

pH-asymmetric bipolar membrane electrolyzer for stable seawater electrolysis toward hydrogen production

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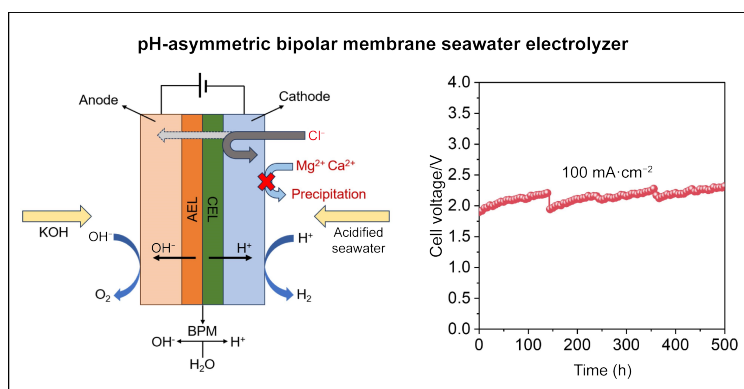


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ABSTRACT: Seawater electrolysis offers a promising route to low-cost, large-scale green hydrogen production without competing for precious freshwater resources. However, it faces two major challenges: the chlorine evolution reaction (CER) at the anode and $\text{Mg}^{2+}/\text{Ca}^{2+}$ precipitation at the cathode. To address these challenges, this work constructs a pH-asymmetric seawater electrolyzer based on a bipolar membrane (BPM), feeding acidified seawater to the cathode and alkaline freshwater to the anode: acidification prevents $\text{Mg}^{2+}/\text{Ca}^{2+}$ precipitation at the cathode, while the BPM blocks chloride ions and thereby prevents CER at the anode. Isotope labeling experiments confirm that the water molecules dissociated within the BPM originate mainly from the cathodic seawater; moreover, the electrolyzer remains stable even when the cathode is fed with saturated seawater. By optimizing the electrolyte concentration and electrode types, this seawater electrolyzer achieves continuous, stable operation for 500 h at a current density of $100 \text{ mA}\cdot\text{cm}^{-2}$, with a voltage rise rate of only $1.76 \text{ mV}\cdot\text{h}^{-1}$, no cathodic scaling, and no anodic chlorine evolution. This work offers valuable insight into advancing seawater electrolysis for hydrogen production.

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KEYWORDS: bipolar membrane, seawater electrolysis, anti-scaling, chlorine evolution free



1 Introduction

Hydrogen, as a clean energy carrier with high energy density, is a cornerstone of a future green, low-carbon energy system¹. However, industrial hydrogen production still relies heavily on fossil fuel reforming, which generates substantial CO_2 emissions². As the cost of renewable electricity (e.g., wind and solar) has continued to decline in recent years, water electrolysis for hydrogen production has attracted increasing attention³. Traditional water electrolysis technologies, however, demand high water quality, which raises hydrogen production costs and consumes precious freshwater resources^{4–5}. Given that seawater resources on Earth far exceed those of freshwater, developing seawater electrolysis technology is of great strategic and practical importance for the large-scale application of water electrolysis for hydrogen production^{6–8}.

The complex composition of natural seawater (impurity ions such as Mg^{2+} and Ca^{2+}) and its high salinity (Cl^- concentration up to $0.5 \text{ mol}\cdot\text{L}^{-1}$) pose great challenges to the operational lifetime and energy conversion efficiency of seawater electrolysis systems^{9–12}. At the anode, the oxygen evolution reaction (OER) faces competition and interference from the chlorine evolution reaction (CER, $\text{Cl}^- + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$), which not only reduces product selectivity but also generates active chlorine that severely corrodes the catalyst and electrolyzer components. At the cathode, H^+ consumption during the hydrogen evolution reaction (HER) causes the local interfacial environment to become alkaline. This readily induces the precipitation of insoluble $\text{Mg}^{2+}/\text{Ca}^{2+}$ hydroxides or carbonates, which then block the active sites and flow channels.

Current research on seawater hydrogen production mainly focuses on anion exchange membrane seawater electrolyzers (AEMSW) and proton exchange membrane seawater electrolyzers (PEMSWE)⁹. AEMSW offers the advantage of using non-noble metal catalysts, but it usually requires seawater alkalization, a process that continuously consumes alkali and increases hydrogen production cost¹³. The acidic environment in PEMSWE increases the risk of CER at the anode, which still relies heavily on expensive noble metal Ir/Ru catalysts^{5, 14–15}. In contrast, the bipolar membrane electrolyzer (BPMWE) shows unique advantages for

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seawater electrolysis^{16–17}. A bipolar membrane (BPM) comprises an anion exchange layer (AEL) and a cation exchange layer (CEL); under reverse bias voltage, water molecules split into H^+ and OH^- at the AEL–CEL interface, and H^+ and OH^- are then transported to the cathode and anode, respectively. A BPM thus allows different pH environments to be coupled on its two sides. During seawater electrolysis, seawater is fed to the cathode side, where the Donnan exclusion effect of the CEL effectively blocks Cl^- permeation into the anode compartment. The anode side thus provides an alkaline reaction environment that enables the use of non-noble metal catalysts and enhances OER activity.

The BPM and electrodes are the key components determining BPMWE performance. Strategies such as tuning AEL/CEL layer thickness and optimizing the water-dissociation catalyst can increase the rate of water-dissociation in the BPM, reduce the water dissociation voltage loss, and raise BPMWE current density^{18–21}. However, when seawater is fed to the cathode, because the water-dissociation efficiency of the BPM is difficult to reach 100%²², the local alkalinity at the cathode increases, inducing $\text{Mg}^{2+}/\text{Ca}^{2+}$ precipitation²³. Furthermore, electrode type strongly influences the voltage and stability of the electrolyzer, yet systematic studies of how electrodes affect the performance of BPM seawater electrolyzers (BPMSWE) remain insufficient. Overall, reported BPMSWEs generally show low current densities (e.g., below $20 \text{ mA}\cdot\text{cm}^{-2}$) or poor stability (e.g., voltage rise rates above $10 \text{ mV}\cdot\text{h}^{-1}$), indicating substantial room for improvement^{13,18,20,23–25}.

To address these limitations, this work constructs a pH-asymmetric BPMSWE in which acidified seawater is fed to the cathode and alkaline freshwater to the anode. Acidification prevents $\text{Mg}^{2+}/\text{Ca}^{2+}$ precipitation at the cathode, while the BPM blocks chloride ions and thereby prevents CER at the anode. Isotope labeling experiments confirm that the water molecules dissociated in the BPM originate mainly from the cathodic seawater. By optimizing the electrolyte concentration and electrode types, this BPMSWE achieves continuous, stable operation for 500 h at a current density of $100 \text{ mA}\cdot\text{cm}^{-2}$, with a voltage rise rate of only $1.76 \text{ mV}\cdot\text{h}^{-1}$, no cathodic scaling, and no anodic chlorine evolution.

2 Experimental section

2.1 Preparation of Ni–Fe anode

This work prepared a Ni–Fe compound electrode, designated HN–NiFe/nickel foam (NF), following a heterogeneous nucleation method reported in the literature²⁶. Briefly, NF (1 mm thick) was cut into $1 \text{ cm} \times 3 \text{ cm}$ pieces and sequentially ultrasonicated in $0.5 \text{ M H}_2\text{SO}_4$ and absolute ethanol for 5 min each to remove the oxide layer and oil contamination from the NF surface, then dried naturally on filter paper at room temperature. Separately, $3.5602 \text{ g Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 60 mL isopropanol, and $0.4875 \text{ g FeSO}_4\cdot 7\text{H}_2\text{O}$ was dissolved in 20 mL ultrapure water; the two solutions were then combined and stirred thoroughly with a magnetic stirrer at 1200 rpm for 10 min. The pretreated NF was immersed in this mixture and left to stand for 24 h at 30°C , after which it was removed, rinsed with deionized water, and dried in a vacuum oven at 25°C for 12 h.

A second Ni–Fe compound electrode, designated E–NiFe/NF, was prepared using an etching method. Briefly, NF was cut into $3 \text{ cm} \times 6 \text{ cm}$ pieces and sequentially ultrasonicated in $0.5 \text{ M H}_2\text{SO}_4$ and absolute ethanol for 5 min each, then dried on filter paper at

room temperature. $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (0.404 g) was dissolved in 100 mL deionized water, and the NF was immersed in this solution and allowed to react at 25°C for 3 h; it was then removed, rinsed repeatedly with deionized water, and dried overnight in a forced-air oven at 60°C .

2.2 Preparation of Pt/C@CP and Au/C@CP cathodes

Carbon paper (CP, TGP-H-060, Toray) was cut into $1 \text{ cm} \times 2 \text{ cm}$ pieces. Commercial Pt/C catalyst (4 mg , 20% Pt, HISPEC3000) was weighed and combined with $400 \mu\text{L}$ absolute ethanol and $10 \mu\text{L}$ Nafion solution (5%, DuPont), followed by ultrasonication to prepare a catalyst ink. This ink was uniformly coated onto both sides of the carbon paper to obtain Pt/C@CP with a loading of $2 \text{ mg}\cdot\text{cm}^{-2}$. Pt/C@CP electrodes with loadings of 1 and $3 \text{ mg}\cdot\text{cm}^{-2}$ were prepared similarly. Au/C@CP was prepared in the same manner, except that Pt/C was replaced with Au/C (20% Au, Premetek), giving an Au/C loading of $2 \text{ mg}\cdot\text{cm}^{-2}$.

2.3 Characterization methods

The crystal structure of the electrodes was analyzed using an X-ray diffractometer (D8 Advance, Bruker), and the morphology and elemental distribution were examined using a scanning electron microscope (SU8600, Hitachi). Chloride ion concentration in the electrolyte was measured using ion chromatography (CIC-D100, Qingdao Shenghan Chromatography Technology Co., Ltd.), with an aqueous KOH eluent ($1.2 \text{ g}\cdot\text{L}^{-1}$) at a flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$; the column oven and conductivity cell were both maintained at 35°C , and the baseline was allowed to equilibrate for 40 min before testing. Cathodic and anodic products of the electrolyzer were analyzed using online mass spectrometry (GMA650, Suzhou Anyeep Precision Instruments Co., Ltd.) under a vacuum of no less than $1 \times 10^{-5} \text{ mbar}$, with ultrapure Ar ($10 \text{ mL}\cdot\text{min}^{-1}$) as the carrier gas and the injection-tube temperature set to 120°C . Hypochlorite ion concentration in the anolyte was measured using the o-tolidine method: the electrolyte was added to an o-tolidine solution, and the absorbance at 436 nm was measured using a UV–Vis spectrophotometer (UV-1800, Shimadzu).

2.4 Three-electrode system electrochemical testing

Three-electrode electrochemical tests were conducted in a single cell using an electrode clip holding the above-prepared electrode (active area, 1 cm^2) as the working electrode, a Pt mesh as the counter electrode, and a reversible hydrogen electrode (RHE) as the reference electrode. A CHI-760E electrochemical workstation was used to control the three-electrode system and to measure current and potential. The OER and HER activities of the electrodes were tested in 2 M KOH prepared with freshwater and $0.5 \text{ M H}_2\text{SO}_4$ prepared with seawater, respectively, both at 25°C . The seawater used in this work was collected from Huizhou, Guangdong Province, China ($22^\circ33'36''\text{N}$, $114^\circ52'48''\text{E}$) and had a Cl^- concentration of $1.98 \times 10^4 \text{ ppm}$. Linear sweep voltammetry (LSV) was performed at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$, and the measured potentials were iR -corrected, with the solution resistance R determined by electrochemical impedance spectroscopy (EIS).

2.5 Assembly and testing of BPMSWE

The BPMSWE mainly consisted of a cathode, an anode, gaskets, a BPM, and titanium end plates with serpentine flow fields (Supplementary Fig. S1). The cathode, anode, and BPM (CJ-BP-1, Zhongke Shenyang Membrane Technology Co., Ltd.) formed a

zero-gap sandwich structure with an active area of 1 cm^2 . The anolyte was KOH solution, and the catholyte was sulfuric acid-acidified seawater. As an extreme working condition, we also used saturated seawater as the catholyte, prepared by adding excess sea salt to $0.5\text{ M H}_2\text{SO}_4$ followed by stirring and standing overnight. The BPMSWE and electrolyte solutions were placed in a constant-temperature water bath, and the electrolytes were circulated using a peristaltic pump at a rotation speed of 40 rpm . Because the maximum stable operating temperature of the BPM used in this work is $40\text{ }^\circ\text{C}$, the water bath temperature was set to $42\text{ }^\circ\text{C}$, allowing the electrolyzer temperature to reach $40\text{ }^\circ\text{C}$. Constant current electrolysis was performed using an IT-6832A DC power supply (ITECH), and EIS spectra were measured at a constant current of $50\text{ mA}\cdot\text{cm}^{-2}$ using a CorrTest electrochemical workstation (CS2350M), over a frequency range of $10^5\text{--}0.01\text{ Hz}$.

3 Results and discussion

3.1 Optimization of electrolytes and electrodes

We first investigated the effect of the catholyte on BPMSWE performance (Fig. 1a), using commercial Pt/TM and Ir/TM as the cathode and anode, respectively, with the anolyte fixed at 2 M KOH and the current density set at $20\text{ mA}\cdot\text{cm}^{-2}$ (Figs. 1b and 1c). When the catholyte was $0.5\text{ M H}_2\text{SO}_4$ prepared with freshwater, the electrolyzer showed a voltage rise rate of $20.6\text{ mV}\cdot\text{h}^{-1}$ over 5 h . Replacing freshwater with seawater in the $0.5\text{ M H}_2\text{SO}_4$ catholyte did not increase this rate ($18.6\text{ mV}\cdot\text{h}^{-1}$), indicating that the complex components in seawater did not markedly affect the cathode reaction or the ion conduction performance of the BPM. However, reducing the H_2SO_4 concentration to 0.05 M markedly increased the electrolyzer voltage by more than 100 mV and raised the voltage

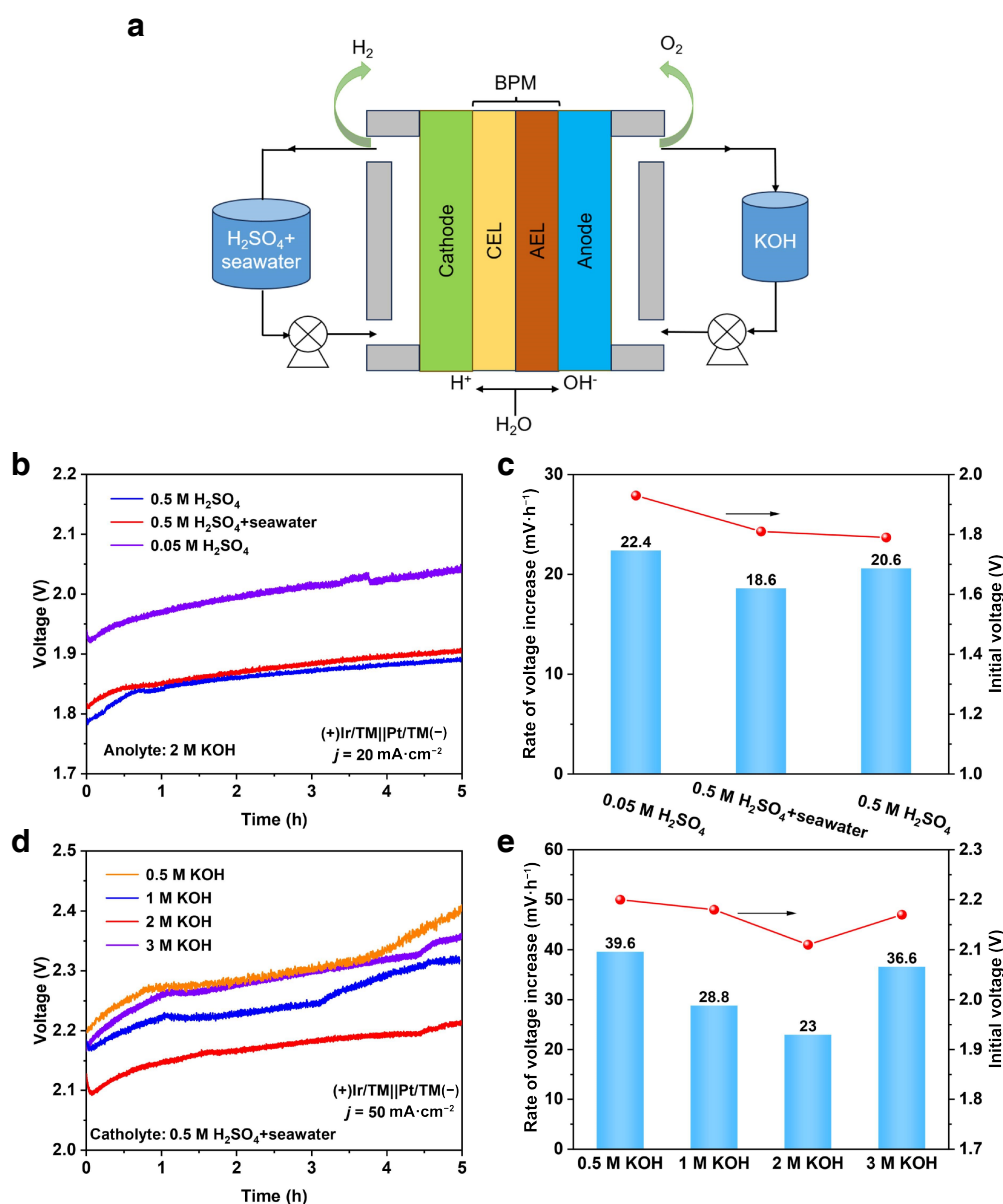


Fig. 1. Optimization of the electrolyte for BPMSWE. **a**, Schematic diagram of BPMSWE. **b**, V - t curves of BPMSWE with different catholytes at $20\text{ mA}\cdot\text{cm}^{-2}$. **c**, Initial voltage and voltage rise rates derived from (b). **d**, V - t curves of BPMSWE with different anolytes at $50\text{ mA}\cdot\text{cm}^{-2}$. **e**, Voltage rise rates derived from (d).

rise rate to $22.4 \text{ mV}\cdot\text{h}^{-1}$, indicating that cathodic acid concentration substantially affects the HER.

We next examined the effect of the anolyte on BPMSWE performance, fixing the catholyte at $0.5 \text{ M H}_2\text{SO}_4$ +seawater and the current density at $50 \text{ mA}\cdot\text{cm}^{-2}$ while varying the anolyte KOH concentration from 0.5 to 3 M (Figs. 1d and 1e). As the KOH concentration increased from 0.5 to 2 M , the initial electrolysis voltage of the BPMSWE gradually decreased from 2.191 to 2.125 V and the voltage rise rate decreased from 39.6 to $23 \text{ mV}\cdot\text{h}^{-1}$, indicating that higher alkali concentration improves BPMSWE performance, likely owing to lower ohmic resistance and enhanced anodic OER activity. However, further increasing the anolyte KOH concentration from 2 to 3 M did not further reduce the electrolysis voltage or voltage rise rate; instead, both increased, a performance regression that may be attributed to BPM interface swelling or reverse ion permeation induced by high-concentration alkaline

solutions. Accordingly, $0.5 \text{ M H}_2\text{SO}_4$ +seawater catholyte and 2 M KOH anolyte were selected as the electrolyte system for subsequent studies.

We next examined the effect of electrode type on BPMSWE performance. For anodes, the OER polarization curves of HN-NiFe/NF, E-NiFe/NF, NF, and Ir/TM (Supplementary Figs. S2–S4) in 2 M KOH are shown in Fig. 2a; based on overpotential and Tafel slope (Supplementary Fig. S5), the OER activity followed the order $\text{HN-NiFe/NF} > \text{E-NiFe/NF} > \text{NF} > \text{Ir/TM}$. These electrodes were assembled as anodes in BPMSWEs, and the corresponding voltage–time curves at a current density of $50 \text{ mA}\cdot\text{cm}^{-2}$ are shown in Fig. 2b. The initial electrolysis voltage of each electrolyzer followed the same order as the anodic OER activity, i.e., higher anode activity led to lower initial voltage; higher anode activity likewise resulted in a lower voltage rise rate, indicating better electrolyzer stability (Fig. 2c).

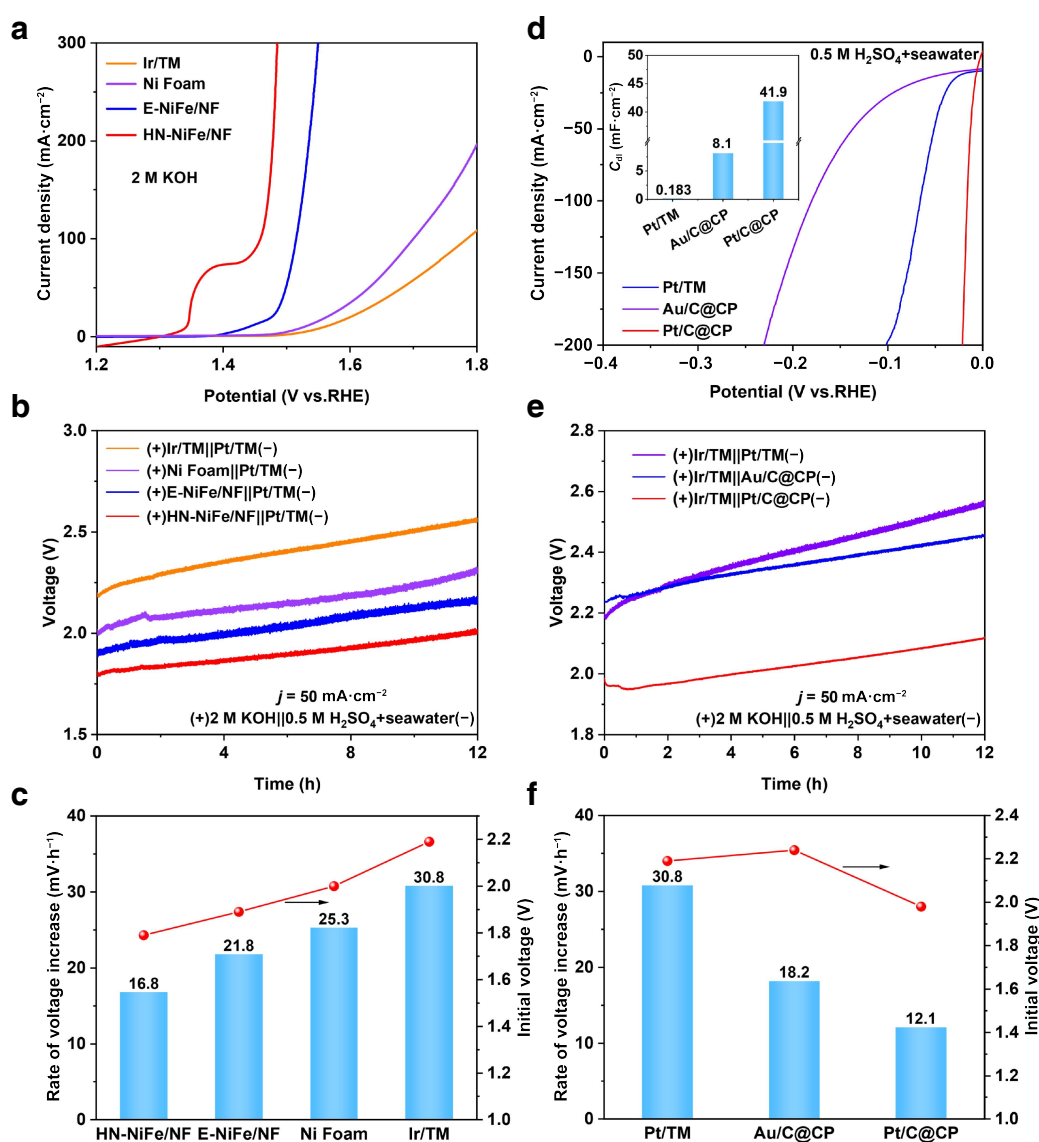


Fig. 2. Optimization of electrodes for BPMSWE. a, OER polarization curves of Ir/TM, NF, E-NiFe/NF, and HN-NiFe/NF in 2 M KOH . b, V - t curves of BPMSWE with different anodes at $50 \text{ mA}\cdot\text{cm}^{-2}$. c, Initial voltage and voltage rise rates derived from (b). d, HER polarization curves of Pt/C@CP, Au/C@CP, and Pt/TM in $0.5 \text{ M H}_2\text{SO}_4$ + seawater; (inset) double-layer capacitance (C_{dl}) of the three electrodes. e, V - t curves of BPMSWE with different cathodes at $50 \text{ mA}\cdot\text{cm}^{-2}$. f, Initial voltage and voltage rise rates derived from (e).

For cathodes, we tested the HER activity of Pt/C@CP and Pt/TM (Supplementary Fig. S6) in 0.5 M H_2SO_4 +seawater. As shown in Fig. 2d, Pt/C@CP exhibited higher HER activity, with an overpotential of only 20 mV at $100 \text{ mA}\cdot\text{cm}^{-2}$, much lower than that of Pt/TM (70 mV); correspondingly, the BPMSWE with Pt/C@CP as the cathode showed a lower initial voltage and a slower voltage rise rate than that with Pt/TM (Figs. 2e and 2f). Regarding catalyst loading, a Pt/C loading of $2 \text{ mg}\cdot\text{cm}^{-2}$ gave the electrolyzer the best stability, and higher loadings did not improve performance further (Supplementary Fig. S7). We further assembled a BPMSWE with Au/C@CP as the cathode, whose HER activity is much lower than that of Pt/TM; as shown in Figs. 2e and 2f, the initial voltage of the Au/C@CP electrolyzer was only slightly higher than that of the Pt/TM electrolyzer, yet it showed a markedly slower voltage rise rate. Compared with Pt/TM, Au/C@CP had much lower HER activity but much higher double-layer capacitance (C_{dl}), which is

positively correlated with active surface area (Fig. 2d and Supplementary Fig. S8)²⁷. This indicates that BPMSWE stability depends not only on electrode activity but also on electrode active area, and that increasing the active area improves electrolyzer stability.

3.2 Investigation of the causes of voltage increase in BPMSWE

To investigate the causes of the voltage increase in the BPMSWE during seawater electrolysis, we paired Pt/TM and Pt/C@CP as cathodes with Ir/TM and HN-NiFe/NF as anodes, constructing BPMSWEs in pairwise combinations and monitoring the evolution of EIS spectra over time. As shown in Figs. 3a and 3b, the (+)HN-NiFe/NF||Pt/C@CP(-) electrolyzer showed the best performance, with an initial voltage of only 1.63 V at $50 \text{ mA}\cdot\text{cm}^{-2}$ and a voltage

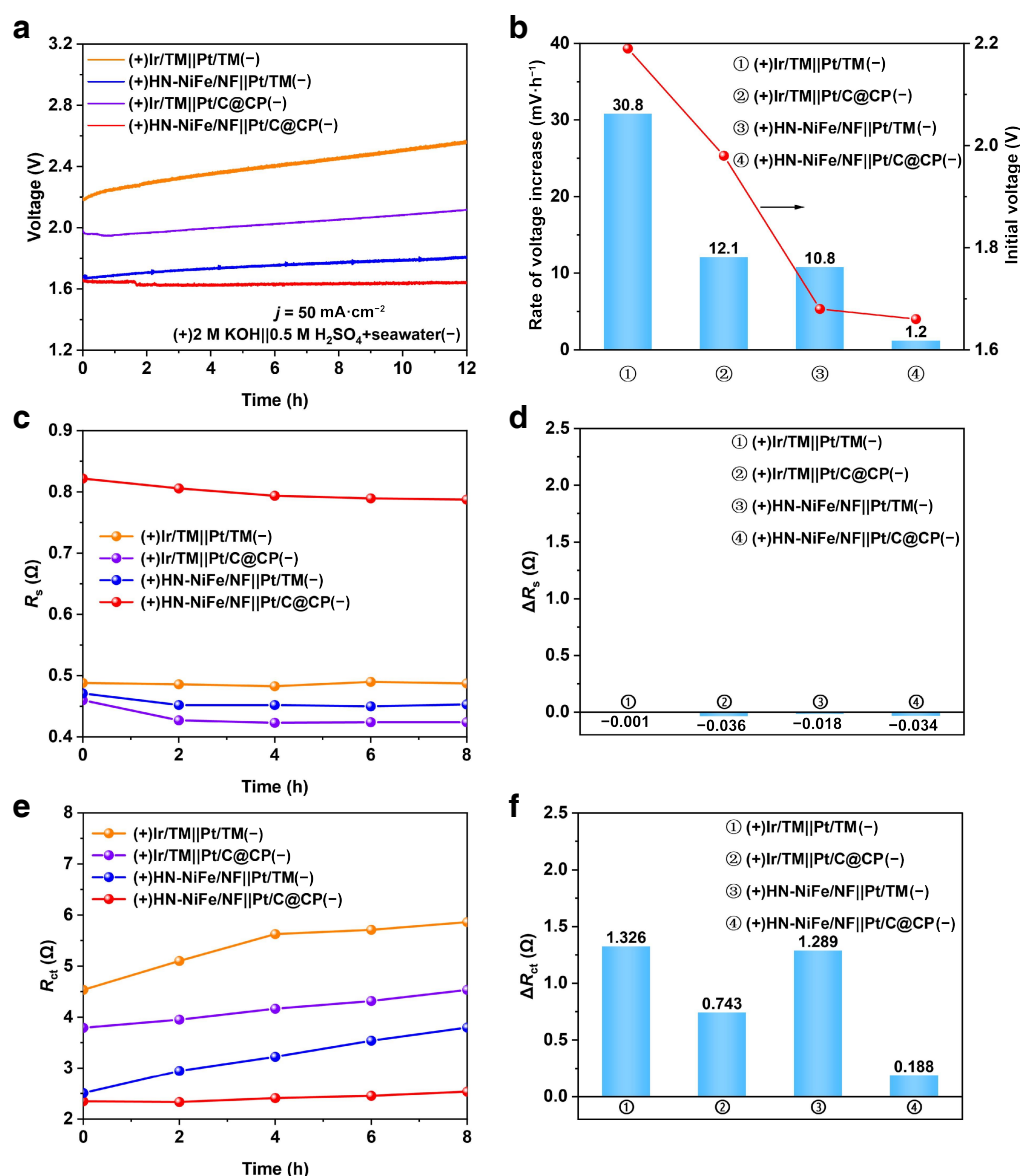


Fig. 3. Ohmic resistance and charge transfer resistance of BPMSWEs. **a**, $V-t$ curves of BPMSWE assembled with different anodes and cathodes at $50 \text{ mA}\cdot\text{cm}^{-2}$. **b**, Initial voltage and voltage rise rates derived from (a). **c**, Ohmic resistance (R_s) of the various BPMSWEs over time. **d**, Change in R_s before and after electrolysis. **e**, Charge transfer resistance (R_{ct}) of the various BPMSWEs over time. **f**, Change in R_{ct} before and after electrolysis.

rise rate of only $1.2 \text{ mV}\cdot\text{h}^{-1}$, much lower than the $30.8 \text{ mV}\cdot\text{h}^{-1}$ of $(+)\text{Ir}/\text{TM}||\text{Pt}/\text{TM}(-)$, consistent with the earlier findings.

EIS spectra were measured for each electrolyzer every 2 h, and the ohmic resistance (R_s) and charge transfer resistance (R_{ct}) were fitted using an equivalent circuit (Supplementary Fig. S9). The results (Figs. 3c and 3d) showed that R_s did not increase for any electrolyzer during continuous electrolysis and varied only slightly (less than 0.04Ω), indicating that ion conduction within the BPM remained essentially stable and ruling out an increase in BPM internal resistance as the cause of the continuous voltage rise. In contrast to the stability of R_s , the R_{ct} of each electrolyzer increased to varying degrees during electrolysis (Figs. 3e and 3f), demonstrating that the gradual retardation of electrochemical reaction kinetics at both electrodes is the main cause of the increase in operating voltage. Electrode type also determined the magnitude of this R_{ct} increase: the $(+)\text{Ir}/\text{TM}||\text{Pt}/\text{TM}(-)$ electrolyzer showed the largest increase, with R_{ct} rising by 1.326Ω after 8 h of operation. Replacing Ir/TM with HN-NiFe/NF reduced this increase to 1.289Ω , and replacing Pt/TM with Pt/C@CP reduced it further to 0.743Ω . The $(+)\text{HN-NiFe/NF}||\text{Pt/C@CP}(-)$ electrolyzer showed the smallest R_{ct} increase, only 0.188Ω .

To clarify the specific changes occurring at the anode and cathode during electrolysis, we used an electrolyzer equipped with an Ag/AgCl reference electrode (Supplementary Fig. S10) to monitor the real-time anode and cathode potentials. The difference between the actual operating voltage and the anode–cathode potential difference can be attributed mainly to the voltage loss caused by BPM internal resistance (i.e., ΔV in Figs. 4a and 4b). For

both the $(+)\text{Ir}/\text{TM}||\text{Pt}/\text{TM}(-)$ and $(+)\text{HN-NiFe/NF}||\text{Pt/C@CP}(-)$ electrolyzers, this BPM voltage loss changed only slightly, consistent with the EIS findings above and confirming that the BPM remains stable during electrolysis. Further analysis of the anode and cathode potentials showed that the Ir/TM anode potential increased by 59 mV after 180 min, whereas the HN-NiFe/NF anode increased by only 5 mV (Fig. 4c). The Pt/TM cathode potential decreased by 139 mV, whereas the Pt/C@CP cathode potential instead increased by 80 mV before eventually stabilizing (Fig. 4d), possibly owing to gradual activation of the Pt/C catalyst within the electrode as its wettability improved. These results indicate that the voltage increase in the BPMSWE during direct seawater electrolysis arises not from BPM degradation but from a gradual increase in electrode overpotential.

3.3 Source of water molecules dissociated in the BPM

Because the BPMSWE is fed acidified seawater at the cathode and alkaline freshwater at the anode, the source of the water molecules dissociated in the BPM determines whether the electrolyzer effectively consumes seawater or freshwater. We therefore used isotope labeling combined with online mass spectrometry (MS) to identify this source (Fig. 5a).

First, the catholyte was $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M NaCl}$ prepared with D_2O as the solvent, and the anolyte was KOH solution prepared with H_2O . At a constant current density of $50 \text{ mA}\cdot\text{cm}^{-2}$, online MS detected three mass-to-charge ratio (m/z) signals among the cathodic products: H_2 , HD, and D_2 (Fig. 5b), with D_2 the most intense, followed by HD and then H_2 . This result indicates that the

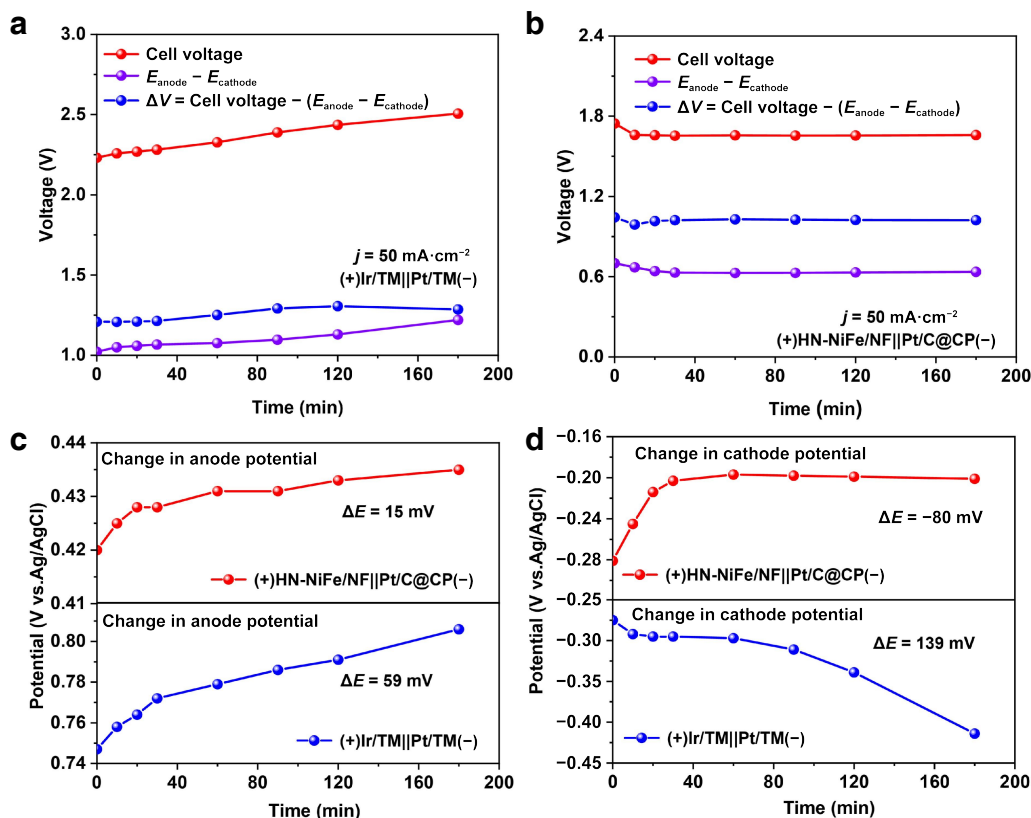


Fig. 4. Anode and cathode potentials of BPMSWEs. a, b, Cell voltage and corresponding anode–cathode potential difference for $(+)\text{Ir}/\text{TM}||\text{Pt}/\text{TM}(-)$ BPMSWE (a) and $(+)\text{HN-NiFe/NF}||\text{Pt/C@CP}(-)$ BPMSWE (b). c, d, Time-dependent potential variation of the anode (c) and cathode (d) for both BPMSWEs.

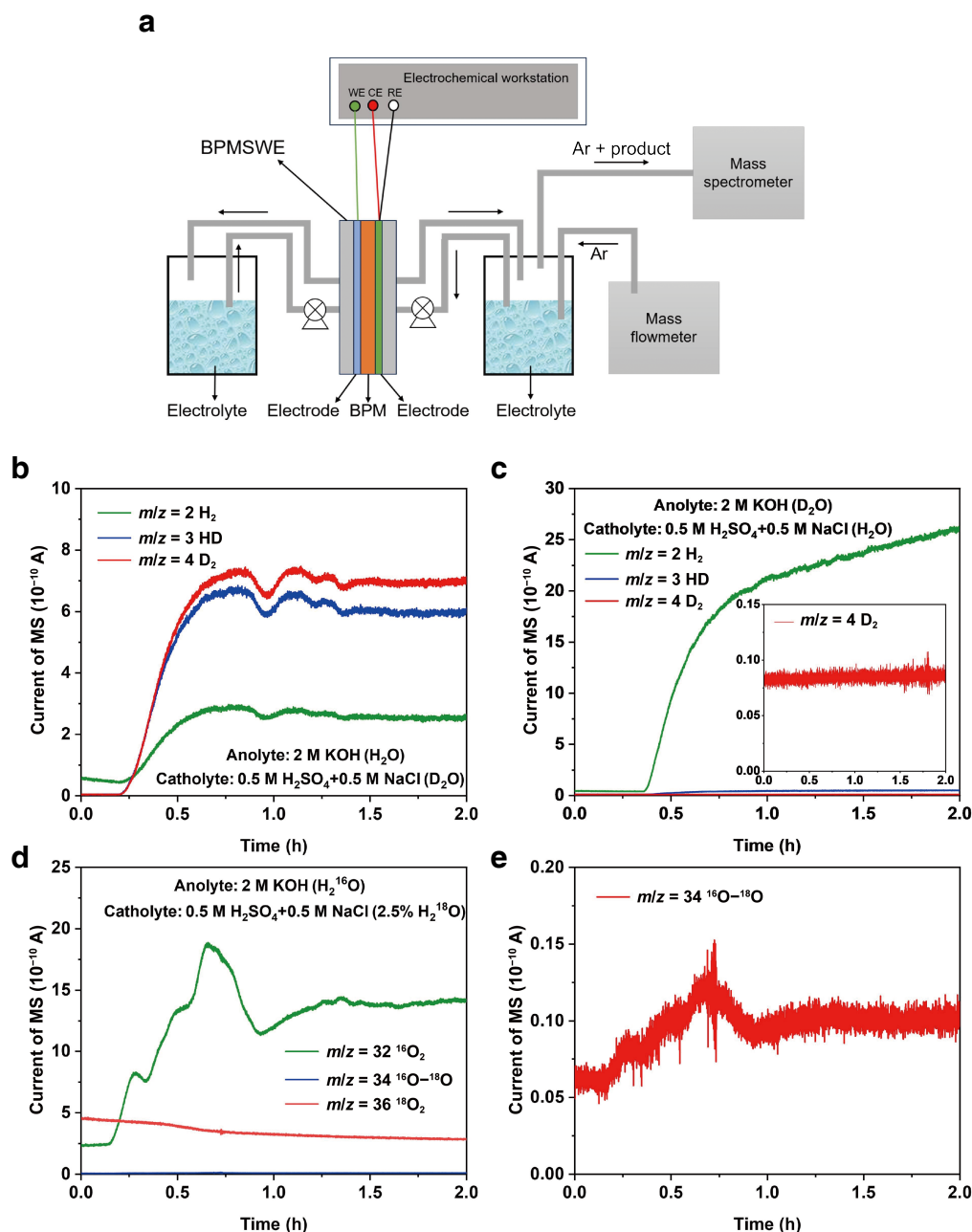


Fig. 5. Isotopic labeling and online mass spectrometry (MS) analysis of the products for identifying the source of water dissociated in the BPM. **a**, Schematic illustration of the online MS setup. **b**, MS ion currents of the cathodic products using H_2O -based anolyte and D_2O -based catholyte. **c**, MS ion currents of the cathodic products using D_2O -based anolyte and H_2O -based catholyte. **d**, MS ion currents of the anodic products using H_2^{16}O -based anolyte and catholyte containing 2.5% H_2^{18}O . **e**, Magnified view of the ^{16}O - ^{18}O signal from (d).

water molecules dissociated in the BPM originate mainly from the catholyte; the HD and H_2 signals arise mainly from H^+ carried by the H_2SO_4 itself, although a minor contribution from anodic H_2O dissociating in the BPM cannot be entirely ruled out.

The electrolytes were then swapped: the anolyte was KOH solution prepared with D_2O , and the catholyte was 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M NaCl prepared with H_2O . Constant current electrolysis was again performed at 50 $\text{mA}\cdot\text{cm}^{-2}$. Online MS showed that the cathodic product consisted almost entirely of H_2 , with only a very weak HD signal and no detectable D_2 (Fig. 5c), indicating that only a very small amount of anodic water dissociates in the BPM.

To further confirm this, 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M NaCl prepared with water containing H_2^{18}O (approximately 2.5 at.%) was used as the catholyte, and KOH solution prepared with H_2^{16}O was used as the anolyte. Electrolysis was performed at a constant current of 50 $\text{mA}\cdot\text{cm}^{-2}$, and the anodic gas products were analyzed online by MS. As shown in Fig. 5d, the anodic products were mainly $^{16}\text{O}_2$ ($m/z = 32$) with trace amounts of ^{16}O - ^{18}O ($m/z = 34$, Fig. 5e). This result indicates that water molecules from the catholyte dissociate in the BPM: the $^{18}\text{OH}^-$ formed from H_2^{18}O dissociation migrates to the anode, where it combines with another OH^- to form ^{16}O - ^{18}O .

Collectively, these online MS results indicate that during operation of this BPMSWE, the water molecules dissociated in the

BPM originate almost entirely from the cathode side seawater, confirming that this system achieves direct seawater electrolysis for hydrogen production.

3.4 Electrolysis of saturated seawater

As noted above, the BPMSWE consumes cathodic seawater during electrolysis, which gradually increases the salt concentration of the catholyte²⁸. We therefore examined whether the BPMSWE can operate normally under the extreme condition of saturated seawater at the cathode (Fig. 6a), prepared by acidifying sea salt.

We first evaluated the effect of electrolyte and electrode type on BPMSWE performance for saturated seawater electrolysis. For the anolyte, 2 M KOH was again the most suitable choice (Supplementary Fig. S11). For the catholyte, the electrolyzer operated normally at a cathodic acid concentration of 0.5 M H₂SO₄; however, reducing this concentration to 0.05 M caused severe Mg²⁺/Ca²⁺ deposition at the cathode (Supplementary Fig. S12), indicating that low acidity cannot maintain cathodic pH stability. Accordingly, 0.5 M H₂SO₄ was retained as the catholyte. For the electrodes, the (+)Ir/TM||Pt/TM(-) electrolyzer showed a fast voltage rise rate, whereas that of the (+)HN-NiFe/NF||Pt/C@CP(-) electrolyzer was only one-sixth as high (Supplementary Fig. S13); the high-activity electrodes were therefore retained for saturated seawater electrolysis as well.

Under these optimal electrolyte and electrode conditions, the BPMSWE operated stably with saturated seawater for 24 h at current densities of 10, 50, and 100 mA·cm⁻² (Fig. 6b), with voltage rise rates of 4.75, 6.9, and 7.8 mV·h⁻¹, respectively (Fig. 6c). The Cl⁻ concentration in the anolyte after 24 h of operation at 100 mA·cm⁻² was only 138.7 ppm (Fig. 6d); although higher than the 1.72 ppm

measured under open-circuit conditions, this value is almost negligible compared with the Cl⁻ concentration of the saturated seawater itself (1.68×10^5 ppm), demonstrating the excellent Cl⁻-blocking capability of the BPM.

3.5 Long-term stability test

Using 0.5 M H₂SO₄ + seawater as the catholyte and 2 M KOH as the anolyte, continuous electrolysis was performed for 500 h at a current density of 100 mA·cm⁻². As shown in Fig. 7a, the initial and final voltages were 1.88 and 2.31 V, respectively, giving an average voltage rise rate of 1.76 mV·h⁻¹, markedly lower than values reported in the literature for BPM electrolyzers (Supplementary Table S1), including the BPM electrolyzer without anolyte (~ 8.75 mV·h⁻¹)¹⁸, the supporting electrolyte-free seawater electrolyzer (~ 8.3 mV·h⁻¹)¹³, and the (+)NiFe@Ni foam|BPM|FeNiCo@lyocell-based CC(-) electrolyzer (~ 2.5 mV·h⁻¹)²⁵. The Cl⁻ and ClO⁻ concentrations in the anolyte were monitored simultaneously during electrolysis. As shown in Fig. 7b, the Cl⁻ concentration gradually increased with electrolysis time but never exceeded 150 ppm, far below that of the catholyte (1.98×10^4 ppm). ClO⁻ was not detected at any point during electrolysis (Fig. 7c and Supplementary Figs. S14–S16). After 500 h of continuous operation, no scaling was observed on the cathode, and the anode remained intact (Supplementary Fig. S17). These stability results demonstrate that the pH-asymmetric BPM electrolysis strategy adopted here enables long-term, stable seawater electrolysis. The activity of both electrodes decreased after 500 h of electrolysis (Supplementary Fig. S18), suggesting that developing more stable anode and cathode materials would further enhance the long-term stability of pH-asymmetric BPMSWE.

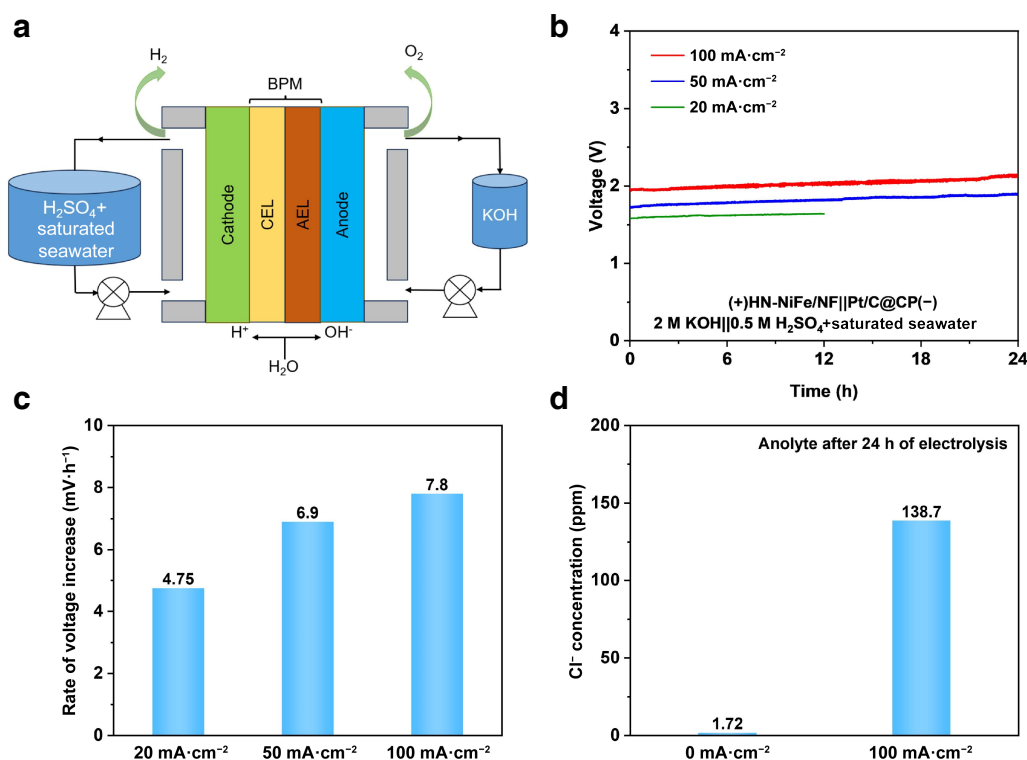


Fig. 6. Performance of BPMSWE using acidified saturated seawater as the catholyte. **a**, Schematic illustration of BPMSWE using saturated seawater. **b**, V - t curves of BPMSWE at different current densities. **c**, Corresponding voltage rise rates derived from (b). **d**, Cl⁻ concentration in the anolyte after 24 h of electrolysis at 0 and 100 mA·cm⁻².

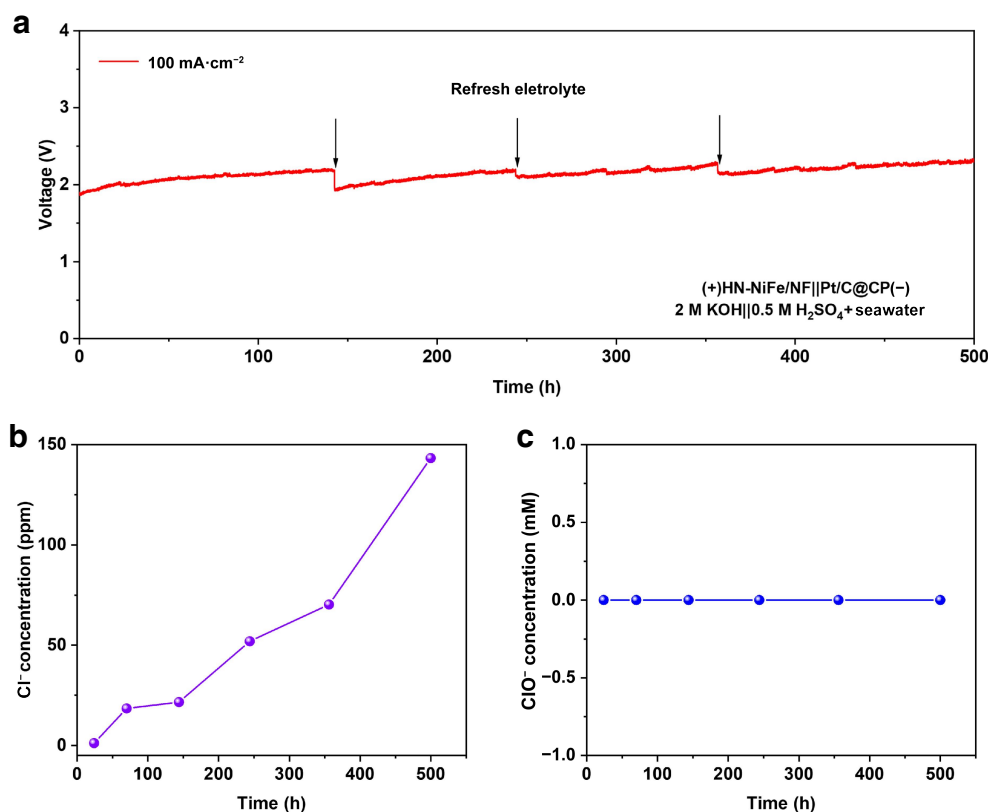


Fig. 7. Long-term stability testing of BPMSWE for 500 h. a, $V-t$ curve of BPMSWE. b, c, Cl^- concentration (b) and ClO^- concentration (c) in the anolyte over time.

4 Conclusions

This work constructed a pH-asymmetric seawater electrolyzer based on a BPM, in which acidified seawater is fed to the cathode and alkaline freshwater to the anode. Acidification prevents $\text{Mg}^{2+}/\text{Ca}^{2+}$ precipitation at the cathode, while the BPM blocks chloride ions and thereby prevents CER at the anode. EIS and anode/cathode potential monitoring indicate that the voltage increase in the BPMSWE originates mainly from an increase in charge transfer resistance rather than from a change in BPM internal resistance; increasing electrode active area and catalytic activity effectively improves electrolyzer stability. Isotope labeling combined with online mass spectrometry confirms that the water molecules dissociated in the BPM come mainly from the cathodic seawater, and the electrolyzer remains stable even when the cathode is fed saturated seawater. By optimizing the electrolyte concentration and electrode types, this BPMSWE achieves continuous, stable operation for 500 h at a current density of $100 \text{ mA} \cdot \text{cm}^{-2}$, with a voltage rise rate of only $1.76 \text{ mV} \cdot \text{h}^{-1}$, no cathodic scaling, and no anodic chlorine evolution.

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Data availability

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

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Author contributions

F.-H. X.: Investigation, formal analysis, writing-original draft; J.-F. L.: Investigation; W.-B. L.: Investigation; F.-F. C.: Supervision, funding acquisition; C. D.: Writing-review and editing, funding acquisition; G. Z.: Conceptualization, supervision, writing-review and editing, funding acquisition.

Competing interests

The authors have no conflicts of interest to declare.

Use of AI statement

None.



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