_2O to H_2 at approximately -1.0 V (vs. Hg/HgO). In Step 2, the discharge voltage of the $\text{NiOOH}/\text{ethanol}$ hybrid cell is approximately 0.95 V, which corresponds to the potential difference between the cathodic reduction of NiOOH back to $\text{Ni}(\text{OH})_2$ (0.4 V vs. Hg/HgO) and the anodic EOR at -0.55 V (vs. Hg/HgO). The drop in cell voltage towards the end of the discharge process indicates that all NiOOH has been reduced to $\text{Ni}(\text{OH})_2$, which can be reused for further hydrogen production, demonstrating a 100% CE.

The amount of $\text{Ni}(\text{OH})_2$ loaded into the cathode of the $\text{NiOOH}/\text{ethanol}$ hybrid cell directly determines its maximum rate capacity. In Step 1, hydrogen and NiOOH were produced over 1000 s at a current density of 1 $\text{A}\cdot\text{g}^{-1}$, emphasizing the system's efficient cycling and hydrogen production capability. A hybrid cell

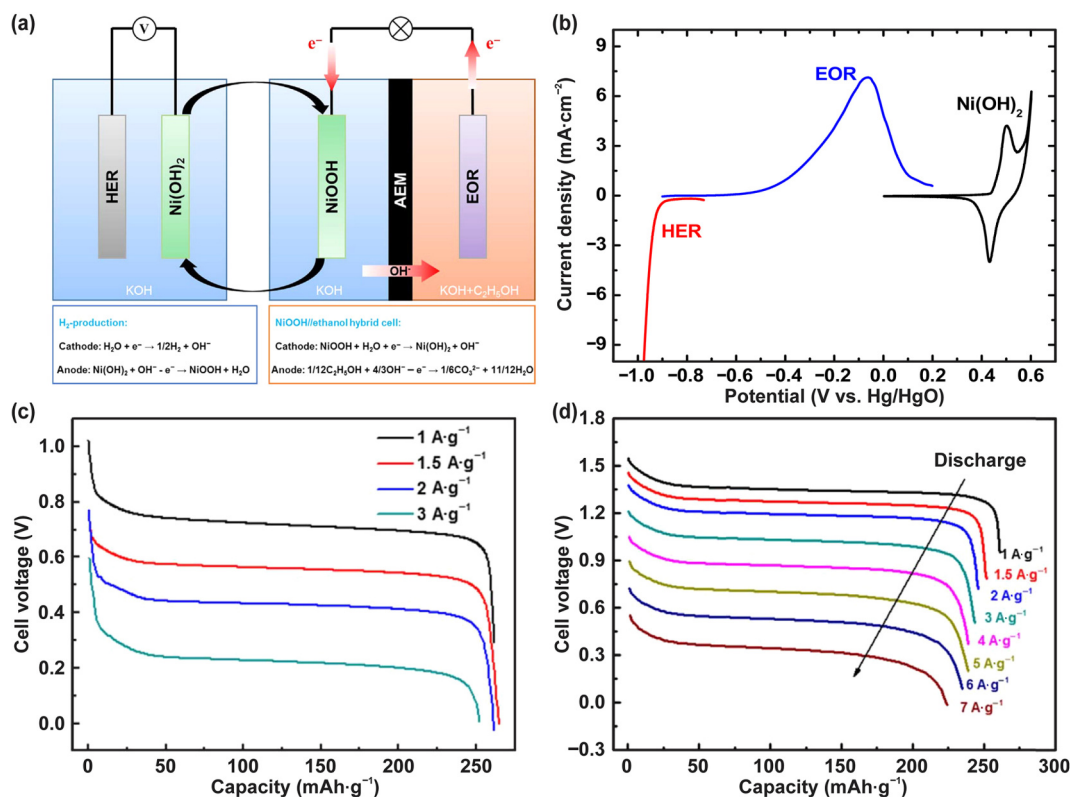


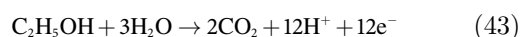
Figure 49 (a) Schematic illustration of hybrid cell with ethanol oxidation by $\text{Ni}(\text{OH})_2$. (b) CV curves of the $\text{Ni}(\text{OH})_2/\text{MWNTs}$ electrode (black) in 1 M KOH, the LSV curve of the Pt-plate electrode for the HER (red) in 1 M KOH, and the PdNiP-based electrode for the EOR in 1 M KOH + 1 M ethanol (blue) at a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$. (c) The discharge capacity of the $\text{NiOOH}/\text{ethanol}$ hybrid cell was evaluated at different current densities, with a $\text{Ni}(\text{OH})_2$ mass loading of 10 $\text{mg}\cdot\text{cm}^{-2}$. (d) Performance of hypophosphite hybrid cell at various current densities for H_2 production. $\text{Ni}(\text{OH})_2$ mass loading of 10 $\text{mg}\cdot\text{cm}^{-2}$ was used to determine specific capacities. Reproduced with permission from Ref. [354], © Elsevier B.V. 2017.

was developed by coupling NiOOH with ethanol and subsequently discharged at varying current densities. The discharge capacity of the NiOOH/ethanol hybrid cell was measured to be 266 mAh·g⁻¹ at a discharge current density of 10 mA·cm⁻², with a corresponding cell voltage of approximately 1.8 V for the Ni(OH)₂/MWNTs electrode during Step 1 with a mass loading of 10 mg·cm⁻² (Fig. 49(c)). Even at a higher current density of 30 mA·cm⁻², the cell delivered a discharge capacity of 243 mAh·g⁻¹, indicating robust performance. The system demonstrated high hydrogen generation rates, with a maximum current density of 148 mA·cm⁻². Additionally, increasing the mass loading of Ni(OH)₂ on the electrode further enhanced the areal capacity, as confirmed by using a commercially available Ni(OH)₂ electrode with a mass loading of 92.7 mg·cm⁻², resulting in a large areal capacity of 26.8 mAh·cm⁻². This configuration allowed the system to operate for nearly 10 h across Steps 1 and 2, showcasing its potential for practical applications. In the hydrogen generation step, a current of 1000 mA (10 mA·cm⁻²) was applied over 100 s, producing H₂ at a rate of 0.121 mL·s⁻¹. The total volume of hydrogen gas collected was 12.1 mL, closely matching the theoretical value of 12.67 mL, resulting in an FE of 95.5% (12.1/12.67). In addition to ethanol, other liquid fuels, such as methanol, formate, isopropanol, and hypophosphite, were also tested, with a bulk loading of 10 mg·cm⁻² applied to the Ni(OH)₂/MWNTs electrode. The system was powered at a constant current density of 100 mA·cm⁻² (10 A·g⁻¹ based on the mass loading of Ni(OH)₂ in Step 1, with a step time of 120 s. After charging in Step 1, the NiOOH/methanol hybrid cell was discharged at varying current densities in Step 2. The cell achieved an estimated capacity of 263 mAh·g⁻¹ at a current density of 10 mA·cm⁻² (1 A·g⁻¹). Even when the current density increased to 40 mA·cm⁻² (4 A·g⁻¹), the cell maintained a discharge capacity of 224 mAh·g⁻¹. The polarization and power density curves of the NiOOH/methanol hybrid cell revealed a maximum power density of 10 mW·cm⁻², highlighting its strong performance even under higher power demands. This performance underscores the potential of the NiOOH-based hybrid cell system for efficient hydrogen production and energy storage across various liquid fuels.

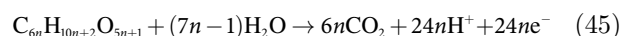
Different liquid fuel hybrid cells i.e., NiOOH/formate, NiOOH/isopropanol, and NiOOH/hypophosphite, exhibit varying rate capacities, with all demonstrating high discharge rate capabilities. Notably, the NiOOH/hypophosphite hybrid cell achieves the highest power density, approximately 35 mW·cm⁻², significantly surpassing the other cells (Fig. 49(d)). This enhanced performance is due to its higher operating voltage, roughly 1.5 V. This hybrid system offers the potential to harness renewable energy for the production of H₂ and NiOOH, which can then be used in a NiOOH-based direct liquid fuel cell to generate stable electricity. However, it is important to note that the Ni(OH)₂ electrode has a considerably lower capacity compared to the O₂ cathode, limiting the hybrid NiOOH/liquid fuel cell's use as a full substitute for conventional direct liquid fuel cells. Consequently, this system is best suited for stationary energy storage and conversion applications. By using a nickel hydroxide electrode as a solid-state redox mediator, the system is capable of both producing hydrogen and powering a direct liquid fuel cell. By repeating the steps of hydrogen generation and energy discharge, this hybrid energy storage and conversion system can transform intermittent renewable energy sources into reliable power using hydrogen fuel cell technology. This approach offers a promising new method for harvesting energy from renewable sources while

also presenting innovative pathways for developing rechargeable batteries and direct liquid fuel cells. This technology could contribute significantly to the integration of renewable energy into stable and efficient energy systems for future energy storage and conversion solutions [354].

To produce hydrogen gas, Hibino et al. [359] used direct electrolysis of discarded newspapers. At the anode, temperatures between 100 and 175 °C facilitated the dissolution and hydrolysis of cellulose and lignin in the newspaper via a phosphoric acid solvent. Using low onset voltages (around 0.2 V) and high current efficiencies, the breakdown products were electrolyzed to H₂ and CO₂. At the anode reaction, carbon black modified with carbonyl groups worked better than a Pt/C catalyst. H₂ generation in a batch cell was around 0.20 g per 1 g of newspaper. H₂ was continuously produced in a flow cell at a current density of 0.15–0.25 A·cm⁻² while the voltage exhibited plateau-like behavior. With a current density of 0.15 A·cm⁻², the energy consumption for electrolysis was as low as 1.27 kWh·Nm⁻³. One of the most plentiful and sustainable feedstocks is woody or herbaceous biomass [360]. Wood chips, paper trash, and raw grass materials are important feedstocks for H₂ generation. Gasification and fermentation are two standard techniques for converting biomass to H₂ [361–364]. Due to the separation cost of H₂ in gasification and fermentation, one method for producing low-cost and highly efficient biomass H₂ is to electrolyze biomass wastes to produce hydrogen in a single step (Eqs. (43) and (44))



Consequently, pure H₂ is produced without the need for a separating step. However, the fermentation of saccharides imposes limitations on this technology. Another issue with this method is that high-calorie lignin is being wasted. It has been shown that cellulose and lignin undergo equivalent anode reactions



Reactions (Eqs. (45) and (46)) are the consequence of numerous intermediary stages at the anode, including cellulose and lignin breakdown in phosphoric acid (H₃PO₄). High current efficiencies of roughly 1.0 for H₂ synthesis at the cathode and around 0.85 for CO₂ formation at the anode were achieved within a temperature range of 100–175 °C, which is thermally self-sustaining due to heat produced by the cell's internal resistance. Biomass wastes are lignocellulosic materials, and because of their more complex structures and higher molecular weights, they are less soluble in the H₃PO₄ solvent than pure cellulose and lignin. The composition of the newspaper is similar to that of wood [365]. The lignin level was around half (11.8%) of that reported (20%–27%) previously because of the differences in the newspaper production procedures. Electrolysis of 15 mg of this mixture of newspaper to hydrogen by the processes mentioned earlier yields 2.4 mg of H₂.

The newspaper was most likely cellulose-rich, according to previous reports [366]. Compared to commercially available cellulose ($M_w = 68,300$, $M_n = 13,600$, and $M_w/M_n = 5.0$, Wako Chemicals), the calculated M_w and number average molecular weight (M_n) of cellulose were 1,810,000 and 220,000, respectively

($M_w/M_n = 8.2$). The Pt/C anode was utilized to electrolyze the newspaper. I - V curves of the electrolysis cell were plotted between a temperature range of 100–175 °C (Fig. 50(a)). Previous research indicated that at a cell voltage of 1 V, current densities of less than 0.01 A·cm⁻² may be achieved without the use of biomass fuels. The beginning voltage for electrolysis also showed a temperature effect, going from around 0.4 V at 100 °C to about 0.2 V at 175 °C. These temperature effects were attributed to reactive carbonyl groups in the decomposition products, which speed up the anode reaction due to the breakdown of cellulose and lignin into small molecules at higher temperatures. Surprisingly, I - V curves indicate that unprinted and printed newspaper fuel did not affect the electrolysis properties. Reflecting its cellulose-rich composition, newspaper I - V values were somewhat lower than those obtained using pure cellulose but higher than those obtained using pure lignin. The amounts of H₂ evolved at the cathode and CO₂ formed at the anode were measured and compared to theoretical values computed using Faraday's law at 175 °C throughout a current-density range of 0–0.3 A·cm⁻² (Fig. 50(b)). H₂ evolution and CO₂ production efficiency (the ratio of actual rates to theoretical values) were approximately 1.0 and 0.9, respectively, similar to those obtained for pure cellulose or lignin. The development of a highly active carbon anode for the oxidation of newsprint and current density was affected by carbon black species in the following order: Ketjen black (KB) > Vulcan > acetylene black. Carbonyl groups on the carbon surface operate as redox-active sites. The observed quantity of H₂ in Ketjen black agreed with the expected value, whereas the measured amount of CO₂ was lower than the theoretical value at 0.3 A·cm⁻² (Fig. 50(c)). The amount of hydrogen gas released was calculated by using those parameters, current and time before water electrolysis, into Faraday's law. At 0.06, 0.10, and 0.15 A·cm⁻², the results were 3.1, 2.5, and 2.2 mg, respectively. The results were consistent with the 2.4 mg estimated from the newspaper content. Hence, 1 g of newspaper can provide 0.15–0.21 g of H₂.

In addition, a flow cell was used to electrolyze newspapers to learn more about the electrolysis process. The voltage–time curves for the flow electrolysis cell at various current densities show lower cell voltages as compared to the batch cell due to a continuous supply of fuel to the anode (Fig. 50(d)). Total electrical resistance dropped to about 2.5 Ω·cm², which was about 1 Ω·cm² less than that achieved in the batch procedure. Hydrogen gas is produced at constant rates by continuous electrolysis at various current densities under uniform conditions (Fig. 50(e)). The H₂ evolution rates also agree with theoretical estimates, which is a noteworthy finding (brown lines). The computed energy was 0.60 kWh·Nm⁻³ for a current density of 0.15 A·cm⁻² (Fig. 50(f)). The average voltage and current of the two cartridge heaters were 2.5 V and 0.0084 A, respectively, for a total power consumption of 0.67 kWh·Nm⁻³. Therefore, the current approach significantly reduces the energy needed to produce H₂. The predicted pH values of 2.45 and 2.40 for the input and output solvents indicate that the H₃PO₄ concentration was relatively stable throughout the process. The results show that H₃PO₄ solvent may be reused even at 175 °C. For oxidizing newspapers between 150 and 175 °C, the modified Ketjen black anode proved more catalytically active and less resistant to mass transfer than a Pt/C anode.

Biomass can be used as a green energy source for hydrogen production through electrolysis. Such kind of exercise was done by Hibino [367] and coworkers, in which electrochemical hydrogen production was done by using rice chaff, cypress sawdust, and bread residue with an onset potential of approximately 0.3 V. 100% H₂ and 90% CO₂ current efficiencies were produced at cathode and anode, respectively (Fig. 51(a)). The lack of high efficiency and other conversion factors hinders its large-scale applications. Within a range of 0.1–0.2 mg, hydrogen was produced with 1 mg of raw biomass. The carbonyl functional group increases the catalytic activity of mesoporous carbon at the anode [368, 369]. Furthermore, different biomass components, i.e., lipid, starch, protein, lignin, and cellulose, were utilized as fuels for

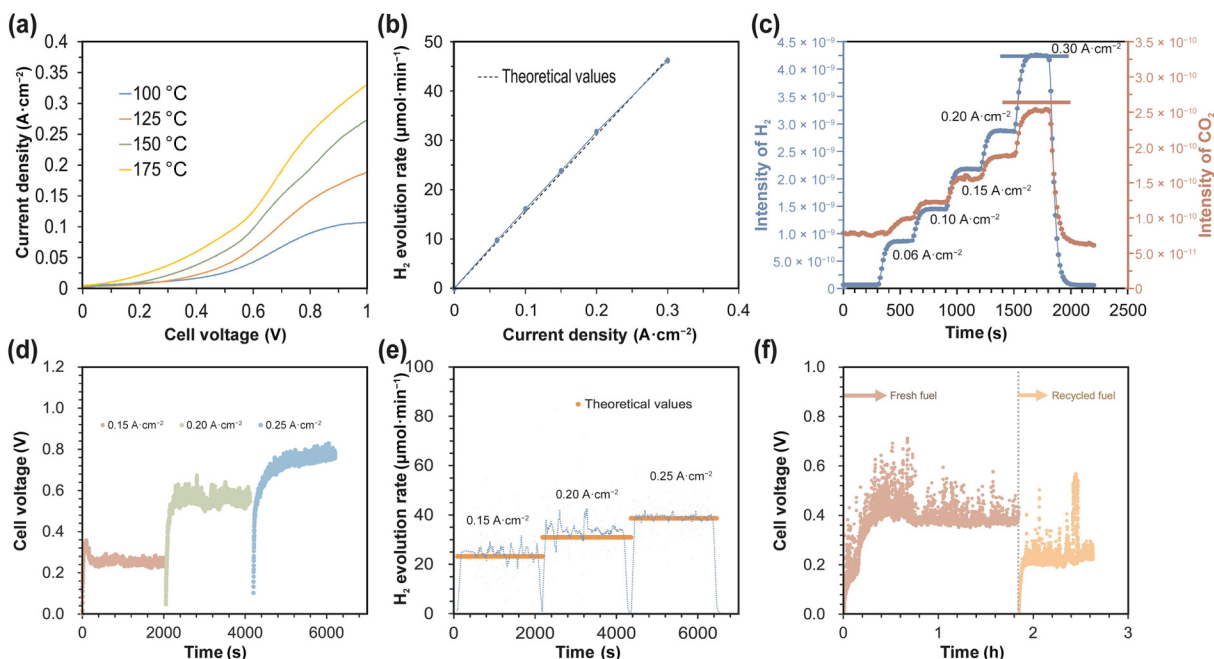
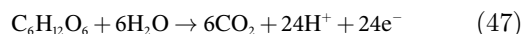


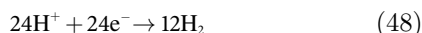
Figure 50 (a) Pt/C anode batch cell I - V curves were measured at temperatures between 100 and 175 °C. (b) The rates of H₂ formation and evolution at 175 °C. Additionally, theoretical values are provided for evaluation. (c) Mass spectrometry for H₂ and CO₂ of the batch cell using the optimized Ketjen black anode. (d) Voltage–time plots of the Ketjen black anode-optimized flow cell. (e) Continuous electrolysis at different current densities leads to varying rates of H₂ evolution. (f) Time–voltage profiles of a flow cell during extended electrolysis times and recycled fuel electrolysis at 0.15 A·cm⁻². Reproduced with permission from Ref. [359], © Elsevier B.V. 2018.

H₂ production. Hibino and coworkers used a new methodology in which biomass was directly introduced at the anode without any pretreatment, while in previous studies, biomass was first pretreated and then presented at the anode for hydrogen production. In this method, a mixed solution of phosphoric acid (H₃PO₄) and the newspaper was constantly supplied (flow operation) or added (batch operation) at an anode for smooth electrochemical electrolysis within the 100–150 °C (Eqs. (47) and (48)).

Anode



Cathode



A bifunctional mesoporous carbon and KB electrodes were employed with Sn_{0.9}In_{0.1}P₂O₇-polytetrafluoroethylene (PTFE) membrane as the electrolyte. Furthermore, for comparison, a commercially available Pt/C electrode was applied. Mass spectroscopy was applied to quantify H₂ and CO₂ production at the cathode and anode. Electrolysis of pure cellulose (15 mg) in the batch cell shows approximately 0.3 V onset cell voltage for all the anodes, but shows variation in current densities, i.e., heated KB anode at 600 °C shows greater current density than others (unheated and heated at 1000 °C anodes) (Fig. 51(b)). Impedance spectra measured at 0.4 V show increased Ohmic and polarization resistance in unheated KB anode because of the presence of carboxyl groups. Because the carboxyl group is removed during the heat treatment of KB anodes at 600 °C, the Ohmic and polarization resistance are greatly reduced without any corresponding loss of carbonyl groups. Within the 100–150 °C

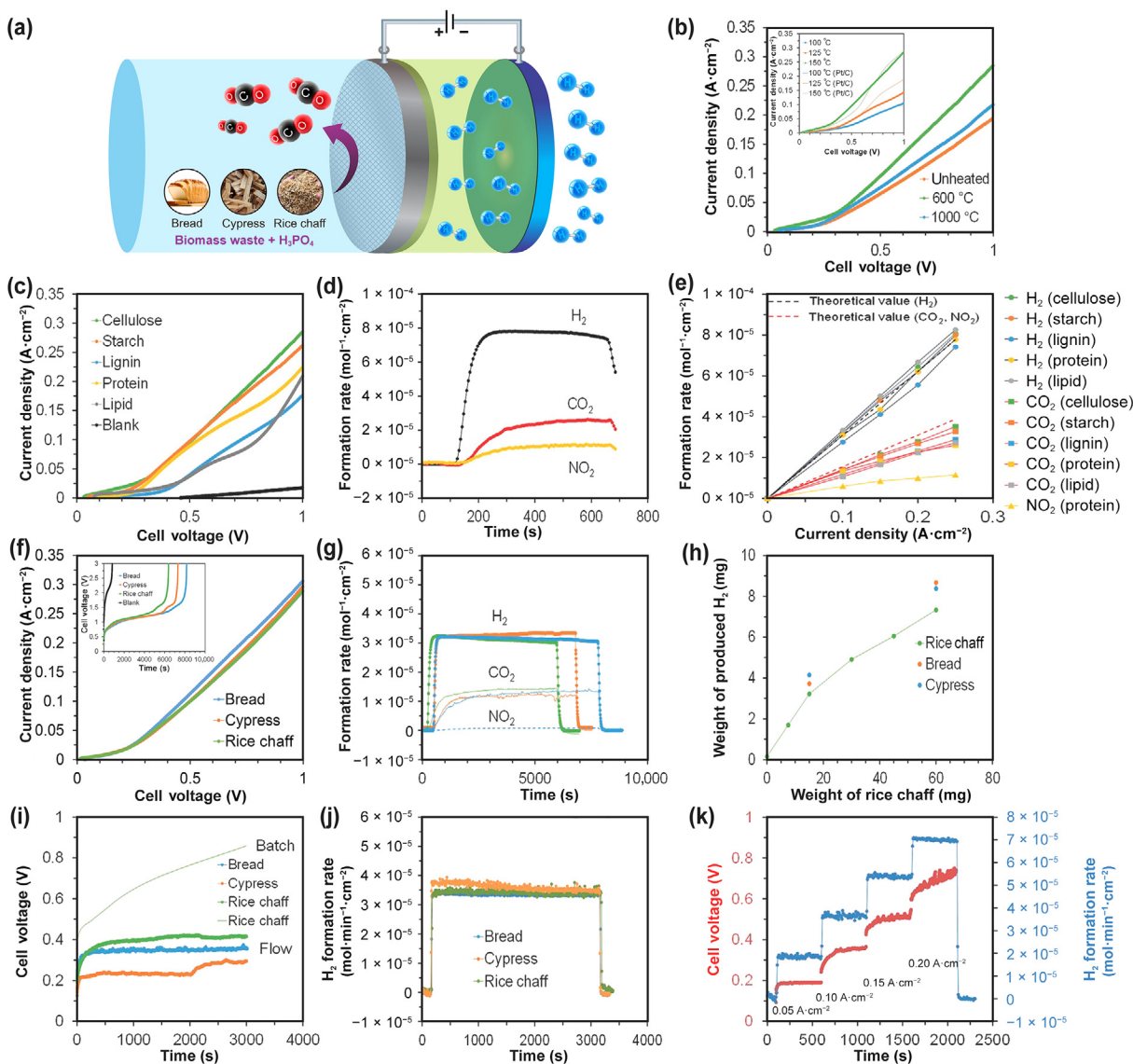


Figure 51 (a) A hybrid electrolysis approach for hydrogen production via waste biomass. (b) *I*–*V* curves of the batch cells at 150 °C using the unheated KB anode and the KB anodes heated at 600 and 1000 °C. Inset *I*–*V* curves of the cell using the 600 °C heated KB anode between 100 and 150 °C. (c) *I*–*V* curves of the batch cell using numerous biomass components as fuels at 150 °C. (d) Production of CO₂ and NO₂ at the anode and hydrogen gas formation at the cathode. (e) Formation rates of H₂, CO₂, and NO₂ during electrolysis of protein for 600 s at 0.25 A·cm^{−2}. (f) *I*–*V* plots the batch cell at 150 °C, with rice chaff, cypress, and bread as fuels. The corresponding voltage–time curves are shown in the inset. (g) During continuous electrolysis, the rates at which H₂ and other gases are formed at the cathode for 15 mg of each at 0.1 A·cm^{−2}. (h) Hydrogen production against rice chaff fuel weight were measured. (i) Voltage–time curves of the flow cell at 150 °C using rice chaff, cypress, and bread fuels. (j) Formation rates of H₂ during continuous electrolysis at the cathode over 0.1 A·cm^{−2}. (k) H₂ production rate and voltage–time plots for continuous bread electrolysis at different current densities. Reproduced with permission from Ref. [367], © American Chemical Society 2018.

temperature range, Ohmic resistance remains unchanged while polarization resistance decreases from 1.5 to 0.3 $\Omega\cdot\text{cm}^2$.

Following the interesting results of cellulose [359], Hibino [367] and coworkers directly introduced other components of pure biomass (15 mg of each component) at the anode in a batch cell for pure hydrogen production without the evolution of oxygen at 150 °C. The electrolysis onset cell voltage was about 0.3 V for starch, cellulose, and protein, whereas for other molecules, lipid, and lignin, it was around 0.4 V (Fig. 51(c)). Anodic onset cell voltage depends on the thermodynamic factor. The *I*-*V* curves show the ascending order of values of lipid = lignin < protein < starch = cellulose. The current efficiency of 95%–106% was obtained for pure biomass components. The hydrogen formation rate was higher than CO₂ and NO₂ (Figs. 51(d) and 51(e)). Finally, it was concluded that most of the hydrogen was produced from pure biomass below 0.5 V onset voltage. Similarly, waste biomass, i.e., bread, cypress, and rice chaff, can be used to produce hydrogen. For this purpose, both batch and flow cells were applied for cross-comparison. In batch cell, electrolysis starts at an onset potential of more than approximately 0.3 V. A current density of approximately 0.3 A·cm⁻² at a cell voltage of 1 V was obtained, similar to starch and cellulose. This waste biomass is rich in starch and cellulose. Bread contains 70% starch, while rice chaff and cypress contain 38% and 35% cellulose, respectively [370–372]. Impedance spectra of these waste biomass were also closer to pure biomass, as reported previously. Hydrogen shows a higher 98%–101% current efficiency than CO₂ (83%–99%) and NO₂ (0%–4%). As the fuel quantity increased, the depletion time and hydrogen production also increased. Hydrogen was extracted from 1 mg of bread, cypress, and rice chaff in a batch cell with a yield of 0.13–0.27, 0.14–0.24, and 0.12–0.22 mg, respectively. Meanwhile, lower cell voltages were seen in the flow cell compared to the batch cell (Figs. 51(f)–51(i)). An unexpectedly small increase in voltage was seen at approximately 2000 s for Cypress fuel, which may be due to disturbance in the fuel flow during electrolysis. At approximately 3000 s, rice chaff has higher cell voltage than bread and cypress. In flow cell electrolysis, the electrical energy consumed by using these fuels as, for rice chaff (0.83 kWh·Nm⁻³ > bread (0.75 kWh·Nm⁻³ > cypress (0.50 kWh·Nm⁻³, which are less than water electrolysis (approximately 5 kWh·Nm⁻³ and ethanol electrolysis (approximately 2 kWh·Nm⁻³ (Figs. 51(j) and 51(k)). The reduction in cell voltage to around 0.4 V at 0.1 A·cm⁻² is the primary reason for this power savings. Finally, it was concluded that introducing any biomass feedstock at the anode can be used to produce hydrogen [367].

Li et al. [373] further spread the idea of hybrid water splitting, leading to a new concept of electroreforming raw biomass coupled with green H₂ production. By replacing the OER with organic products, i.e., oxidation of amino biopolymer chitin (found in crustacean shells, insect skeleton, and fungi with 100 billion tons annual production naturally) [374, 375] at anode, produces acetate with 90% yield in hybrid electrolysis with a 15% decrease in energy consumption (Fig. 52(a)). Alkaline water electrolysis produces 4% of 2–3 million metric tons of hydrogen globally each year [376]. Hydrogen obtained from alkaline water electrolysis at a large scale is more expensive (> 10 USD·kg⁻¹) than traditional methane reforming technology (> 2 USD·kg⁻¹). Nearly 90% of electricity was consumed by OER as compared to HER. The authors replaced OER with chitin oxidation reaction (COR), an organic species, to get value-added products. As a safety measure, when a 2% hydrogen concentration is reached in the oxygen

compartment, the electrolysis process and hydrogen gas are stopped. This hybrid water electrolysis has some advantages like (1) high scalability on both anode and cathode, (2) COR is more promising rather than OER in conventional alkaline water electrolysis, (3) removes partial load issues because by-product obtained at the anode can easily be dissolved in electrolyte (4) membrane free electrolyzer, (5) valuable organic product which can be further upgraded to protein, (6) chitin is generally a solid waste having significant eco-friendly benefits by using COR. COR occurs at the anode, and HER occurs at the cathode to produce acetate and hydrogen. In the beginning, the depolymerization of anodic species (chitin) yielded N-acetylglucosamine (NAG) monomer, further decomposing to HAC and glucosamine by deacetylation. Both products were soluble in electrolytes. The redox potential of HAC lies between -0.4 and +1.7 V vs. RHE. Hierarchical porous-nickel/nickel foam (hp-Ni/NF) as an anode, Ni₂P/NF or Pt wire as a cathode, whereas Ag/AgCl reference electrodes were employed. When exposed to a Ni₂P/NF cathode at a current density of 100 mA·cm⁻² over -180 mV vs. RHE in 1.0 M KOH electrolyte, HER exhibits respectable activity.

Cyclic voltammetry curves show an onset potential of +1.55 V vs. RHE of OER at the anode in the absence of chitin (Fig. 52(b)). LSV curves of anodic reactions at 5 mV·s⁻¹ in 1.0 M KOH are shown in (Figs. 52(c) and 52(d)). Oxidation of Ni²⁺ to Ni³⁺ occurs around 1.40 V vs. RHE, where Ni³⁺ is an active site for water oxidation. Conversely, in the presence of chitin (33.3 mg·L⁻¹), anodic peak shifts earlier rather than OER with a current density of ~ 600 mA·cm⁻² at 1.7 V vs. RHE and a potential of ~ 80 mV lower at 0.4 A·cm⁻² (Fig. 52(e)). As a reference to these results, COR is more promising than OER. Introducing chitin at the anode leads to a decrease in oxygen generation. Because of the rapid kinetics of the reactions, COR current densities are greater than OER. GC analysis shows that the theoretical value of oxygen is deficient (i.e., O₂:H₂ = 1:2). At 1.6 V vs. RHE, the FE of oxygen was about 30%. The chitin anode shows the best stability and can be used several times during a COR reaction (Fig. 52(g)). Mechanochemical pretreatment process (M-COR) and NAG oxidation reaction (NOR) verify the increased solubility of chitin in alkaline electrolyte. Oxidation of 3.5 g·L⁻¹ milled chitin shows higher current density during the M-COR reaction than oxidation of 2.2 g·L⁻¹ NAG during NOR, with redox potential ranging from 1.24–1.49 V vs. RHE. GC shows that no oxygen was detected up to 1.45 V vs. RHE. Powdered potassium acetate hydrate (CH₃CO₂K·xH₂O) was obtained at the anode as a final product. Different extraction methods, i.e., solid-phase extraction (SPE) and liquid–liquid extraction (LLE) methods, were applied to get oxidation products (e.g., HAC with minor formic acid (< 5%) and N-containing chemicals like N-methyl-2-pyrrolidone (NMP)) at the anode as major products. At the same time, other intermediates are unstable and act as small organic acids, and identification was done using GC-MS. Complete conversion of 133.3 mg·L⁻¹ of chitin during COR output 0.5 mM concentration of HAC (Fig. 52(h)).

Furthermore, the authors demonstrated the safe production of hydrogen in gas bags driven by solar irradiation via PV solar panels. The higher the reactant concentration, the lower the oxygen concentration in the gaseous product. Overall, 0.073 L·min⁻¹ hydrogen gas is collected over an electrode with an area of 28 cm² (Fig. 52(f)). Cyclic performance indicates that the anode is stable for both OER and COR. Finally, HAC, a useful product, was obtained at anode in a range of 73.7%–77.5% with pure hydrogen gas evolution. In addition to the advantages of

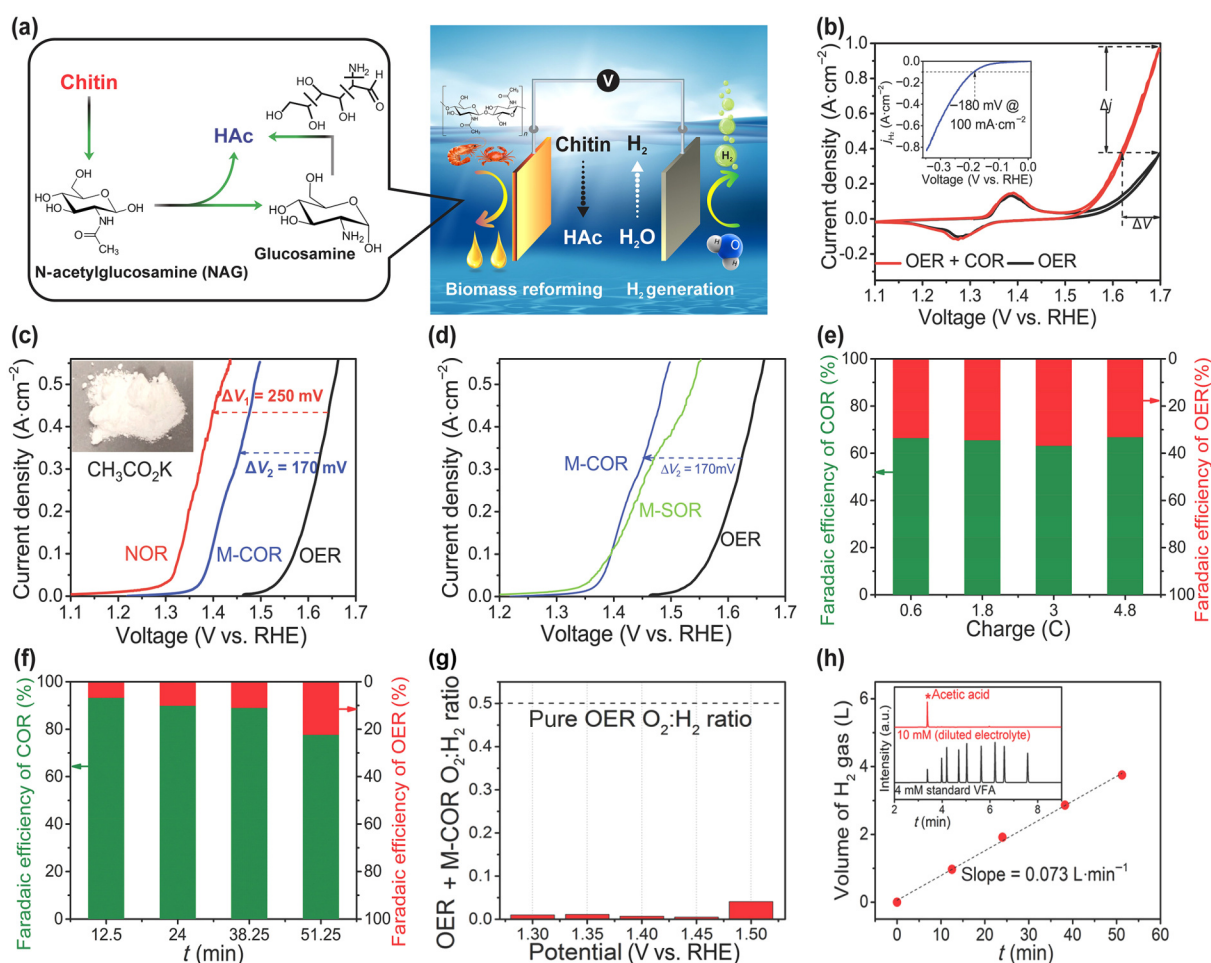


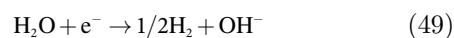
Figure 52 (a) Conceptual model of hybrid electrolysis by utilization of raw biomass (chitin) to HAC, a value-added product, together with hydrogen production. (b) Comparison of anodic reactions in 1.0 M KOH before (OER: black) and after the addition of 33.3 mg·L⁻¹ of chitin (OER + COR: red) using CV at a scan rate of 10 mV·s⁻¹. Inset: LSV curve of HER using Ni₂P/NF catalyst. (c) LSV curves of anodic reactions at 5 mV·s⁻¹ in 1.0 M KOH (OER: black) and at the condition of containing 2.2 g·L⁻¹ N-acetyl glucosamine (red) and 3.5 g·L⁻¹ milled chitin (blue). Shifts the potential after adding the correlating biomass. Inset: 436 mg of potassium acetate (CH₃CO₂K). (d) LSV curves of anodic reactions at 5 mV·s⁻¹ in 1.0 M KOH with 6.0 g·L⁻¹ milled shrimp shell (green). The anodic OER (black) and M-chitin oxidation reaction (blue) curves are also plotted for comparison. (e) The HWS Faradaic efficiency of COR and OER under 33.3 mg·L⁻¹ chitin added at a constant potential of 1.6 V vs. RHE. (f) FE of COR and OER for solar-powered single-compartment hybrid electrolysis at varied reaction times. (g) The hybrid NOR/HER electrolysis O₂:H₂ ratio at different potentials. (h) H₂ production rate (0.073 L·min⁻¹) through solar energy-driven single-compartment hybrid electrolysis. Reproduced with permission from Ref. [373], © The Author(s), 2021.

such a hybrid electrolysis, it has some shortcomings like (1) energy consumption during the ball milled process, (2) use of cocatalysts to reduce energy consumption, and (3) increasing the processing scale may lead to increase in the cost. That is why the practical importance of such proposed hybrid electrolysis has lessened. Moreover, shrimp shells and other seafood were applied as an alternative to chitin to support hybrid electrolysis with good results [377–379].

Xia et al. [354] introduced an HWS system that utilizes Ni(OH)₂ as a solid-state redox mediator. In this system, the cathodic reduction of NiOOH to Ni(OH)₂ is paired with an anodic oxidation reaction with a lower potential, replacing the conventional OER. Ethanol was chosen as the anodic reactant because the ethanol oxidation reaction is widely used in alkaline media, particularly in direct ethanol fuel cells (DEFCs). This choice leverages ethanol's well-established electrochemical behavior, allowing for a more efficient and lower-potential anodic process, making the overall system more energy-efficient while coupling hydrogen production with ethanol oxidation [357, 358]. The NiOOH formed during the hydrogen production step can react with ethanol to form a NiOOH/ethanol hybrid cell. In this

process, Ni(OH)₂ is oxidized to NiOOH while hydrogen is produced, and NiOOH then reacts with ethanol, converting back to Ni(OH)₂ as ethanol undergoes oxidation. The discharge product, Ni(OH)₂, can be reused to produce hydrogen in subsequent cycles. This anodic ethanol EOR can also be integrated with other liquid fuels, such as hypophosphite, formate, isopropanol, or methanol, resulting in the formation of various NiOOH/liquid fuel hybrid cells. These hybrid cells offer flexibility by utilizing different fuels, while the Ni(OH)₂ acts as a solid-state redox mediator, enabling repeated cycles of hydrogen generation and fuel cell operation (Eqs. (49)–(52)).

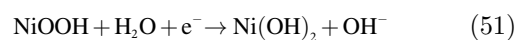
Cathode



Anode



Cathode



Anode



Using a three-electrode system, the electrochemical profiles of HER and EOR were examined in an alkaline electrolyte, with 1 M KOH used for HER and a mixture of 1 M KOH and 1 M ethanol for EOR. The system employed a Pt electrode as the counter electrode, a PdNiP-based film electrode for EOR, and a Ni(OH)₂/MWNTs redox electrode, with a Hg/HgO electrode as the reference. The CV scan of the Ni(OH)₂/MWNTs electrode at a scan rate of 5 mV·s⁻¹ in 1 M KOH (black line) revealed a pair of redox peaks within the range of 0.35 to 0.5 V (vs. Hg/HgO). The onset potential for HER was approximately -0.9 V (red line), while for EOR, it was about -0.55 V (blue line) vs. Hg/HgO. In the absence of OER, a driving voltage of 1.5 V was necessary to produce hydrogen. The NiOOH/ethanol hybrid cell demonstrated a discharge capacity of 266 mAh·g⁻¹ at 1 A·g⁻¹ and 243 mAh·g⁻¹ at 3 A·g⁻¹, while chronoamperometry data indicated a maximum current density of 148 mA·cm⁻², highlighting the high rate of hydrogen production. Similarly, the NiOOH/methanol hybrid cell exhibited discharge capacities of 263 mAh·g⁻¹ at 1 A·g⁻¹ and 224 mAh·g⁻¹ at 4 A·g⁻¹. The maximum current density for this system also reached 148 mA·cm⁻². Notably, the NiOOH/hypophosphite hybrid cell achieved a maximum power density of approximately 35 mW·cm⁻², which was significantly higher than the other cells, likely due to its higher operating voltage of around 1.5 V. This direct liquid fuel cell system, based on a solid-state redox mediator using nickel hydroxide architecture, integrates efficient hydrogen production. Cycling through both the hydrogen production and energy discharge steps results in a hybrid energy storage and conversion system capable of transforming renewable energy into both hydrogen energy and stable electrical energy, with the OER step further enhancing its efficiency.

Despite the development of many types of electrocatalysts, their performance remains unsatisfactory, even when noble metal catalysts like IrO₂ and RuO₂ are used [380–385]. One of the significant challenges in conventional water electrolysis is that the oxygen produced at the anode is of limited value since it can be easily obtained from the air. Recent efforts have focused on integrating the oxidation of small organic molecules with the decoupled HER in water splitting to enhance efficiency. Various small organic molecules, such as aloe extract, ethanol, 5-hydroxymethylfurfural, and benzyl alcohol, have been employed for H₂ production via oxidation [70, 181, 333, 386–389]. MOFs have significant potential in catalysis [390, 391]. Methanol is relatively inexpensive and offers great potential for hydrogen production. Shi et al. [392] introduced an ultrathin 2D bi-MOF nanosheets (UMOFNs) for electrocatalytic hydrogen production in methanol aqueous solutions. Notably, the onset potential (10 mA·cm⁻²) of the anode reaction in methanol solution was more than 200 mV lower than that required for water electrolysis. Mass spectroscopy confirms that the hydrogen evolution mechanism was methanol-assisted water splitting. The anodic potential of CoCu-UMOFNs in methanol solution was significantly reduced by 232 mV at a current density of 10 mA·cm⁻².

Furthermore, the anodic potentials at different current densities of 20, 50, and 100 mA·cm⁻² are also much lower than those of OER. Co-UMOFNs and Cu-UMOFNs also show similar results. FE for hydrogen evolution in methanol solution is nearly 100%. CoCu-UMOFNs exhibit a low onset potential of (1.365 V vs.

RHE) as compared to Cu-UMOFNs (1.495 V vs. RHE) and Co-UMOFNs (1.427 V vs. RHE). CoCu-UMOFNs show good stability, as concluded by CV for 2000 cycles and chronoamperometry. During the chronoamperometry test at an applied potential of 1.38 V, H₂ bubbles were visible on the surface of graphite carbon, and no significant decrease in current density was observed over 12 h. CV and chronoamperometry tests confirmed the excellent stability of CoCu-UMOFNs for hydrogen evolution in methanol. This indicates that CoCu-UMOFNs could be highly effective for electrocatalytic hydrogen production.

HWS is more favorable than conventional water splitting due to (1) the generation of pure hydrogen, (2) the simultaneous production of value-added organic compounds, and (3) a lower overpotential for electrooxidation reactions [69, 393, 394]. The electrochemical reforming of small organic molecules is a promising approach to producing hydrogen. Geng et al. [395] introduced a Mo–Ni alloy nanoparticles hybrid system that exhibits a Pt-like electronic structure with highly active HER catalysts in alkaline media. Ni is responsible for oxidizing small organic molecules to yield value-added products by BA oxidation in 1.0 M KOH. Experiments confirmed that the OER performance of hierarchical Mo–Ni nanoparticle catalysts was superior to commercially available Mo_{0.6}Ni_{0.4}/Ti, RuO₂/NF, NiMoO₄/NF, and treated/untreated Ni foams in 1.0 M KOH. LSV shows that in the presence of 10 mM, BA onset potential is shifted from 1.55 to 1.31 V vs. RHE, having a current density of 15 mA·cm⁻² for OER. The *in situ* formed NiOOH species confirm that NiOOH serves as the active site for BA oxidation. Anodic oxidation reaction resulted in a lower Tafel slope of 23.2 mV·dec⁻¹, compared to 154.8 mV·dec⁻¹ for the OER. Below 1.28 V, no oxidation products were detected. In the potential range of 1.30 to 1.36 V, benzoic acid achieves nearly 100% FE. At a higher potential of 1.38 V, the FE decreased to 98% due to the onset of the OER. As the potential increased to 1.42 V, the OER became more significant, leading to a sharp drop in FE to 60% for benzoic acid formation. We further assessed the influence of organic compounds, including 10 mM BA, benzaldehyde, and benzoic acid, on the cathode chamber, which had a negligible effect on HER kinetics, as indicated by minimal changes in the LSV curves. The FE for hydrogen production remained close to unity across all cases. The FE for hydrogen production remained close to 100%, with 1.7 mL of H₂ generated for every 15 C of charge passed. 3-methylbenzyl alcohol and 2-methylbenzyl alcohol also exhibit similar results. Long-term stability tests for five cycles (10 h) show 90% capacity retention after each cycle. The cell voltage of 1.39 V produces 10.4 mL of H₂ from 0.25 mmol of BA within 4.5 h with no OER during this process.

The electrocatalytic oxidation of HMF to FDCA is an essential chemical for the renewable polymer industry. Wang et al. [396] reported that nickel borides (NiB_x) doped with varying amounts of phosphorus were applied to HMF electrocatalysis. The FDCA yield using phosphorus-doped NiB_x (NiB_x-P_y) initially increased with phosphorus content but declined as doping levels rose. The NiB_x-P_{0.07} catalyst (η_P/η_{Ni} = 0.07; where η_P/η_{Ni} represents the atomic ratio of P to Ni) exhibited the highest FDCA yield of 90.6%, with a FE of 92.5% at a potential of 1.464 V (vs. RHE). XPS analysis revealed that phosphorus doping caused electron displacement from surface nickel, which increased the presence of surface nickel hydroxide species beneficial for electrocatalytic performance. Furthermore, the phosphorus dopant enhanced the charge transfer capability of NiB_x-P_y, thus improving catalytic activity. The NiB_x-P_{0.07} catalyst also demonstrated good stability,

showing no significant deactivation after three cycles. The electrocatalytic performance of $\text{NiB}_x\text{-P}_y$ with different phosphorus content was evaluated using LSV curve of HMF in 0.1 M KOH. The FDCA yield increased initially with phosphorus content, peaking at 90.6% on $\text{NiB}_x\text{-P}_{0.07}$, with a FE of 92.5%, compared to 75.5% yield and 80.1% efficiency on undoped NiB_x . EIS confirmed that phosphorus doping improves the charge transfer capability of $\text{NiB}_x\text{-P}_y$, further enhancing its electrocatalytic performance.

Wang et al. [397] designed and prepared efficient electrocatalysts for biomass upgrading. The electrocatalytic oxidation activity of $\text{Ni}_3\text{S}_2/\text{NF}$ for HMF conversion was evaluated using a three-electrode system. $\text{Ni}_3\text{S}_2/\text{NF}$ served as WE, Ag/AgCl as RE, and a graphite rod as CE using an H-type cell. The anode compartment contained 15 mL of 1 M KOH with 10 mM HMF, while the cathode compartment held 10 mL of 1 M KOH. Water oxidation on the $\text{Ni}_3\text{S}_2/\text{NF}$ electrode occurred at approximately 1.63 V vs. RHE at a $10 \text{ mA}\cdot\text{cm}^{-2}$ current density. When HMF was added, the required potential decreased to 1.43 V vs. RHE, representing a 0.2 V reduction compared to the OER. This result indicates that the $\text{Ni}_3\text{S}_2/\text{NF}$ catalyst exhibits high electrocatalytic activity for HMF oxidation. Furthermore, a comparison with nickel foam, NiC, NiO, and NiS revealed that $\text{Ni}_3\text{S}_2/\text{NF}$ outperformed in HMF oxidation activity. The $\text{Ni}_3\text{S}_2/\text{NF}$ has a lower Tafel slope compared to other catalysts, suggesting superior electrochemical activity. LSV results show that HMF oxidation occurs at a constant potential of 1.498 V vs. RHE. High-performance liquid chromatography (HPLC) monitors the concentrations of HMF and its oxidation products. After 120 min, the conversion rate of HMF reached 100%, with a yield of 98.3% and a FE of 93.5%, outperforming many previously reported Ni and Co catalysts. HMF solution changed color from light yellow to colorless, reflecting the oxidation process. The NF exhibits poor oxidation efficiency for HMF, yielding only 51.7% FDCA. The oxidation mechanism of HMF can follow two pathways: Path I involves the oxidation of hydroxyl groups to aldehyde groups, producing DFF, which is then oxidized to FFCA. Path II consists of the oxidation of aldehyde groups to carboxyl groups, producing HMFCFA, which is subsequently oxidized to FFCA. Both pathways ultimately generate FDCA. However, in this study, Path II was more favorable because HMFCFA and FFCA were detected, not DFF. The reaction rate of $\text{Ni}_3\text{S}_2/\text{NF}$ was $0.15 \text{ mM}\cdot\text{min}^{-1}$, significantly higher than NiS ($0.08 \text{ mM}\cdot\text{min}^{-1}$), NiO ($0.08 \text{ mM}\cdot\text{min}^{-1}$), NF ($0.07 \text{ mM}\cdot\text{min}^{-1}$), and NiC ($0.06 \text{ mM}\cdot\text{min}^{-1}$), which further highlights the superior catalytic activity of $\text{Ni}_3\text{S}_2/\text{NF}$. The conversion rate of HMF, the yield of FDCA, and FE remained consistently above 99%, 96%, and 93%, respectively. These results demonstrate that $\text{Ni}_3\text{S}_2/\text{NF}$ is a highly efficient and stable electrocatalyst for HMF oxidation.

Electrochemical oxidation of ethylene glycol (EG) offers a promising alternative to the sluggish OER in thermodynamics, enabling energy-efficient hydrogen production alongside the generation of valuable glycolic acid. In line with this approach, PtRh nanowires (NWs) modified with Rh atoms ($\text{PtRh}_{0.02}/\text{Rh}$ NWs) were designed and synthesized. Wang et al. [398] reported that these nanowires demonstrated exceptional performance in both HER and the EG oxidation reaction (EGOR). The $\text{PtRh}_{0.02}/\text{Rh}$ NWs exhibited remarkable HER activity with overpotentials as low as 30.6 mV in alkaline water and 45.8 mV in seawater, along with Tafel slopes of 39.1 and 39.5 $\text{mV}\cdot\text{dec}^{-1}$, respectively. In the EGOR, the nanowires achieved peak current densities of 1.25 and $1.17 \text{ A}\cdot\text{mg}^{-1}$ in alkaline and seawater electrolytes, respectively. Furthermore, the stability of $\text{PtRh}_{0.02}/\text{Rh}$

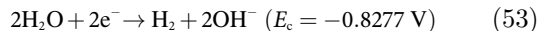
NWs is better than that of commercially available Pt black (JM-Pt black) from Johnson Matthey Corporation. When $\text{PtRh}_{0.02}/\text{Rh}$ NWs were used as both the cathode (for HER) and the anode (for EGOR), the cell required only 0.66 V to reach a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, significantly lower than the 1.57 V needed for the HER/OER combination. The Rh atoms on the surface of the Pt nanowires introduced a strain effect, optimizing the active sites and offering a general strategy for designing highly efficient, durable bifunctional catalysts. Their application as electrocatalysts enables EG to serve as an anodic feedstock for hydrogen production from seawater while simultaneously producing high-value chemical products with minimal energy consumption. $\text{PtRh}_{0.1}/\text{Rh}$ NWs and $\text{PtRh}_{0.34}/\text{Rh}$ NWs were also synthesized using the same method, but $\text{PtRh}_{0.02}/\text{Rh}$ NWs showed the best performance. The electrochemical performance of these samples was evaluated in N_2 -saturated 0.1 M KOH solution and seawater containing 0.1 M KOH (pH = 13.8) with a standard three-electrode system at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. LSV curves revealed that $\text{PtRh}_{0.02}/\text{Rh}$ NWs exhibited the highest HER activity in both electrolytes. The $\text{PtRh}_{0.02}/\text{Rh}$ NWs achieved an overpotential of 30.6 mV, which is significantly lower than that of Pt NWs (99.7 mV) and commercial JM-Pt black (122.3 mV) at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. The Tafel slope from the LSV curves further confirmed that $\text{PtRh}_{0.02}/\text{Rh}$ NWs with a Tafel slope of $39.1 \text{ mV}\cdot\text{dec}^{-1}$ displayed faster HER kinetics. After 3000 cycles, the ECSA of $\text{PtRh}_{0.02}/\text{Rh}$ NWs retained 96.5% of its initial value, with only a 10.1 mV negative shift in overpotential. In contrast, JM-Pt black retained only 20.9% of its original ECSA and exhibited a 102.8 mV degradation in overpotential for HER. In long-term stability tests, $\text{PtRh}_{0.02}/\text{Rh}$ NWs maintained 98.2% of their initial current density, while JM-Pt black dropped to 81.4%. Since coupling EGOR with HER can enhance water splitting efficiency, $\text{PtRh}_{0.02}/\text{Rh}$ NWs were employed as the cathodic and anodic electrodes in a two-electrode electrolyzer. When replacing OER with EGOR during water splitting, the required cell voltage was only 0.66 V, considerably lower than the 1.57 V needed for the HER–OER system.

Wang et al. [399] proposed a novel rechargeable Zn–Hz battery, utilizing a bifunctional electrocatalyst that enables two distinct cathodic reactions: hydrogen evolution (discharge: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) and hydrazine oxidation (charge: $1/2\text{N}_2\text{H}_4 \rightarrow 1/2\text{N}_2 + 2\text{H}_2\text{O} + 2\text{e}^-$). This Zn–Hz battery operates via temporally decoupled electrochemical hydrazine splitting at the cathode during the discharge and charge processes, allowing for hydrogen generation without the need for purification. When paired with a highly active bifunctional three-dimensional (3D) carbon decorated with core–shell $\text{Mo}_2\text{C}/\text{C}$ and Ni/C ($\text{Mo}_2\text{C}/\text{Ni}/\text{C}/\text{CS}$) cathode and a Zn foil anode, the Zn–Hz battery achieves efficient hydrogen production with a minimal energy input of less than 0.4 V ($77.2 \text{ kJ}\cdot\text{mol}^{-1}$) and a high energy efficiency of 96%. Notably, the battery demonstrates excellent long-term stability over 600 cycles (200 h), maintaining continuous, on-demand hydrogen production, highlighting its potential for practical applications. In traditional water electrolysis, the high energy consumption is primarily due to the sluggish kinetics of the anodic OER, which requires an energy input more significant than 1.6 V due to the theoretical water splitting voltage of 1.23 V [400–403]. Recently, small organic molecules, such as alcohols, urea, glucose, and hydrazine, have been explored as alternative fuel sources to replace OER, given their lower overpotentials. Among these, hydrazine, a carbon-free and environmentally friendly liquid fuel, can be oxidized by transition metal catalysts at a low voltage of -0.33 V ,

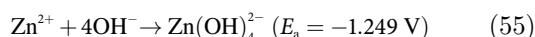
significantly reducing the electrical energy input [404–412]. The HzOR releases only inert, environmentally benign nitrogen as a byproduct [413]. A rechargeable alkaline Zn–Hz battery, based on decoupled hydrazine splitting via two temporally separate cathodic reactions (HzOR during charging and HER during discharging), can achieve efficient and segregated hydrogen production. Unlike typical decoupled electrolysis, this process is enabled by bifunctional electrocatalysts in a two-electrode system, facilitating hydrogen generation without the need for purification through temporal separation. Hydrazine decomposition is an exothermic reaction, releasing a ΔG of $-111.54 \text{ kJ}\cdot\text{mol}^{-1}$, which can be reused by the system to further lower electrical energy input. This Zn–Hz battery operates with a bifunctional electrocatalyst as the cathode, Zn foil as the anode, and a 1 M KOH aqueous electrolyte. The bifunctional electrocatalyst, consisting of 3D $\text{Mo}_2\text{C}/\text{Ni@C}/\text{CS}$, demonstrates exceptional performance for both HER and HzOR. In this system, Mo_2C serves as the active site for HER, while Ni exposes favorable active sites for HzOR. HER tests were conducted using a 1 M KOH electrolyte with 0.2 M N_2H_4 to ensure consistency in the Zn–Hz battery. According to the LSV curves, the $\text{Mo}_2\text{C}/\text{Ni@C}/\text{CS}$ catalyst delivers a small overpotential of 76 mV to reach a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, which is slightly higher than Pt/C but significantly lower than Mo_2C (237 mV) and Ni nanoparticles (258 mV). Additionally, the corresponding Tafel slope for $\text{Mo}_2\text{C}/\text{Ni@C}/\text{CS}$ is approximately $48.4 \text{ mV}\cdot\text{dec}^{-1}$, nearly half that of Mo_2C , indicating favorable and fast electrochemical HER kinetics for the $\text{Mo}_2\text{C}/\text{Ni@C}/\text{CS}$ catalyst.

The overall discharge reaction of the Zn–Hz battery is represented as follows (Eqs. (53)–(58)):

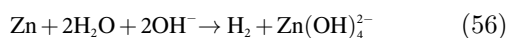
Cathode



Anode



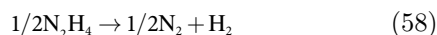
Overall discharge



$$E_{\text{dis}} = E_c - E_a = 0.4213 \text{ V} \quad (57)$$

where E_c , E_a , and E_{dis} denote the cathodic potential, anodic potential, and discharge voltage, respectively.

The overall reaction for the aqueous rechargeable Zn–Hz battery during hydrazine oxidation is



Furthermore, the Zn–Hz battery exhibits outstanding long-term stability, maintaining performance over 600 cycles at a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$, confirming its potential for practical applications. Summary of recent studies on hybrid water splitting can be seen in Table 5.

6 Challenges in decoupled water splitting

Further research on the redox mediators is necessary to enhance charge storage capacity, thereby increasing the efficiency and output of hydrogen production. Current research remains

confined to laboratory-scale studies, highlighting the gap between fundamental discoveries and industrial implementation. While significant progress has been made in developing electrocatalysts for HER and OER reactions, critical challenges persist in decoupled water electrolysis. The long-term stability of non-noble metal catalysts under industrial conditions remains unresolved, with mechanical degradation, gas-induced deactivation, and impurity interference posing major hurdles. When transitioning from laboratory-scale research to industrial applications, both practicality and efficiency must be optimized. Redox mediators, central to decoupled systems, face compatibility issues with cell components (e.g., membranes and electrodes) and structural instability during repeated electron/proton cycling. While this challenge is not insurmountable, further research efforts are required to enhance RM performance. These challenges demand advanced *in-situ* characterization techniques (synchrotron spectroscopy, XPS, Raman) to probe active sites and dynamic reconstruction processes, coupled with computational modeling to guide catalyst optimization. Hybrid water splitting systems, which pair HER with alternative anodic reactions (e.g., biomass oxidation, UOR, AOR, SOR, HzOR, and pollutant degradation), offer a promising route to reduce energy input and bypass corrosive side reactions like chloride oxidation in seawater electrolysis. However, their viability hinges on designing selective catalysts for value-added products (e.g., organics over CO_2) and addressing pH-dependent kinetics, as HER favors acidic media while most oxidations thrive in alkaline conditions.

Transition metal catalysts (Ni, Fe, and Co), leveraging tunable d-orbital electronics and nanostructured morphologies, show potential for cost-effective scalability but require tailored designs beyond conventional OER-based strategies. However, despite these advantages, the high cost of electrochemical oxidation substrates and the low economic value of gaseous byproducts hinder the overall feasibility of such systems. The choice of oxidation reaction is critical and should balance cost, energy savings, and product value. However, the competing ClOR at the anode generates corrosive chlorine species that degrade catalysts and cell components, severely limiting practical implementation. Notably, small molecule oxidation occurs at substantially lower potentials than both OER and ClOR, suggesting its potential to enable high-current-density seawater electrolysis while circumventing chloride interference. Transitioning to industrial applications necessitates reactor innovations, such as flow electrolyzers, to sustain high current densities ($> 1 \text{ A}\cdot\text{cm}^{-2}$) while suppressing competing reactions. The downstream separation and purification of anodically generated products represent critical challenges for industrial implementation of electrocatalytic systems. While gas-phase products can be readily separated using dual-compartment reactors, liquid-phase products often require energy-intensive purification processes, particularly when present at low concentrations in electrolyte solutions. Downstream product separation remains a critical bottleneck, particularly for hydrophilic liquid-phase products, driving research toward hydrophobic intermediates or *in-situ* precipitation strategies. Concurrently, ion-exchange membranes with enhanced selectivity are vital to prevent reactant crossover. Economically, system feasibility relies on balancing visible costs (materials, catalysts) with hidden expenditures (energy, purification), emphasizing the integration of renewable energy sources (solar, wind) and earth-abundant catalysts. From an economic perspective, the viability of coupled electrocatalytic processes depends on a comprehensive cost-benefit analysis that accounts for both direct and indirect

Table 5 Summary of recent studies on hybrid water splitting

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
NiFeRh-LDH nano sheets		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	100	1.471	100	62 h at 1.47 V	[414]
Co _{0.26} -Ni(OH) ₂ NPs/CF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.42	100	38 h	[415]
Ni(OH) ₂ /NiO-C/WO ₃ HAs		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.37	—	60 h at 20 mA·cm ⁻²	[416]
F-P-Co ₃ O ₄ /NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.427	—	15 h	[417]
NiCoB@C		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.34	—	10 h at 20 mA·cm ⁻²	[418]
N-NiS/NiS ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.62	100	8 h	[419]
Ni ₉ S ₈ /CuS/Cu ₂ O/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.47	—	20 h	[420]
NiMoV LDH/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	100	1.63	—	15 h at 15 mA·cm ⁻²	[421]
P-CoNi ₂ S ₄ YSSs		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.402	—	100 h	[422]
N-Co ₉ S ₈ /Ni ₃ S ₂ /NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.4	98	50 h at 200 mA·cm ⁻²	[423]
Ni ₂ Fe(CN) ₆		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	100	1.5	90	—	[424]
NF/NiMoO-H ₂ as a HER and NF/NiMoO-Ar as a UOR		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.55	100	50 h	[425]
P-CoS ₂ /Ti		H ₂ + N ₂ + CO ₂	1 M KOH + 0.3 M urea	10	1.375	—	18 h	[426]
CoS ₂ -MoS ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.29	—	60 h	[427]
FeNi-MOF NSs		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.431	—	10 h	[428]
NiCoP _x @NiFeCo-MOF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.54	—	42 h	[429]
Ni ₃ N/Mo ₂ N	HER + urea electrolysis	H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.36	—	50 h	[430]
Ni-WO _x		H ₂ + N ₂	1 M KOH + 0.33 M urea	100	1.42	98	10 h	[431]
Ni ₃ Se ₄ nanorod array		H ₂ + N ₂ + CO ₂	1 M KOH + 0.1 M urea	10	1.38	—	24 h	[432]
V-FeNi ₃ N/Ni ₃ N		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.46	—	25 h at 50 mA·cm ⁻²	[433]
Ni-S-Se/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.47	100	24 h at 20 mA·cm ⁻²	[434]
Mo-Co-S-Se/CC		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.4	—	11 h	[435]
Zn _{0.08} Co _{0.92} P/TM		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.38	100	10 h	[436]
CoS _x /Co-MOF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.48	—	10 h	[437]
Fe-Co _{0.85} Se/FeCo LDH		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	300	1.57	98.2	60 h	[438]
NiSe ₂ /MoSe ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.44	—	48 h	[439]
Ni 3N NA/CC		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.44	—	10 h	[440]
Co ₂ Mo _{0.2} CH		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.40	—	40 h	[441]
F-NiO/Ni@C		H ₂ + N ₂ + CO ₂	1 M KOH + 0.3 M urea	10	1.37	—	100 h at 1000 mA·cm ⁻²	[442]
NiF ₃ /Ni ₂ P@CC-2		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	50	1.83	—	10 h at 10 mA·cm ⁻²	[443]
20% Pt/C as a HER and Ce Ni ₃ N@CC as a UOR		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.34	100	15 h at 40 mA·cm ⁻²	[444]
Ni@NCNT-3		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.56	—	10 h	[445]
W-NiS ₂ /MoO ₃ @CC		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.372	—	24 h	[446]
N-NiZnCu LDH/rGO		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.668	—	40 h	[447]
Ni-Mo nanotube		H ₂ + N ₂ + CO ₂	1 M KOH + 0.1 M urea	10	1.43	98.7	24 h at 10 mA·cm ⁻²	[448]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Co ₃ O ₄ /Ti ₃ C ₂ MXene	HER + Hz electrolysis	H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	50	1.49	97.9	40 h	[449]
Ni ₂ P NF/CC		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	50	1.35	100	8 h at 100 mA·cm ⁻²	[450]
Ni ₃ N/Mo ₂ N		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.36	—	50 h	[430]
V-Ni ₃ N/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.416	—	200 h	[451]
Ni ₂ P/Ni _{0.96} S/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.453	90	50 h at 20 mA·cm ⁻²	[452]
Ni(OH) ₂ -NiMoO _x /NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.42	—	40 h at 50 mA·cm ⁻²	[453]
Ni ₃ N/Ni _{0.2} Mo _{0.8} N/F		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.348	100	500 h	[454]
Ru-Co ₂ P/N-C/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.58	—	20 h at 1.6 V	[455]
P-mAuRh film/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	100	1.47	—	35 h	[456]
O-NiMoP/NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	50	1.55	96.8	10 h at 20 mA·cm ⁻²	[457]
Fe-Ni ₃ S ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	100	1.57	100	500 h at 500 mA·cm ⁻²	[458]
NiSe ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.33 M urea	10	1.39	95	25 h	[459]
Ru/P-NiMoO ₄ @NF		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea + seawater	500	1.73	—	145 h at 100 mA·cm ⁻²	[460]
N-WS ₂ /Co ₃ N		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	500	1.72	94	45	[461]
NiCo ₂ S ₄ /CC		H ₂ + N ₂ + CO ₂	1 M KOH + 0.3 M urea	10	1.45	—	10 h	[462]
CoMn/CoMn ₂ O ₄		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.51	95.7	~ 17 h at 100 mA·cm ⁻²	[463]
Cu ₂ S@Ni ₃ Se ₂		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.48	92	20	[464]
Ni/MoC/Ti ₃ C ₂ T ₂ @C		H ₂ + N ₂ + CO ₂	1 M KOH + 0.3 M urea	10	1.56	—	20 h	[465]
Tb _{8A} @d-Co ₃ O ₄		H ₂ + N ₂ + CO ₂	1 M KOH + 0.5 M urea	10	1.22	97.5	100 h	[466]
Ni ₃ Se ₄ nanorod array		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	10	0.37	—	24 h	[432]
Fe/F-Ni ₃ P@NC		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	1000	0.568	100	100 h at 100 mA·cm ⁻²	[467]
Ni ₃ N-Co ₃ N PNAs/NF		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	400	0.76	100	20 h at 0.14 V	[468]
Ni NCNAs		H ₂ + N ₂	1 M KOH + 0.3 M N ₂ H ₄	892	0.485	—	20 h at 50 mA·cm ⁻²	[469]
Ni-SN@C		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	10	0.336	100	24 h	[470]
Ni-C HNAs		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	200	0.4	100	30 h at 50 mA·cm ⁻²	[471]
RuP ₂ /C		H ₂ + N ₂	1 M KOH + 0.3 M N ₂ H ₄	10	0.023	99.5	20 h	[472]
N-NiZnCu LDH/rGO		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.106	—	40 h	[447]
Mn-SA/BNC		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	10	0.41	100	24	[473]
RP-CPM		H ₂ + N ₂	1 M KOH + 0.3 M N ₂ H ₄	100	0.227	99.5	20 h	[472]
WS ₂ /Ru SAs		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	200	0.4	100	100 h at 10 mA·cm ⁻²	[413]
Au@Rh ultra-NWs		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	10	0.18	—	12 h	[474]
CoFeNiCrMnP/NF		H ₂ + N ₂	1 M KOH + 0.4 M N ₂ H ₄	200	0.14	98	20 h	[475]
Ni(Cu) CNPs		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.339	99.2	24 h	[476]
N-Ni ₅ P ₄ @CoP/CFP		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	10	0.037	—	10 h	[477]
RhRu _{0.5} -alloy		H ₂ + N ₂	1 M KOH + 1 M N ₂ H ₄	853	0.60	94.1	80 h at 100 mA·cm ⁻²	[478]
Cu ₁ Ni ₂ -N		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	10	0.24	95	75 h	[479]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Rh/N-CBs		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	20	0.20	—	~ 3 h	[480]
Ni ₂ P/Zn-Ni-P		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	400	0.532	—	—	[481]
CoSe ₂		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	10	0.164	98.3	14 h	[409]
Ru-Cu ₂ O/CF		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	10	0.0174	—	18 h at 0.03 V	[482]
NiCo-MoNi ₄ HMNAs/NF		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	250	0.63	100	10 h at 20 mA·cm ⁻²	[483]
PWCo ₃ N NWA/NF		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	10	0.028	96	10 h at 30 mA·cm ⁻²	[484]
Rh/RhO _x NSs		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.279	—	65 h	[485]
D-MoP/rGO		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.74	100	12	[486]
Mo-Ni ₃ N/Ni/NF		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	300	0.423	100	10 h at 50 mA·cm ⁻²	[487]
Cu ₃ P/CF		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.72	—	3 h at 10 mA·cm ⁻²	[488]
Ni ₂ P/NF		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	500	1.0	100	10 h at 100 mA·cm ⁻²	[408]
PW-Co ₃ N NWA/NF		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	200	0.607	96	10 h at 30 mA·cm ⁻²	[484]
RhIr MNs		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.604	—	—	[489]
Ru-FeP ₄ /IF		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	1000	0.90	100	80 h at 100 mA·cm ⁻²	[490]
Ni(Cu)/NF		H ₂ + N ₂	1 M KOH + 0.5 M N ₂ H ₄	100	0.41	100	10 h	[491]
Fe-doped CoS ₂ nanosheets		H ₂ + N ₂	1 M KOH + 0.1 M N ₂ H ₄	500	0.95	98	20 h	[492]
3D PF-NiCoP/NF nanoarrays		H ₂	1 M KOH + seawater	10	0.287	96.5	20 h	[493]
Ni ₃ S ₂ /Co ₃ S ₄	HER + seawater electrolysis	H ₂	1 M KOH + seawater	100	1.73	100	100 h at 800 mA·cm ⁻²	[494]
S-(Ni,Fe)OOH		H ₂	1 M KOH + seawater	800	2.08	100		
Co-Se		H ₂	1 M KOH + seawater	100	1.661	100	100 h	[495]
N-CoO _x		H ₂ + formic acid	1 M KOH + 0.1 M glycerol	10.3	1.8	—	12 h	[496]
Ni-Mo-N/CFC		H ₂ + formate	1 M KOH + 0.1 M glycerol	10	1.59	100	15 h	[497]
Au/Ni(OH) ₂		H ₂ + lactic acid	3 M KOH + 1 M glycerol	10	1.36	99.7	12 h	[498]
NiCo hydroxide		H ₂ + formic acid	3 M KOH + 1 M glycerol	217	1.40	47	—	[499]
CNs@CoPt		H ₂ + formate	1 M KOH + 0.1 M glycerol	100	1.35	100	90 h	[500]
MnO ₂ /CP	HER + glycerol oxidation reaction	H ₂ + formate	1 M KOH + 10 mM glycerol	100	1.71	97	70 h	[501]
MoO _x /Pt		H ₂ + formate	5 mM H ₂ SO ₄ + 0.2 M glycerol	10	1.38	100	865 h	[502]
NiVRu-LDHs NAs/NF		H ₂ + glycerate	1 M KOH + 0.1 M glycerol	10	0.70	100	—	[503]
HEA-CoNiCuMnMo		H ₂ + formic acid	1 M KOH + 0.1 M glycerol	100	1.62	96	50 h at 50 mA·cm ⁻²	[504]
Ni ₃ N/Co ₃ N-NWs		H ₂ + formate	1 M KOH + 0.1 M glycerol	10	0.55	100	12 days at 50 mA·cm ⁻²	[505]
Ni-phen-NO ₂		H ₂ + formate	1 M KOH + 0.1 M glycerol	50	1.47	100	200 h at 1 A·cm ⁻²	[506]
VP-Ni ₂ P-Pt/CC		H ₂ + formate and Oxalate	2 M KOH + 0.1 M glycerol	20	1.675	100	—	[507]
MoNi ₄ /Fe ₂ O ₃ /NiO	HER + Methanol oxidation reaction	H ₂ + formic acid	1 M KOH + 2 M methanol	50	1.10	100	6 h	[508]
CNFs@NiSe/CC		H ₂ + formate	1 M KOH + 1 M methanol	10	1.381	100	15 h	[509]
NiCu@Cu		H ₂ + formate	1 M KOH + 1 M methanol	100	1.43	97.90	20 h	[510]
		H ₂ + formate	1 M KOH + 2 M methanol	10	1.45	96.50	16 h at 50 mA·cm ⁻²	[511]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Mo-Co ₄ N		H ₂ + formate	1 M KOH + 3 M methanol	10	1.427	100	60 h	[512]
NiS ₂ /CFC		H ₂ + acetone	1 M KOH + 0.45 M 2-propanol	20	1.41	100	13 h	[513]
NiSe/MoSe ₂ /CC		H ₂ + formate	1 M KOH + 1 M methanol	10	1.50	—	24 h	[514]
Co(OH) ₂ @HOS/CP		H ₂ + formate	1 M KOH + 3 M methanol	10	1.497	100	20 h	[515]
Ni _{0.33} Co _{0.67} (OH) ₂ /NF		H ₂ + formate	1 M KOH + 0.5 M methanol	100	1.75	100	20 h	[516]
NiIr-MOF/NF		H ₂ + formate	1 M KOH + 4 M methanol	10	1.39	100	20 h	[517]
Ni ₂ Co ₁ Cu LDH/NF 0.008		H ₂ + formate	1 M KOH + 0.5 M methanol	10	1.47	94	24 h	[518]
PdRh bimetallic		H ₂ + formate	1 M KOH + 1 M methanol	10	0.657	99	20 h	[519]
Pt-CoSe/NC		H ₂ + CO ₂	0.5 M H ₂ SO ₄ + 1 M methanol	10	0.67	—	12 h	[520]
Co ₃ P@NiCo-LDH/NF		H ₂ + formate	1 M KOH + 0.5 M methanol	10	1.43	100	20 h	[521]
NiMn		H ₂ + formate	1 M KOH + 3 M methanol	100	1.43	100	20 h	[522]
Ni ₅₀ Co ₁₅ Fe ₃₀ Cu ₅ MEAAs		H ₂ + formate	1 M KOH + 1 M methanol	10	1.476	—	7 h	[523]
Cu ₂ O-Cu@Ni ₂ P/NF		H ₂ + formate	1 M KOH + 1 M methanol	10	1.40	—	25 h	[524]
Au@PdRu RNs		H ₂ + carbonate	1 M KOH + 1 M methanol	10	0.88	—	20 h	[525]
mPtRh NSs		H ₂ + formate	3 M KOH + 1 M methanol	10	0.51	—	20 h	[526]
CC@NiCo ₂ S ₄		H ₂ + formate	1 M KOH + 1 M methanol	100	1.81	100	12 h	[527]
Ru&Fe-WO		H ₂ + formate	1 M KOH + 3 M methanol	500	1.62	100	36 h	[528]
NiFe ₂ O ₄ /NF		H ₂ + formate	1 M KOH + 0.5 M methanol + seawater	100	1.74	96	6 h at 700 mA·cm ⁻²	[529]
NiFe _x P@NiCo-LDH/CC		H ₂ + formate	1 M KOH + 0.5 M methanol	50	1.42	100	10 h	[530]
Pt-CoTe/NC		H ₂ + CO ₂	0.5 M H ₂ SO ₄ + 1 M methanol	10	0.68	—	18 h	[531]
NiCo		H ₂ + formate	1 M KOH + 2 M methanol	20	1.47	98	15 h	[532]
Co-Rh ₂		H ₂ + formate	1 M KOH + 1 M methanol	10	1.545	—	10 h	[533]
Pd/TNTA-web		H ₂ + sodium acetate	2 M KOH + 2 M ethanol	1000	0.69	—	—	[176]
PtIr NWs		H ₂ + 1,1-diethoxyethane	0.5 M H ₂ SO ₄ ethanol	10	0.61	94	—	[534]
Anode = LC-Ni(OH) ₂ ·xH ₂ O and cathode = Ni ₄ Mo-MoO ₂		H ₂ + formate	6 M KOH + 3 M ethanol	> 500	2.0	90	50 h	[535]
SA In-Pt NWs/C		H ₂ + HAc	1 M KOH + 0.5 M ethanol	10	0.62	100	5 h	[536]
Co(OH) ₂ @Ni(OH)		H ₂ + HAc	1 M KOH + 1 M ethanol	100	1.464	97.9	100 h at 50 mA·cm ⁻²	[537]
CoS ₂ -MoS ₂ //CoNi-PHNS	HER + EOR	H ₂ + acetate	1 M KOH + 1 M ethanol	50	1.80	90.50	2 h	[538]
F-modified β-FeOOH		H ₂ + acetate	15:5 volume ratio of ethanol to water	10	1.43	91.66	—	[539]
Cu ₁ Ni ₂ -N//Cu ₁ Ni ₂ -S/G		H ₂ + ethyl acetate	1 M KOH + 1 M ethanol	10	1.495	96	44 h	[540]
Co ₃ O ₄ nanosheets/CP for anode and Ni-Mo nanopowders/NF for cathode		H ₂ + ethyl acetate	1 M KOH + 1 M ethanol	10	1.5	98	10 h	[541]
PtCu NF/C		H ₂ + HAc	1 M KOH + 0.5 M ethanol	10	0.58	92	—	[542]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Pt-NCs	HER + ammonia electrolysis	H ₂ + N ₂	1 M KOH + 0.1 M NH ₄ OH	5	0.68	—	5 h	[543]
Pt ₆ Ru-NCs		H ₂ + N ₂	0.1 M KOH + 0.1 M NH ₃	10	0.72	—	20 h	[544]
N-NiZnCu LDH/rGO		H ₂ + N ₂	1 M KOH + 0.3 M NH ₄ Cl	100	0.964	—	40 h	[447]
NiCo-NiCoP@PCT/CC	HER + others electrolysis	H ₂ + CO ₂	1 M KOH + 14 mg·mL ⁻¹ HCHO	50	1.76	—	10 h	[545]
NF//Au/CoOOH		H ₂ + benzoic acid	3 M KOH + 0.2 M BA	4.8 A	2	99.9	24 h at > 250 mA·cm ⁻²	[546]
NC@CuCo ₂ N _x /CF		H ₂ + benzaldehyde	1 M KOH + 0.015 M BA	10	1.55	97.4	60 h	[386]
Rh/RhOOH metallene		H ₂ + glycolate and carbonate	1 M KOH + 6 M EG	10	0.678	99	20 h	[547]
PtO ₂ /h-Ni(OH) ₂ /Ni(OH) ₂		H ₂ + benzoic acid	1 M KOH + 40 mM BA	10	1.48	192.9	—	[548]
Anode = Cu _x O/CF and cathode = h-Ru-Cu _x O/CF		H ₂ + formic acid	1 M KOH + 0.5 M EG	10	1.25	90	25 h	[549]
ys-ZIF@CoFe-LDH NCs		H ₂ + formic acid	1 M KOH + 0.5 M EG	50	1.47	91	16 h	[550]
hp-Ni		H ₂ + benzoic acid	1 M KOH + 10 mM BA	10	1.50	100	18 h	[551]
Anode = PdAg/NF and cathode = Pt plate		H ₂ + glycolic acid	1 M KOH + 1 M EG	20	1.02	100	20 h	[552]
Ni ₂ P/NF		H ₂ + genzoic acid	1 M KOH + 50 mM BA	10	1.45	96	500 h	[553]
Anode = Au/Ni(OH) ₂ and cathode = Ni foam		H ₂ + glycolic acid	3 M KOH + 1 M EG	157	1.4	96	10 h	[499]
PtRh _{0.02} @Rh NWs		H ₂ + glycolic acid	1 M KOH + 1 M EG	10	0.66	90	50 h	[398]
A-Ni-Co-H/NF		H ₂ + benzoic acid	1 M KOH + 0.1 M BA	20	1.30	90	—	[554]
CC@NiO/Ni ₃ S ₂		H ₂ + benzoic acid	1 M KOH + 0.2 M BA	50	1.806	94	—	[555]
Pt/C//Fe ₂ P/SSM		—	1 M KOH + 0.5 M glucose	10	1.22	100	24 h	[556]
Mo-Ni alloy		H ₂ + benzoic acid	1 M KOH + 10 mM BA	20	1.40	100	10 h	[395]
α-MoO ₃		H ₂ + CO ₂	1 M KOH + 14 mg·mL ⁻¹ methylene blue (MB)	20	1.557	—	2 h at 40 mA·cm ⁻²	[557]
Pt-Co ₃ O ₄		H ₂ + 2-furoic acid	1 M KOH + 50 mM BA	10	1.83	66.1	—	[558]
Ru@Ni-B/NF		H ₂ + glucaric acid	1 M KOH + 0.1 M glucose	50	1.36	—	24 h	[559]
Co@NPC		H ₂ + lactic acid	1 M KOH + 0.1 M glucose	10	1.56	98.9	15 h	[560]
Co _{0.5} Ni _{0.5} /CC		H ₂ + gluconic acid/gluconolactone	1 M KOH + 0.1 M glucose	50	1.52	94.6	32 h at 10 mA·cm ⁻²	[561]
Ni ₂ P/Ni/NF		H ₂ + 2-furoic acid	1 M KOH + 30 mM BA	10	1.48	100	—	[562]
Ni-SVs SBs/CoP/CoSe ₂		H ₂ + butyronitrile	1 M KOH + 20 mM butylamine	10	1.37	98.9	4 h	[563]
Ni ₃ N/Ni//Cu ₃ Ag ₇ /CF		H ₂ + formate	1 M KOH + 0.6 M HCHO	500	0.60	100	8 h	[564]
Co@CoO-1/rGO		H ₂ + lactic acid and formic acid	1 M KOH + 0.1 M glucose	10	1.34	98	80 h at 100 mA·cm ⁻²	[565]
VR-Ni(OH) ₂ /CoS ₂ -MoS ₂		H ₂ + propionitrile	1 M KOH + 10 mmol propylamine	10	1.48	96.5	—	[301]
CNTs@Co/CoP		H ₂ + glucaric acid and gluconic acid	1 M KOH + 0.5 M glucose	10	1.42	—	50 h	[566]
NiFeN _x /NiFeO _x		H ₂ + glucaric acid	1 M KOH + 0.5 M glucose	100	1.39	87	24 h	[567]
Fe _{0.1} -CoSe ₂ /CC		H ₂ + gluconate	1 M KOH + 0.5 M glucose and 0.5 M H ₂ SO ₄	10	0.72	86.7	20 h	[568]
Fe ₃ O ₄ /Au/CoFe-LDH		H ₂ + gluconate	1 M KOH + 0.5 M glucose and 0.5 M H ₂ SO ₄	10	0.48	100	2 h at 300 mA·cm ⁻²	[569]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Pt/C//metallic Cu		H ₂ + 2-furoic acid	1 M KOH + 0.1 M HMF 1 M KOH + 0.2 M furfural	100	0.27 0.31	200	—	[570]
Cu _x S@NiCo-LDH		—	1 M KOH + 10 mM HMF	10	1.34	100	20 h	[571]
Anode = Pd/NF and cathode = NF		H ₂ + terephthalate and carbonate	10 M KOH + 0.5 g PET hydrolysate	100	1.01	98	20 h	[572]
Anode = Cu foam and cathode = CC@MoSe ₂ /Ru		H ₂ + 5,5'-azotetrazolate	1 M KOH + 0.20 M 5-amino-1H-tetrazole	10	1.34	98.9	100 h	[573]
Fe-CoP/CC		H ₂	50 mL KOH + 5 mL aloe extract	50	1.62	100	15 h at 40 mA·cm ⁻²	[574]
Co-Ni ₂ P/NF		H ₂ + formate	1 M KOH + 5 g·L ⁻¹ PET hydrolysate	10	1.43	85	10 h	[575]
Anode = hp-Ni/NF and cathode = Ni ₂ P/NF		H ₂ + potassium acetate	1 M KOH + chitin hydrolysate (N-acetylglucosamine)	535	3.6	90	24 h	[373]
OMS-Ni ₁ -CoP		H ₂ + formate	2 M KOH + 6.3 g PET hydrolysate	10	1.57	100	12 h	[576]
CoNi _{0.25} P/NF		H ₂ + formate	1 M KOH + PET hydrolysate (EG)	500	1.77	91.7	60 h	[577]
Ni ₃ N/W ₅ N ₄		H ₂ + formate	1 M KOH + seawater + 2 g PET	50	1.47	100	300 h at 200 mA·cm ⁻²	[578]
CoNi _{0.2} P-uNS/NF		H ₂ + formate	1 M KOH + 0.3 g·L ⁻¹ PET hydrolysate	50	1.24	92	10 h	[579]
Ni ₂ P		H ₂ + dihydroisoquinolines	1 M KOH + 0.5 mmol tetrahydroisoquinolines	20	1.49	100	—	[580]
Co ₂ P ₄ O ₁₂ /NF		H ₂ + benzonitrile	1 M KOH + 1 mmol benzylamine	100	1.472	100	27 h	[581]
Ni ₂ P-UNMs/NF		H ₂ + benzonitrile	1 M KOH + 0.125 M benzylamine	20	1.41	100	20 h	[302]
Anode = NiSe and cathode = CoP		H ₂ + benzonitrile	1 M KOH + 1 mmol benzylamine	20	1.49	100	16 h	[300]
Anode = Ni ₃ N and cathode = Ni-Ni ₃ N		H ₂ + benzonitrile	1 M KOH + 2 mmol benzylamine	50	1.61	95	36 h at 150 mA·cm ⁻²	[582]
E-CoAl-LDH-NSA		H ₂ + FDCA	1 M KOH + 10 mM HMF	50	1.74	100	—	[583]
Ni ₃ N-V ₂ O ₃		H ₂ + FDCA	1 M KOH + 10 mM HMF	10	1.40	100	12 h	[584]
MoO ₂ -FeP@C		H ₂ + FDCA	1 M KOH + 10 mM HMF	10	1.486	100	24 h	[585]
NiCoN ₈₈ /Cu _{NW5}		H ₂ + FDCA	1 M KOH + 10 mM HMF	10	1.44	—	20 h	[586]
CoP-CoOOH		H ₂ + FDCA	1 M KOH + 150 mM HMF	100	1.14	98.2	55 h	[587]
Ni ₃ N@C		H ₂ + FDCA	1 M KOH + 10 mM HMF	50	1.55	99	15 h	[588]
Ni ₃ S ₂ -MoS ₂ /NF		H ₂ + FDCA	1 M KOH + 10 mM HMF	10	1.44	99	24 h	[589]
Ni ₂ P NPA/NF		H ₂ + FDCA	1 M KOH + 10 mM HMF	50	1.58	100	12 h	[70]
NF@Mo-Ni _{0.85} Se		H ₂ + FDCA	1 M KOH + 10 mM HMF	50	1.50	100	12 h	[590]
Ni ₃ S ₂ /NF		H ₂ + FDCA	1 M KOH + 10 mM HMF	100	1.64	100	18 h	[181]
Co-Ni ₃ S ₂		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S	100	0.95	96.7	24 h at 50 mA·cm ⁻²	[591]
Cu ₂ S/NF		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S	100	0.64	97	140 h at 10 mA·cm ⁻²	[592]
WS ₂ NSs		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S	10	1.17	99.22	192 h	[593]
NiSe/NF		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S	106	1	99.9	500 h at 30 mA·cm ⁻²	[594]
Anode = IF and cathode = Fe@N-CNT/IF		Flocculent precipitate	0.5 M Na ₂ SO ₄	20	1.09	—	12 h	[595]

(Continued)

Hybrid water splitting								
Catalyst	Decoupling mechanism	Value added products	Electrolyte	Current density (mA·cm ⁻² vs. RHE)	Cell voltage (V)	Faradaic efficiency (%)	Stability (cycle or h)	References
Co ₃ S ₄		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S and 1 M NaOH + 0.5 M NaCl	100	0.496	95	100 h	[596]
CuCoS/CC		H ₂ + sulfur powder	1 M KOH + 4 M Na ₂ S	100	0.75	100	144 h	[597]
CoS ₂ @C/MXene/NF		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S and 1 M NaOH + seawater	300	0.97	96	240 h at 300 mA·cm ⁻²	[598]
CoP NA/TM		H ₂ + sulfur powder	1 M NaOH + 50 mM Na ₂ S	15	1.49	100	10 h at 20 mA·cm ⁻²	[599]
Anode = NiS ₂ and cathode = v-NiS ₂		H ₂ + sulfur powder	0.1 M NaOH + 0.05 M Na ₂ S	20	0.65	96.5	100 h	[600]
Anode = Ni-Co-S/NF and cathode = Pt-C/CP		H ₂ + sulfur powder	1 M NaOH + 1 M Na ₂ S	100	0.531	97–98	40 h	[601]
Anode = NiFe@ACF and cathode = Ni-Mo@ACF		H ₂	1 M KOH	10	1.6	—	36 h	[602]

expenses. Beyond the apparent costs of raw materials, catalysts, and equipment (visible consumption), critical but frequently overlooked factors include energy inputs, product/pollutant treatment, and electrolyte maintenance (invisible consumption). A holistic approach combining moderate operational conditions, aqueous electrolytes, and techno-economic analysis will bridge the gap between laboratory-scale breakthroughs and scalable, sustainable hydrogen production.

6.1 Current limitations

Decoupled water-splitting systems, while promising for flexible and safe hydrogen production, face several technical and operational challenges. The performance of redox mediators is often limited by their stability across redox states, diffusivity, and undesired reactivity with electrodes. Many mediators and catalysts have been characterized only over short-term cycles, leaving long-term durability, turnover numbers, and degradation pathways largely unexplored. Device complexity further constrains commercialization, as DWS often requires auxiliary components, such as pumps, flow manifolds, and catalyst beds, increasing the balance-of-plant burden. Membranes and separators in conventional systems are susceptible to thinning, gas crossover, and reactive oxygen species formation, leading to efficiency losses and potential safety hazards. Efficiency of decoupled electrolysis is generally lower than that of conventional water splitting, partly due to voltage drops at high current densities, limitations of electrode gaps, and slow kinetics of non-spontaneous reactions. Integration with renewable energy is complicated by intermittency, while pressurization and storage of hydrogen remain energy-intensive. Finally, cost analyses indicate that current DWS setups often require higher capital investment due to additional cells or mediators, despite potential electricity cost reductions.

6.2 Potential solutions

Strategies to overcome these limitations focus on improving materials, system design, and operational flexibility. Tailored redox mediators with optimized redox potentials, stability, and diffusivity could enhance reaction kinetics and system reliability. Electrocatalysts with high surface area or earth-abundant

compositions can reduce reliance on precious metals and improve hydrogen evolution rates. Modular configurations, such as battery–electrolyzer hybrids and advanced decoupled architectures, allow separation of half-reactions, pressurized hydrogen generation without membranes, and integration with intermittent solar or wind energy. Catalyst beds can minimize bubble-induced losses, while mediators can serve as safe hydrogen carriers, facilitating centralized production and transport. Membrane-free designs or replacement with low-cost, high-performance membranes could enhance system longevity and safety. Further, pairing hydrogen evolution with alternative high-value oxidation reactions instead of oxygen evolution may improve economic feasibility. Continued research on long-term stability, degradation analysis, and techno-economic optimization is essential for scaling DWS technologies from laboratory demonstrations to commercially viable hydrogen production systems.

7 Conclusion and future outlook

This review has highlighted recent achievements in innovative decoupled water splitting. The hydrogen economy is a promising energy storage and conversion system, where researchers are interested in producing H₂ for carbon neutrality. We can foresee various future developments based on current research trends in decoupled water splitting. DWS provides several benefits compared to traditional water electrolysis. First and most importantly, it allows for the spatial and/or temporal isolation of the H₂ and O₂ evolution processes. In conventional systems like PEM, AEM, alkaline, and solid oxide electrolyzers, H₂ and O₂ are often generated simultaneously in the same cell, necessitating a membrane or separator to prevent the gases from mixing and recombining with water. The production of H₂ and O₂ through DWS reduces these issues. DWS also allows solar and wind power to safely generate hydrogen from water. Various mediators, separators, light absorbers, catalysts, engineering optimizations, and electrochemical environments have been introduced in the last few decades.

An ideal redox mediator would have a negligible difference between its oxidation and reduction potentials. In industrial

electrolyzers, high current densities of 1 or 2 A·cm⁻² are needed for anodic and cathodic reactions, but the vast majority of reported electrocatalysts have either been examined at current densities below 100 mA·cm⁻² or are unable to supply such quantities. In both OER/HER, the design of effective catalysts plays a crucial role in reducing the overpotential and increasing the energy efficiencies necessary to make industrial water splitting a reality. The synthetic cost of redox mediators needs to be reduced to make large-scale DWS economically viable. Solubility, stability, and high electron transfer kinetics are crucial properties of effective redox mediators. For instance, a redox flow battery with certain modifications may be integrated with decoupled water splitting to produce hydrogen gas for chemical fuel or to store an electrical charge for later use. Some significant obstacles must be overcome before DWS can reach its full potential, i.e., overall system stability and device complexity. While linked techniques are often easier, DWS systems typically need a more complicated balance of plant infrastructure.

Decoupling agents in solution are often more viscous than water, which results in the need for supplementary pumps and flow systems. The commercial use of PEM electrolyzers may reach pressures of up to 30 bar, while alkaline electrolyzers typically operate at up to 10 bar pressures. Hydrogen is usually stored in tanks at 350 or 700 bar pressure. Yet when the pressure rises, the hydrogen and oxygen bubbles shrink, making them more soluble in the solution and allowing them to pass through the barrier. Overpotential losses over the mediated redox processes are sensitive to various factors, including current density, mediator chemical composition, electrode construction, temperature, and electrolyte concentration. Therefore, the system and the redox mediator might be adjusted to reduce these losses.

Recently, several new redox mediators have been developed for DWS in acidic, basic, or neutral electrolytes. The flowing nature of soluble redox mediators gives them the benefit of adaptable redox capacity. To create high-efficiency DWS systems, soluble redox mediators should have good reversibility, solubility, and low molecular weight. Transportation of charged liquid or solid mediators is a common need of decoupled splitting systems, which adds system complexity and expense. Solution-phase mediators offer the convenience of easy movement between cells or reactors. However, decoupled systems based on soluble redox mediators still need a membrane to block redox shuttling. At room temperature, the optimal range for the redox potential of the mediator is between 0 and 1.23 V vs. RHE. In addition, solid-state redox mediators allow membrane-free operation, which simplifies the electrolyzer design and sealing, necessitates less maintenance, and might reduce material and construction costs. Many solid-state redox mediators have slow redox reactions because ion diffusion in the crystalline framework slows the electrolysis rate. Given these issues, significant work is needed to boost DWS efficiency. There has been a lot of research into finding solid-state redox mediators that use electrode materials with high reversibility and kinetics. To maximize the benefits of hybrid water electrolysis, it is important to achieve high selectivity for desirable products from carefully chosen organic oxidations and plan accordingly for their future separation and purification. As organic electrocatalysis and electrosynthesis are on the cusp of a revival, we expect to see a rise in incorporating several potential organic oxidation processes. Recent research shows that a DWS technique may be used for additional organic transformations outside water splitting, suggesting its extensive relevance in many sectors. Organic materials are seen as a promising contender that may fulfill high

reversibility, high capacity, and low cost because of their chemical diversity and metal-free nature, which provides considerable design freedom of molecule and crystal structure, whether soluble or solid-state redox mediators. It is more economically advantageous to replace the OER process with the high-value O₂ process rather than the low-value HER process since O₂ can be created from liquid air at a minimal cost.

To that end, we are publishing this review to inspire researchers to put more time and effort toward creating cutting-edge electrocatalysts and designing cutting-edge techniques for H₂ generation and, more critically, organic upgrading under benign settings. The future of DWS is bright because of the quick growth and enormous inventiveness already shown in the sector. After more than two centuries of research on conventional water electrolysis, decoupled water electrolysis promises high efficiency, durability, low cost, and high-pressure hydrogen production from renewable sources. Further investigation is required to find more redox mediators, evaluate their performance and stability, and bring this exciting new industry to fruition so that the promise of DWS for hydrogen production at commercial scales can be fully realized. The development of redox mediators allows for various electrolyzer designs, increasing the efficiency of water electrolysis with other electrochemical processes, such as battery charging, fuel cell battery charging, and electrosynthesis. There is a lot of room for progress in this area. Furthermore, practical implementation of such systems can benefit greatly from studies that quantify their long-term performance, whether through deeper investigation of degradation routes or thorough study of failure. It is hoped that many of the difficulties associated with DWS that are alluded to here will be resolved by the community through the creative experimentation that we believe we have shown in this field in recent years. This applies to both solution-phase and solid-state mediators.

Figure 53 depicts the concept of DWS for green hydrogen production, stressing its progression from laboratory to industrial scales. Key breakthroughs in the laboratory include the design of effective catalysts, the improvement of reaction kinetics, the achievement of stable redox reactions, and the investigation of processes within a close-packed and flexible structural configuration. Molecular and solid-state redox mediators with hybrid water splitting techniques can be utilized to generate hydrogen. As technology develops into industrial applications, the focus shifts to guaranteeing system compatibility and integrity, optimizing cell topologies, scaling up the process, assessing practical feasibility, and reducing environmental concerns. The ultimate goal of these advances is to lower the cost of producing green hydrogen, allowing it to be used in a range of applications, such as electric vehicles, aerospace, and storage systems.

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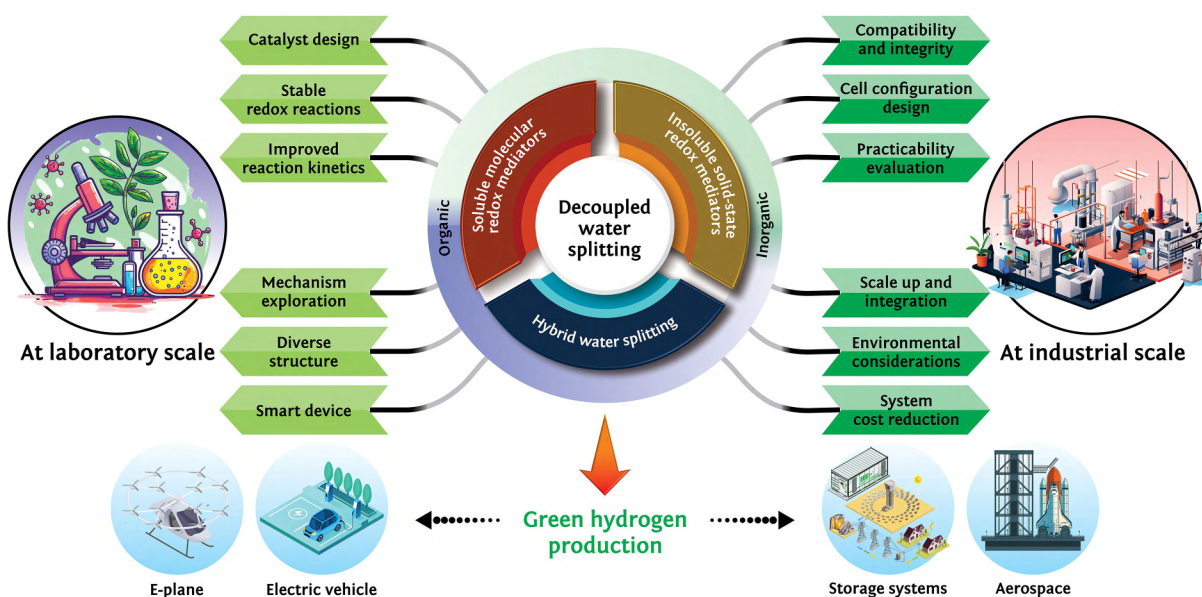


Figure 53 A roadmap to future developments for green hydrogen generation through decoupled water splitting.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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