



Metal-Organic Xerogel Binder Enables Strong Chemisorption and Fast Conversion Kinetics towards Shuttle-Suppressed Zn–I₂ Batteries

Xinxin Han¹, Yicai Pan², Min Chen¹(✉), Haoran Tu¹, Wenlong Wang¹, Lu Chen¹(✉), Yongqiang Yang³(✉)

¹ School of Materials Science and Engineering, Dongguan University of Technology, Dongguan 523808, China

² Department of Materials Science and Engineering & Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong 999077, China

³ Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong SAR 999077, China

Nano Research Energy, **Just Accepted Manuscript** • <https://doi.org/10.26599/NRE.2026.9120286>

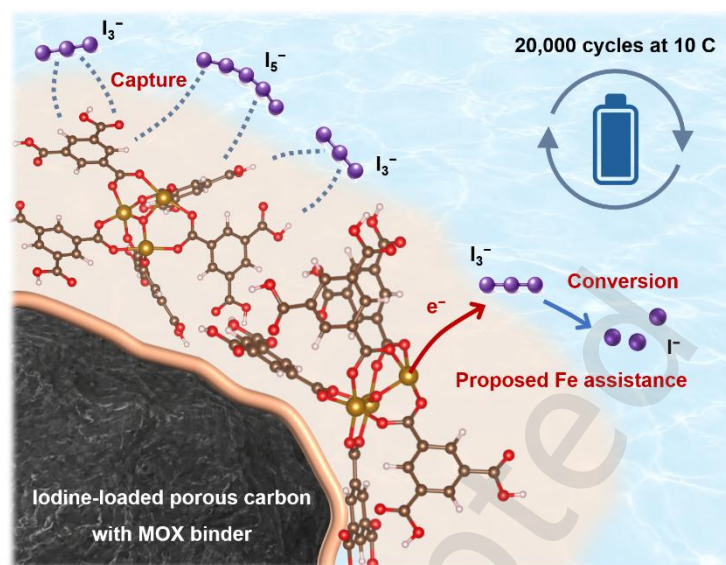
<https://www.sciopen.com/journal/2791-0091> on Oct. 21, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research Energy*, 2025, 4, e9120191). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Table of Contents



An amorphous Fe–BTC metal–organic xerogel functions as a redox-responsive interfacial binder that couples polyiodide capture with Fe-assisted interfacial conversion in aqueous Zn–I₂ cathodes. This capture-conversion coupling suppresses polyiodide accumulation, improves apparent iodine redox kinetics, and sustains stable cycling for 20,000 cycles at 10 C.

Metal-Organic Xerogel Binder Enables Strong Chemisorption and Fast Conversion Kinetics towards Shuttle-Suppressed Zn–I₂ Batteries

Xinxin Han¹, Yicai Pan², Min Chen^{1, *}, Haoran Tu¹, Wenlong Wang¹, Lu Chen^{1, *}, and Yongqiang Yang^{3, *}

¹ School of Materials Science and Engineering, Dongguan University of Technology, Dongguan, 523808, China

² Department of Materials Science and Engineering & Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong 999077, China

³ Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong SAR 999077, China

© The Author(s) 2026

Received: 28 August 2026 / **Revised:** 29 September 2026 / **Accepted:** 1 October 2026

* Corresponding authors' email addresses: chenmin@dgut.edu.cn; chl2008051160@163.com; yong-qiang.yang@polyu.edu.hk

Abstract

The loss and incomplete conversion of soluble polyiodide intermediates limit the long-term cycling stability of aqueous Zn–I₂ batteries. Conventional functional binders can restrict polyiodide migration but generally do not promote the conversion of the retained species. Here, an amorphous iron-benzene-1,3,5-tricarboxylate (Fe–BTC) metal–organic xerogel (MOX) is used as a redox-responsive binder to couple polyiodide capture with interfacial redox conversion. Its heterogeneous electrostatic environment retains iodine species near the cathode, while the mixed-valence Fe centers electronically interact with the adsorbed intermediates and are proposed to assist interfacial electron transfer. This capture-conversion coupling suppresses polyiodide accumulation and migration, reduces interfacial polarization, and preserves electrochemically accessible iodine during cycling. Consequently, the MOX-based cell retains 122.8 mAh g^{−1} after 20,000 cycles at 10 °C. Its robustness is further demonstrated at a high iodine loading of 7 mg cm^{−2}, at temperatures of −10 and 60 °C, and in pouch cells. These results demonstrate that redox-responsive metal coordination within the binder phase provides an effective strategy for regulating both the location and reactivity of soluble intermediates in aqueous Zn–I₂ batteries.

Keywords: Aqueous zinc–iodine batteries; Metal-organic xerogel; Redox-responsive binder; Polyiodide capture-conversion; Interfacial redox conversion

1. Introduction

Aqueous zinc–iodine (Zn–I₂) batteries are attractive because of their relatively low material costs, high safety, and favorable iodine redox chemistry.^{1–2} The conventional I[–]/I₂ redox couple involves a two-electron transfer, corresponding to a theoretical Zn–I₂ cell voltage of approximately 1.29 V and a theoretical capacity of 211 mAh g^{–1} based on iodine.^{3–4} During charge and discharge, however, soluble I₃[–] and I₅[–] intermediates are formed.⁵ Their diffusion from the cathode into the electrolyte promotes active-iodine loss and self-discharge. Polyiodides reaching the Zn anode may also induce parasitic reactions, resulting in lower Coulombic efficiency and poor cycling stability.^{6–7} Suppressing their migration is therefore essential.⁸ However, immobilization alone does not ensure that the retained intermediates remain electrochemically accessible or are efficiently reintegrated into the iodine redox cycle.

Early cathode designs mainly relied on physical confinement to reduce the loss of iodine species.⁹ Microporous carbons and starch-derived hosts retain polyiodides through pore confinement, adsorption, and noncovalent interactions.^{10–11} These approaches restrict intermediate migration, but retention alone does not intrinsically promote interfacial electron transfer or the subsequent conversion of the adsorbed intermediates. Catalytically active motifs have therefore been introduced to promote polyiodide conversion, including open Co/Fe sites in Prussian blue analogues,¹² Fe–N–C single-atom motifs,¹³ and molecular Fe centers in hemin.¹⁴ Cathode architectures combining confinement, chemisorption, and catalysis have also been reported.¹⁵ In most cases, however, these functions are provided by the iodine host or by additional catalytic components rather than being integrated into the binder phase.

Binders provide another interfacial platform for regulating iodine chemistry because they are distributed throughout the cathode and contact both the active material and the electrolyte. Their role in Zn–I₂ cathodes has consequently expanded beyond mechanical adhesion. LA133 anchors iodine species through amide and carboxyl groups,¹⁶ while Janus and gelatin binders regulate iodine-species adsorption and redox behavior.^{17–18} Polysaccharide binders restrict polyiodide migration through hydrogen bonding and chemisorptive interactions,^{19–20} and mixed ionic–electronic conducting binders provide chemical affinity together with charge transport.²¹ Most reported binders nevertheless rely on organic functional groups to retain polyiodides, with few incorporating metal centers that can

participate in the subsequent redox conversion of adsorbed intermediates.

Metal-organic materials provide a direct way to introduce such coordination sites into the binder phase. Metal-organic gels have been used in Zn–I₂ batteries, but mainly as catholyte hosts to limit iodine diffusion rather than as electrode binders.²² Separately, ferrocene/ferrocenium chemistry has shown that metal-centered redox couples can participate in polyiodide conversion.²³ These findings raise the possibility that a metal-organic binder could simultaneously retain soluble intermediates and facilitate their subsequent conversion within the same interfacial phase.

In this study, we employ an amorphous iron-benzene-1,3,5-tricarboxylate (Fe–BTC) metal-organic xerogel (MOX) as a redox-responsive binder for aqueous Zn–I₂ cathodes. Its heterogeneous electrostatic environment provides favorable binding sites for iodine species, while its mixed-valence Fe centers electronically interact with the adsorbed intermediates and are proposed to assist interfacial electron transfer. This combination suppresses polyiodide accumulation, reduces interfacial polarization and improves the apparent iodine redox kinetics. During long-term cycling at 10 C, the MOX-based cell retains 122.8 mAh g^{−1} after 20,000 cycles. The effectiveness of MOX is further demonstrated in high-loading cathodes containing 7 mg cm^{−2} of iodine, at temperature extremes of −10 and 60 °C, and in pouch cells subjected to static bending. These results establish a binder design in which polyiodide retention and interfacial conversion are coupled through redox-responsive metal coordination centers.

2. Results and Discussion

The structure of MOX was examined by X-ray diffraction (XRD) and Fe K-edge X-ray absorption spectroscopy. The XRD pattern was dominated by broad scattering features, consistent with limited long-range structural order (**Fig. 1a**). Such broad scattering is commonly observed in nonperiodic metal–carboxylate networks formed during gelation and subsequent drying.²⁴ Despite the limited long-range order, local coordination around the Fe centers was preserved. The Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectrum was dominated by the first-shell Fe–O contribution, with fitted Fe–O distances of 1.98–2.13 Å (**Fig. 1b**). A strong Fe–O feature was also observed in the WT-EXAFS map, whereas no distinct higher-shell contribution attributable to Fe–Fe scattering was resolved within the measured range (**Fig. 1c**). Together, these

results identify MOX as a nonperiodic Fe–carboxylate network with preserved local Fe–O coordination and no evident extended Fe–Fe connectivity within the measured range.

The affinity of this network for soluble polyiodides was compared with that of poly(vinylidene fluoride) (PVDF). After MOX was added to an I_3^- solution, the yellow color was largely removed, while the solution treated with PVDF remained visibly darker. The absorption band centered at approximately 288 nm²⁵ showed a consistent trend, with only a slight decrease after PVDF treatment but a pronounced decrease after MOX treatment (**Fig. 1d**). The recovered binders were then examined by Raman spectroscopy. Signals at approximately 110 and 162 cm⁻¹, assigned to I_3^- and I_5^- , respectively,²⁶ were present in both samples but were considerably stronger for MOX (**Fig. 1e**). Because ultraviolet-visible (UV–Vis) spectroscopy probes the depletion of polyiodides from the liquid phase whereas Raman spectroscopy detects iodine species retained in the recovered solids, the consistent results from these complementary measurements support substantially greater polyiodide uptake by MOX. The decrease in solution-phase polyiodide signals may also include a contribution from chemical conversion, as suggested by the Fe 2p X-ray photoelectron spectroscopy (XPS) results discussed below. The calculated electrostatic potential (ESP) of MOX was unevenly distributed over the model surface (**Fig. 1f**), revealing spatially heterogeneous electronic environments that can interact differently with iodine species. Area-weighted surface analysis showed a broader ESP distribution for MOX than for PVDF, with variances of 448.7 and 120.6 (kcal mol⁻¹)², respectively, and a higher fraction of negative-ESP surface area (48.6% versus 37.6%; **Fig. S1**). The adsorption energies of I^- , I_2 , I_3^- and I_5^- on MOX were -0.21, -1.63, -1.40 and -1.67 eV, respectively. The corresponding values on PVDF were -0.07, -0.12, -0.14 and -0.37 eV (**Fig. 1g**). The difference was relatively small for I^- but became much larger for I_2 , I_3^- and I_5^- . The substantially more favorable adsorption energies for the molecular and polyiodide species are consistent with the UV–Vis and Raman results and provide an energetic basis for their preferential retention by MOX. Independent gradient model based on Hirshfeld partition (IGMH) maps of the optimized adsorption configurations further visualize contacts around the Fe–O/carboxylate region and adjacent ligands of MOX, whereas the PVDF contacts are localized near the polymer chain (**Figs. S2 and S3**).

Fig. 1h illustrates the proposed function of MOX within the iodine cathode. The xerogel binder forms an interfacial network around the iodine-loaded porous carbon particles, placing its

heterogeneous electrostatic regions close to the active material. These interfacial binding environments favor the retention of I_3^- and I_5^- near the cathode, thereby limiting their migration into the bulk electrolyte. The proposed local electron exchange between Fe centers and iodine species can be expressed as $2\text{Fe}^{2+} + \text{I}_3^- \rightleftharpoons 2\text{Fe}^{3+} + 3\text{I}^-$. During discharge, Fe^{2+} is proposed to donate electrons to I_3^- , forming Fe^{3+} and I^- . During charging, Fe^{3+} is proposed to accept electrons released during the oxidation of I^- to I_3^- , regenerating Fe^{2+} . The electronic response of the Fe centers and the dynamic evolution of polyiodides during cycling are therefore examined next to evaluate this proposed capture-conversion coupling.

The proposed electronic role of the Fe centers was examined by comparing MOX before and after exposure to I_3^- . The principal Fourier-transform infrared (FTIR) bands remained at similar wavenumbers after adsorption (**Fig. 2a**), indicating that the primary Fe–carboxylate coordination environment remained largely unchanged upon polyiodide uptake. A clearer change appeared in the Fe 2*p* XPS spectra. For pristine MOX, the fitted Fe^{3+} components were located at approximately 712.4 and 725.9 eV, while the Fe^{2+} components appeared at approximately 711.1 and 724.5 eV (**Fig. 2b**).²⁷ After exposure to I_3^- , the fitted relative Fe^{2+} fraction decreased from 17.7% to 5.9%, accompanied by an increase in the Fe^{3+} fraction from 82.3% to 94.1% (**Fig. 2b, c**). This redistribution is consistent with oxidation of Fe^{2+} centers upon interaction with I_3^- and supports the proposed interfacial electron-transfer process. The C 1*s* and O 1*s* spectra showed much smaller changes (**Fig. S4**), supporting a predominantly Fe-centered electronic response rather than extensive perturbation of the organic ligand environment. Additional ex situ XPS measurements were performed on MOX-containing cathodes collected after discharge to 0.6 V and subsequent recharge to 1.6 V (**Fig. S5**). The fitted relative $\text{Fe}^{2+}/\text{Fe}^{3+}$ fractions changed from 10.5%/89.5% in the discharged state to 22.5%/77.5% after recharging. These state-dependent changes support the proposed involvement of the Fe centers in Fe-assisted iodine conversion.

The charge-density-difference calculation provided a molecular-level view of this interaction. Electron accumulation and depletion appeared across the interface between I_3^- and the MOX model, including the region close to the Fe coordination center (**Fig. 2d**). The redistribution was more pronounced for the MOX–polyiodide configurations than for the corresponding PVDF systems (**Fig. S6**). This more pronounced interfacial charge redistribution is consistent with stronger electronic

coupling between MOX and the adsorbed iodine species. Taken together with the adsorption-induced redistribution of the fitted $\text{Fe}^{2+}/\text{Fe}^{3+}$ components, these results indicate that the Fe coordination centers are electronically responsive to polyiodide binding and support their involvement in interfacial electron transfer.

Operando Raman and UV–Vis spectroscopy were then used to follow polyiodide evolution during charge and discharge. In the Raman maps, the bands near 110 and 162 cm^{-1} assigned to I_3^- and I_5^- remained pronounced for the PVDF electrode but were markedly weaker for the MOX electrode throughout the same electrochemical cycle (**Fig. 2e, f**). The operando UV–Vis maps showed a similar difference. Strong absorption responses near 288 and 354 nm developed in the PVDF cell, whereas the corresponding responses were much weaker in the MOX cell (**Fig. 2g, h**). These complementary observations are consistent with lower detectable polyiodide accumulation near the cathode and reduced migration into the electrolyte probed by UV–Vis spectroscopy. Whereas static exposure over 24 h allows cumulative polyiodide retention, operando cycling involves continuous electrochemical formation and consumption of these intermediates.

This dynamic behavior is consistent with the calculated binding-energy hierarchy: MOX binds I_2 , I_3^- and I_5^- much more strongly than I^- . The stronger affinity for oxidized iodine species favors their retention near the cathode during charging, while reduction to the more weakly bound I^- favors product release and regeneration of the binding sites. Together, these results suggest that MOX couples polyiodide retention with subsequent conversion while maintaining reversible iodine redox.

The electrochemical response of the two electrodes was first compared by cyclic voltammetry (CV). Both electrodes showed one main pair of iodine redox peaks over scan rates from 0.2 to 1.0 mV s^{-1} (**Fig. 3a, b**). The peak currents increased and the peak positions shifted as the scan rate increased. The MOX electrode generally produced larger absolute peak currents than the PVDF electrode. A direct comparison at 0.2 mV s^{-1} also showed a smaller separation between the anodic and cathodic peaks for MOX, indicating lower electrochemical polarization (**Fig. S7**). Because peak current is also affected by the amount of electrochemically accessible iodine, the larger peak currents alone should not be interpreted as direct evidence of faster charge-transfer kinetics. The apparent anodic Tafel slope decreased from 62.1 mV dec^{-1} for PVDF to 47.2 mV dec^{-1} for MOX, whereas the magnitudes of the cathode slopes remained similar at 156.4 and 155.6 mV dec^{-1} , respectively (**Fig.**

S8). Thus, under the present measurement conditions, the kinetic advantage of MOX was more evident for the anodic iodine conversion, whereas the cathodic branch showed little difference in the apparent Tafel response.

The dependence of peak current (i_p) on scan rate (v) was fitted using $|i_p| = av^b$. Here, a and b are adjustable parameters. Both redox peaks of the MOX electrode gave a b value of 0.82, while the corresponding values for PVDF were 0.722 and 0.735 (**Fig. 3c, d**). A b value near 0.5 is associated with a predominantly diffusion-controlled response, whereas a value approaching 1 indicates a larger scan-rate-proportional or surface-controlled contribution.²⁸ The b values between these two limits show that both processes contributed to the iodine reaction. The higher b values of MOX therefore indicate a greater relative contribution from rapidly responding surface or near-surface electrochemical processes. Current separation using $i(V) = k_1v + k_2v^{1/2}$ gave the same trend, where $i(V)$ is the current at potential V and k_1 and k_2 are fitting coefficients. The scan-rate-proportional contribution of the MOX electrode increased from 66.6% at 0.2 mV s⁻¹ to 81.9% at 1.0 mV s⁻¹, compared with an increase from 58.7% to 76.3% for PVDF (**Fig. 3e-h**). This contribution includes both non-Faradaic charging and fast surface or near-surface Faradaic reactions and therefore should not be interpreted exclusively as electric-double-layer capacitance.

The peak-current response was further examined by plotting i_p against $v^{1/2}$. Linear fitting yielded slopes of 2.12 and -2.90 for the MOX electrode and 1.51 and -2.30 for PVDF (**Fig. S9**). The larger absolute slopes for MOX indicate a greater variation in peak current with $v^{1/2}$ and a stronger overall current response over the scan-rate range investigated. This observation complements the higher b values because the two parameters describe different aspects of the electrochemical response: the b value reflects the relative scan-rate dependence of the total peak current, whereas the $i_p-v^{1/2}$ slope reflects the magnitude of its variation with scan rate. Together, these results show that MOX produces a larger peak-current response while increasing the relative contribution of rapidly responding surface or near-surface processes.

Electrochemical impedance spectroscopy (EIS) was used to determine whether the lower CV polarization was accompanied by reduced interfacial impedance. From the initial state to 50 cycles, the Nyquist arcs of the MOX electrode remained smaller than those of the PVDF electrode (**Fig. 3i-k**). Distribution of relaxation times (DRT) analysis resolved four relaxation features, denoted

P1–P4 (**Fig. 3I**). The shorter-time P1–P3 responses can contain overlapping contributions from electrode contact, interfacial charge transfer, and ion transport within the porous electrode, whereas the long-time P4 response is primarily attributed to slow interfacial exchange and electrolyte/polyiodide mass transport.^{29–30} The MOX electrode showed lower amplitudes than PVDF across all four relaxation regions, both initially and after 50 cycles, indicating that the reduction in polarization extends across multiple electrochemical relaxation processes rather than being confined to a single characteristic time scale.

The reaction energetics were first compared using stepwise free-energy calculations. After formation of the first adsorbed intermediate, the free-energy profile on MOX fell below that on PVDF and remained lower through the subsequent reduction steps (**Fig. 4a**). These calculations indicate that the MOX interface provides a thermodynamically more favorable sequence of interfacial states for the reduction of I_2 to I^- . Temperature-dependent EIS measurements showed progressively smaller impedance arcs as the temperature increased from 35 to 55 °C (**Fig. 4b, c**). Over the full temperature range, the MOX electrode also displayed lower impedance than PVDF. Arrhenius fitting yielded apparent activation energies of 33.19 and 43.91 kJ mol⁻¹ for the MOX and PVDF electrodes, respectively (**Fig. 4d**). The lower apparent activation energy and consistently lower impedance of the MOX electrode over the measured temperature range are consistent with facilitated interfacial charge transfer under the present measurement conditions.

The influence of polyiodide retention was examined under open-circuit conditions. After full charging, both cells showed a rapid initial voltage decrease followed by a slower decay (**Fig. 4e**). After 48 h, the MOX cell remained at 1.325 V, while the PVDF cell decreased to 1.296 V. The higher open-circuit voltage retained by the MOX cell indicates slower self-discharge, consistent with more effective retention of soluble iodine species within the cathode region and reduced polyiodide-mediated active-material loss.

Rate and long-term cycling tests were then conducted to assess whether this interfacial regulation translated into sustained iodine utilization under demanding operating conditions. The rate capability of the cells was measured from 1 to 50 C. The MOX cell delivered discharge capacities of 157.9, 141.6, 136.4, 127.7, 111.5 and 100.2 mAh g⁻¹ at 1, 3, 5, 10, 25 and 50 C, respectively. Under the same conditions, the PVDF cell delivered 100.9, 90.9, 83.8, 70.3, 58.6 and 52.0 mAh g⁻¹,

respectively (**Fig. 4f**). Thus, the MOX cell retained 63.5% of its 1 C capacity at 50 C. Upon returning to 1 C, its capacity recovered to 150.3 mAh g⁻¹, corresponding to 95.2% of the initial value. Consistent with the rate data, the voltage-capacity profiles show that the MOX cell preserves better-defined discharge plateaus and higher capacities as the current density increases (**Fig. 4h, i**). The preservation of the discharge plateau and capacity at increasing rates is consistent with the lower electrochemical polarization and interfacial impedance observed by CV and EIS, indicating that a larger fraction of iodine remained electrochemically accessible under rapid cycling conditions.

Long-term cycling was examined at 2 and 10 C. At 2 C, the MOX cell started with a discharge capacity of 190.1 mAh g⁻¹ and retained 129.9 mAh g⁻¹ after 5000 cycles, giving a capacity retention of 68.3% (**Fig. 4g**). The initial capacity of the PVDF cell was 101.6 mAh g⁻¹, and the cell could no longer be cycled after approximately 1350 cycles. At 10 C, the MOX cell still delivered 122.8 mAh g⁻¹ after 20,000 cycles. The PVDF cell ceased operating after approximately 3700 cycles (**Fig. 4j**). The voltage profiles of the MOX cell retained visible charge–discharge plateaus at different cycling stages (**Fig. S10**), indicating that reversible iodine redox remained electrochemically accessible even after prolonged cycling. Taken together with the self-discharge and rate results, the long-term cycling behavior supports the ability of MOX to preserve active iodine within the cathode while maintaining its participation in the redox process.

The performance comparison was extended to cathodes with a higher iodine loading. At an iodine loading of 7 mg cm⁻² and 2 C, the MOX cell retained 166.9 mAh g⁻¹ after 500 cycles, corresponding to an areal capacity of approximately 1.17 mAh cm⁻², while the capacity of the PVDF cell remained below 100 mAh g⁻¹ (**Fig. 5a**). The Coulombic efficiency of the MOX cell stayed close to 100% during the test. At the 100th cycle, its charge–discharge profile showed a longer and more distinct voltage plateau than that of the PVDF cell (**Fig. 5b**). These results show that the capacity advantage of MOX was preserved when the iodine loading was increased, indicating that its beneficial interfacial regulation was not limited to low-loading cathodes. The cells were also cycled at -10 and 60 °C. After 1000 cycles at 10 C, the MOX cell delivered 122.9 mAh g⁻¹ at -10 °C, compared with 71.3 mAh g⁻¹ for the PVDF cell (**Fig. 5c**). At low temperature, sluggish ion transport and interfacial charge transfer limit the accessibility and conversion of iodine species. By retaining polyiodide intermediates close to the conductive cathode interface, the distributed MOX binder helps

maintain their participation in the iodine redox process under transport-limited conditions. At 60 °C, the MOX and PVDF cells retained 118.3 and 87.6 mAh g⁻¹, respectively, after 1000 cycles at 10 C, while exhibiting comparable Coulombic efficiencies (**Fig. 5d**). Elevated temperature accelerates iodine dissolution and migration, and the stronger affinity of MOX for molecular iodine and polyiodides helps preserve electrochemically accessible iodine within the cathode region during prolonged cycling.

MOX was further used as the binder in pouch cells. At 5 C, the pouch cell retained 99.2 mAh g⁻¹ after 1000 cycles with a Coulombic efficiency close to 100% (**Fig. 5e**). It also maintained 93.3 mAh g⁻¹ after 2000 cycles at 10 C (**Fig. S11**). The pouch cell powered a hygrometer in the flat, 90°-bent, and 180°-bent states, and voltage output was retained during static bending (**Fig. 5f-j**). These results demonstrate the operation of the MOX-based cathode in a larger-format cell and its ability to maintain electrical output under static mechanical deformation; repeated bending or mechanical-fatigue durability, however, was not evaluated. Anode-side interfacial engineering has demonstrated that regulating the local Zn reaction environment can improve Zn reversibility.³¹ In the present cells, the benefit of cathode-side regulation was also reflected at the Zn anode. After 500 cycles at 10 C, the Zn surface from the MOX cell was more uniform than that from the PVDF cell (**Fig. S12**). Energy-dispersive X-ray spectroscopy (EDS) showed a lower O content for MOX (2.08 versus 7.03 wt.%) and no detectable S, whereas the PVDF sample contained 0.86 wt.% S (**Fig. S13**). Together, the more uniform Zn morphology and the lower abundance of O- and S-containing surface species are consistent with less severe parasitic surface reactions in the MOX-based cell, although the specific chemical nature of these surface products cannot be established from EDS alone.

Collectively, MOX retains soluble iodine species near the cathode while providing electronically responsive Fe coordination centers throughout the cathode interfacial network. By coupling polyiodide retention with an electronically responsive interfacial environment, MOX suppresses detectable polyiodide accumulation and migration while reducing electrochemical polarization and self-discharge. The accompanying mitigation of Zn-side surface degradation further suggests reduced cathode-to-anode chemical crosstalk. Together, these coupled effects help preserve electrochemically accessible iodine during prolonged cycling and underpin the improved rate capability, cycling stability, and tolerance to varied operating conditions.

3. Conclusion

In summary, we establish an amorphous Fe–BTC metal-organic xerogel as a redox-responsive binder that transforms the conventionally passive binder phase into a distributed reaction interface for aqueous Zn–I₂ cathodes. Within its nonperiodic Fe–carboxylate network, heterogeneous electrostatic regions favor polyiodide retention near the active material, while adsorption-induced changes in the fitted Fe²⁺/Fe³⁺ contributions, together with interfacial charge redistribution, provide evidence for electronic coupling between the coordination centers and retained iodine species. The spatial integration of polyiodide affinity and electronically responsive Fe coordination centers couples intermediate retention with interfacial electron transfer and subsequent redox conversion, thereby suppressing detectable polyiodide accumulation, reducing electrochemical polarization, and preserving the electrochemical accessibility of iodine. These coupled interfacial effects enable the MOX-based cell to retain 122.8 mAh g⁻¹ after 20,000 cycles at 10 C, with the robustness of the binder further demonstrated through separate high-loading, extreme-temperature, and pouch-cell tests. By recasting the binder as an active regulator of both intermediate transport and interfacial charge transfer, this work establishes a binder-design strategy for coupling intermediate retention with subsequent conversion in multistep conversion electrodes involving soluble intermediates.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (22309029), the Guangdong Basic and Applied Basic Research Foundation (2024A1515140011, 2024A1515110010) and the Dongguan Social Development Technology Foundation (20231800907933). The authors also acknowledge the Dongguan University of Technology Analytical and Testing Center for characterization support.

Conflict of Interest

The authors declare no competing interests.

Supporting Information

Supporting Information is available from the authors.

References

1. Wu, H.; Hao, J.; Zhang, S.; Jiang, Y.; Zhu, Y.; Liu, J.; Davey, K.; Qiao, S.-Z., Aqueous

- Zinc–Iodine Pouch Cells with Long Cycling Life and Low Self-Discharge. *J. Am. Chem. Soc.* **2024**, *146* (24), 16601-16608.
2. Zhang, S.-J.; Hao, J.; Wu, H.; Kao, C.-C.; Chen, Q.; Ye, C.; Qiao, S.-Z., Toward High-Energy-Density Aqueous Zinc–Iodine Batteries: Multielectron Pathways. *ACS Nano* **2024**, *18* (42), 28557-28574.
 3. Zou, Y.; Liu, T.; Du, Q.; Li, Y.; Yi, H.; Zhou, X.; Li, Z.; Gao, L.; Zhang, L.; Liang, X., A four-electron Zn-I₂ aqueous battery enabled by reversible I⁻/I₂/I⁺ conversion. *Nat. Commun.* **2021**, *12* (1), 170.
 4. Li, Q.; Abdalla, K. K.; Xiong, J.; Song, Z.; Wang, Y.; Zhao, Y.; Liu, M.; Fan, Y.; Zhao, Y.; Sun, X.-M., High-energy and durable aqueous Zn batteries enabled by multi-electron transfer reactions. *Energy Mater.* **2024**, *4* (4), 400040.
 5. Zhao, H.; Yin, D.; Qin, Y.; Cui, X.; Feng, J.; Zhang, Y.; Zhao, L.; Gao, N.; Cui, M.; Xiao, C.; Feng, G.; Su, Y.; Xi, K.; Ding, S., Highly Electrically Conductive Polyiodide Ionic Liquid Cathode for High-Capacity Dual-Plating Zinc–Iodine Batteries. *J. Am. Chem. Soc.* **2024**, *146* (10), 6744-6752.
 6. Yan, W.; Liu, Y.; Qiu, J.; Tan, F.; Liang, J.; Cai, X.; Dai, C.; Zhao, J.; Lin, Z., A tripartite synergistic optimization strategy for zinc-iodine batteries. *Nat. Commun.* **2024**, *15* (1), 9702.
 7. Wang, Y.; Cui, Y.; Zhao, M.; Wang, J.; Liu, X.; Zhu, Y.; Yang, Y., Zwitterion-mediated interface chemistry for practical Zn-iodine batteries. *Nat. Commun.* **2025**, *16* (1), 5565.
 8. Wu, J.; Guo, S.; Xie, X.; Qin, M.; Liang, S.; Fang, G., Zinc-compound iodine battery chemistry with dual functional oxalate-based electrolyte. *Adv. Powder Mater.* **2026**, *5* (3), 100385.
 9. Wen, H.; Wen, H.; Sun, Y.; Li, J.; Zhuang, C.; Liu, M.; Li, H.; Fan, H.; Yin, B.; Zhang, S.; Ma, T., The Frontiers of Aqueous Zinc–Iodine Batteries: A Comprehensive Review on Mechanisms, Optimization, and Industrial Prospects. *Adv. Funct. Mater.* **2025**, *35* (31), 2500323.
 10. Pan, H.; Li, B.; Mei, D.; Nie, Z.; Shao, Y.; Li, G.; Li, X. S.; Han, K. S.; Mueller, K. T.; Sprengle, V.; Liu, J., Controlling Solid–Liquid Conversion Reactions for a Highly Reversible Aqueous Zinc–Iodine Battery. *ACS Energy Lett.* **2017**, *2* (12), 2674-2680.
 11. Zhang, S.-J.; Hao, J.; Li, H.; Zhang, P.-F.; Yin, Z.-W.; Li, Y.-Y.; Zhang, B.; Lin, Z.; Qiao, S.-Z., Polyiodide Confinement by Starch Enables Shuttle-Free Zn–Iodine Batteries. *Adv. Mater.* **2022**, *34*

(23), 2201716.

12. Ma, L.; Ying, Y.; Chen, S.; Huang, Z.; Li, X.; Huang, H.; Zhi, C., Electrocatalytic Iodine Reduction Reaction Enabled by Aqueous Zinc-Iodine Battery with Improved Power and Energy Densities. *Angew. Chem. Int. Ed.* **2021**, *60* (7), 3791-3798.
13. Liu, M.; Chen, Q.; Cao, X.; Tan, D.; Ma, J.; Zhang, J., Physicochemical Confinement Effect Enables High-Performing Zinc–Iodine Batteries. *J. Am. Chem. Soc.* **2022**, *144* (47), 21683-21691.
14. Chen, Z.; Wang, F.; Ma, R.; Jiao, W.; Li, D.; Du, A.; Yan, Z.; Yin, T.; Yin, X.; Li, Q.; Zhang, X.; Yang, N.; Zhou, Z.; Yang, Q.-H.; Yang, C., Molecular Catalysis Enables Fast Polyiodide Conversion for Exceptionally Long-Life Zinc–Iodine Batteries. *ACS Energy Lett.* **2024**, *9* (6), 2858-2866.
15. Gao, Y.; Chen, C.; Zhang, J.; Chen, M.; Shan, L.; Luo, Q.; Xing, Z.; Zhao, Z.; Li, J.; Rao, P.; Kang, Z.; Tian, X.; Shi, X., Integrated confinement-chemisorption-catalysis cathode for highly stable zinc-iodine batteries. *Nano Mater Sci.* **2026**, *8* (1), 175-182.
16. Wang, K.; Li, H.; Xu, Z.; Liu, Y.; Ge, M.; Wang, H.; Zhang, H.; Lu, Y.; Liu, J.; Zhang, Y.; Tang, Y.; Chen, S., An Iodine-Chemisorption Binder for High-Loading and Shuttle-Free Zn–Iodine Batteries. *Adv. Energy Mater.* **2024**, *14* (17), 2304110.
17. Yang, J.-L.; Liu, H.-H.; Zhao, X.-X.; Zhang, X.-Y.; Zhang, K.-Y.; Ma, M.-Y.; Gu, Z.-Y.; Cao, J.-M.; Wu, X.-L., Janus Binder Chemistry for Synchronous Enhancement of Iodine Species Adsorption and Redox Kinetics toward Sustainable Aqueous Zn–I₂ Batteries. *J. Am. Chem. Soc.* **2024**, *146* (10), 6628-6637.
18. Chen, M.; Han, X.; Pan, Y.; Tu, H.; Zhu, J.; Shao, M.; Zheng, K.; Wang, W.; Li, K.; Qiao, X.; Shan, L.; Shi, X., Boosting iodine redox kinetics through the inherent electrostatic interaction and electron donor capability of gelatin binder. *Nano Mater Sci.* **2025**, *7* (5), 719-725.
19. Yu, Z.-T.; Gong, Z.-S.; Wen, R.-H.; Hou, Y.-J.; Luo, Z.-Q.; Yuan, Z.-H.; Zhang, N., Gelatinized starch as a low-cost and bifunctional binder enables shuttle-free aqueous zinc–iodine batteries. *Rare Met.* **2024**, *43*, 6351-6361.
20. Zhang, J.; Qiu, C.; Zhou, C.; Guo, S.; Gao, Y.; Li, F.; Wang, X.; Zhao, Z.; Xing, Z.; Li, J.; Rao, P.; Kang, Z.; Tian, X.; Shi, X., Liner-chain polysaccharide binders with strong chemisorption capability for iodine species enables shuttle-free zinc-iodine batteries. *Nano Energy* **2025**, *133*, 110519.

21. Han, X.; Shan, L.; Chen, M.; Li, G.; Zheng, K.; Shao, M.; Chen, Z.; Wang, W.; Qiu, C.; Xing, Z.; Tu, H.; Shi, X., Rational design of an organic mixed ionic-electronic conductor binder for shuttle-suppressed zinc-iodine batteries. *Energy Stor. Mater.* **2026**, *89*, 105179.
22. Machhi, H. K.; Sonigara, K. K.; Bariya, S. N.; Soni, H. P.; Soni, S. S., Hierarchically Porous Metal–Organic Gel Hosting Catholyte for Limiting Iodine Diffusion and Self-Discharge Control in Sustainable Aqueous Zinc–I₂ Batteries. *ACS Appl. Mat. Interfaces* **2021**, *13* (18), 21426-21435.
23. Zhang, S.-J.; Hao, J.; Wu, H.; Hu, Y.; Chen, Q.; Johannessen, B.; Ma, Q.; Luo, D.; Qiao, S.-Z., Electroactive ferrocene/ferrocenium redox coupling for shuttle-free aqueous zinc–iodine pouch cells. *Nat. Chem.* **2026**, *18*, 266–274.
24. Chen, L.; Wang, X.; Rao, Z.; Tang, Z.; Shi, G.; Wang, Y.; Lu, G.; Xie, X.; Chen, D.; Sun, J., One-pot Synthesis of the MIL-100 (Fe) MOF/MOX Homojunctions with Tunable Hierarchical Pores for the Photocatalytic Removal of BTXS. *Appl. Catal., B* **2022**, *303*, 120885.
25. Zhang, S.-J.; Hao, J.; Wu, H.; Chen, Q.; Ye, C.; Qiao, S.-Z., Protein Interfacial Gelation toward Shuttle-Free and Dendrite-Free Zn–Iodine Batteries. *Adv. Mater.* **2024**, *36* (35), 2404011.
26. Wu, C.; Pan, Y.; Jiao, Y.; Wu, P., α -Methyl Group Reinforced Amphiphilic Poly(Ionic Liquid) Additive for High-Performance Zinc–Iodine Batteries. *Angew. Chem. Int. Ed.* **2025**, *64* (21), e202423326.
27. Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C., Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **2011**, *257* (7), 2717-2730.
28. Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P.-L.; Tolbert, S. H.; Abruña, H. D.; Simon, P.; Dunn, B., High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat. Mater.* **2013**, *12* (6), 518-522.
29. Zhong, W.; Cheng, H.; Zhang, S.; Li, L.; Tan, C.; Chen, W.; Lu, Y., Cation-driven phase transition and anion-enhanced kinetics for high energy efficiency zinc-interhalide complex batteries. *Nat. Commun.* **2025**, *16* (1), 4586.
30. Zhao, Y.; Kumteveli, V.; Ludwig, S.; Jossen, A., Investigation of the distribution of relaxation times of a porous electrode using a physics-based impedance model. *J. Power Sources* **2022**, *530*, 231250.

31. Liu, Z.; Fu, B.; Xie, X.; Li, M.; Li, L.; Liang, S.; Fang, G., Bimetallic Cladding-Constructed Interfacial Microenvironment Enabled Highly Reversible Powder Anode for Zn Metal Batteries. *Adv. Mater.* **2026**, 38 (12), e18003.

Just Accepted

Figures and captions

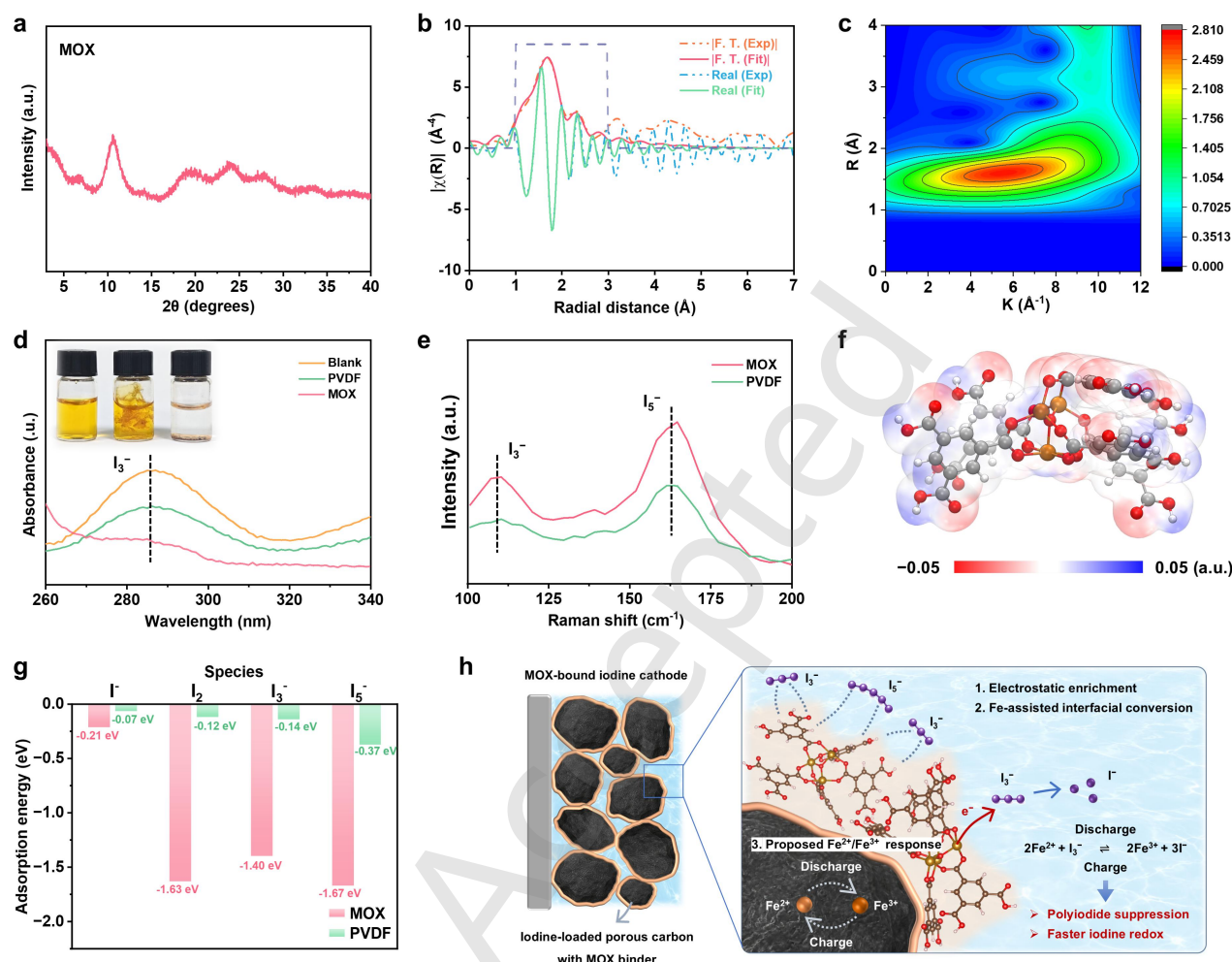


Figure 1. Structure of MOX and its interaction with iodine species. (a) XRD pattern of MOX. (b) Fourier-transformed Fe K-edge EXAFS spectrum and corresponding fit in R space. (c) Fe K-edge WT-EXAFS contour map. (d) Photographs and UV-Vis spectra of the initial I_3^- solution and the solutions after treatment with PVDF or MOX. (e) Raman spectra of PVDF and MOX recovered after exposure to I_3^- , with bands assigned to I_3^- and I_5^- . (f) ESP map of the MOX model. (g) Calculated adsorption energies of I^- , I_2 , I_3^- and I_5^- on MOX and PVDF. (h) Schematic illustration of the proposed arrangement and interfacial function of MOX in the iodine cathode. MOX surrounds the iodine-loaded porous carbon particles, provides heterogeneous electrostatic environments that favor polyiodide retention near the cathode, and contains mixed-valence Fe^{2+}/Fe^{3+} coordination centers proposed to assist interfacial electron transfer and subsequent iodine conversion.

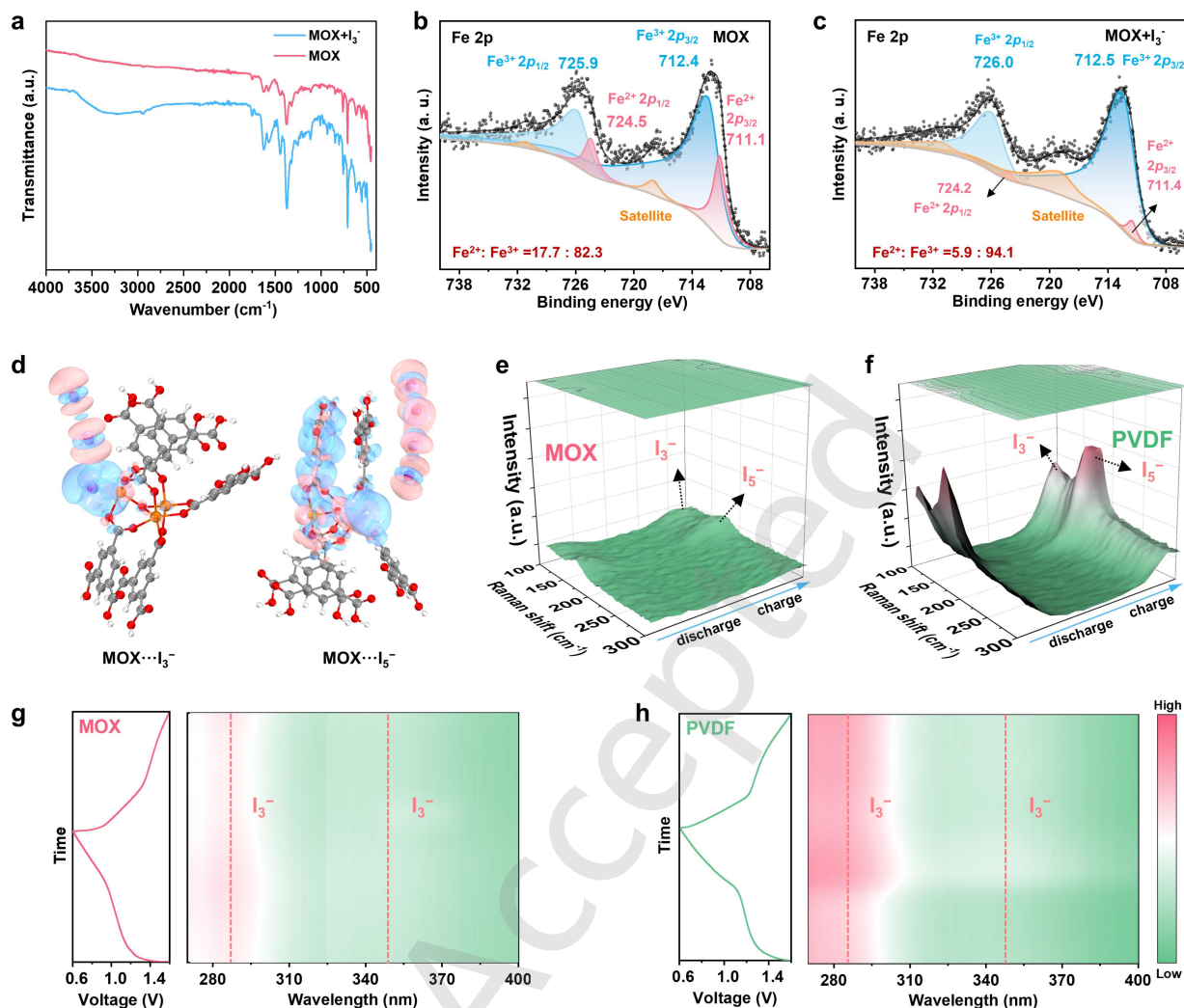


Figure 2. Electronic response of the Fe centers and operando evolution of polyiodide species. (a) FTIR spectra of pristine MOX and MOX after exposure to I_3^- . High-resolution Fe 2p XPS spectra with fitted Fe^{2+} , Fe^{3+} and satellite components for (b) pristine MOX and (c) MOX after exposure to I_3^- . (d) Charge-density-difference maps for I_3^- and I_5^- adsorbed on the MOX model, with cyan and pink regions representing electron depletion and accumulation, respectively. Operando Raman intensity maps collected during charge and discharge of the (e) MOX and (f) PVDF electrodes. Voltage profiles and corresponding operando UV-Vis intensity maps for the (g) MOX and (h) PVDF cells, showing the evolution of soluble polyiodide species over one charge-discharge cycle. The Raman bands at approximately 110 and 162 cm^{-1} are assigned to I_3^- and I_5^- , respectively, while the UV-Vis absorption bands at approximately 288 and 354 nm are assigned to I_3^- .

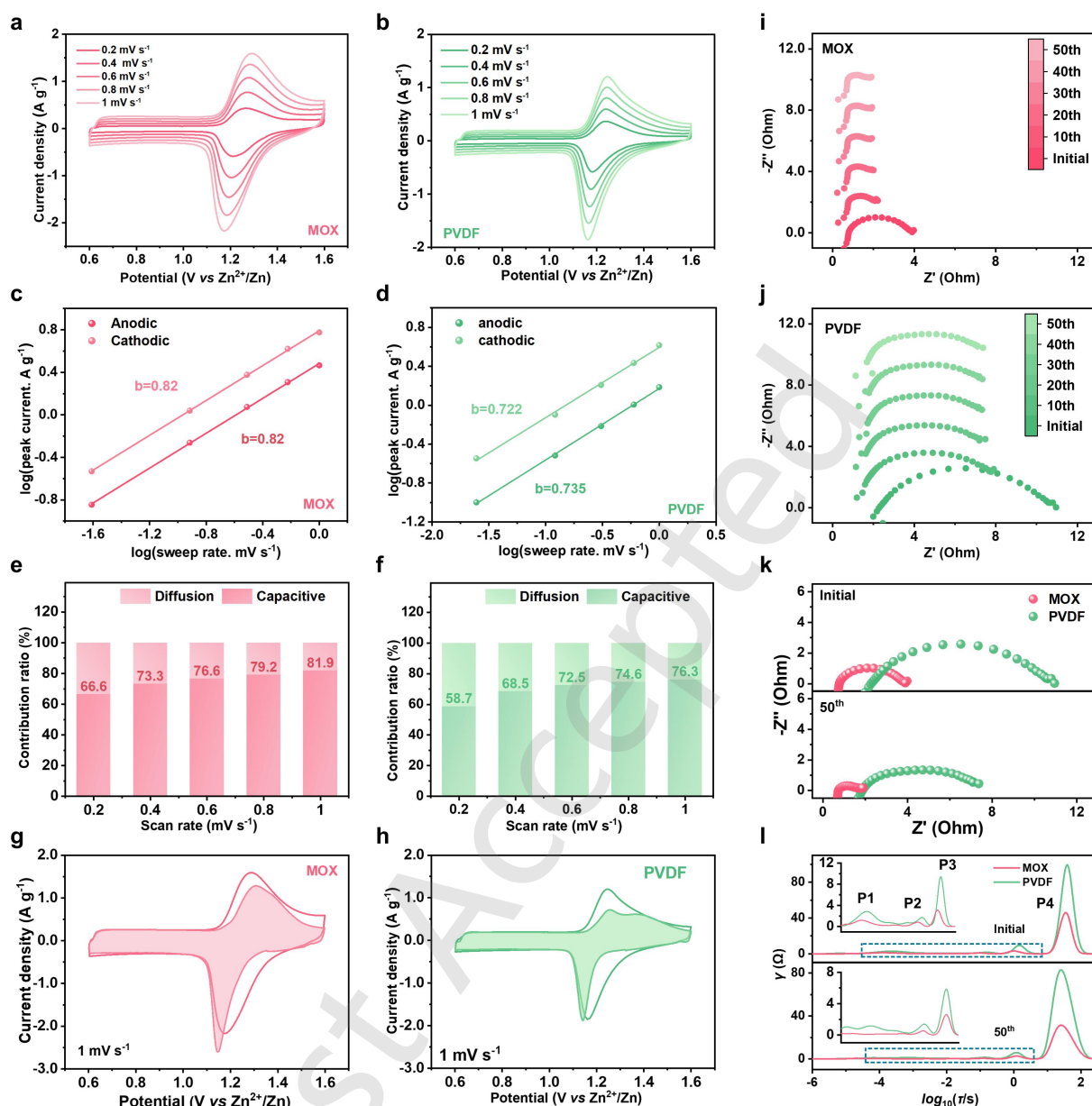


Figure 3. Electrochemical response and apparent iodine redox kinetics of the MOX and PVDF electrodes. CV curves of the (a) MOX and (b) PVDF electrodes recorded at scan rates from 0.2 to 1.0 mV s^{-1} . Logarithmic plots of absolute peak current versus scan rate for the (c) MOX and (d) PVDF electrodes, with b values obtained from $|i_p| = av^b$. Relative $v^{1/2}$ -associated and scan-rate-proportional (k_1v) current contributions of the (e) MOX and (f) PVDF electrodes at different scan rates. CV curves and separated scan-rate-proportional contributions at 1.0 mV s^{-1} for the (g) MOX and (h) PVDF electrodes, with the shaded areas representing the scan-rate-proportional current contribution. Nyquist plots of the (i) MOX and (j) PVDF electrodes from the initial state to

50 cycles. The Nyquist plots collected after 10, 20, 30, 40 and 50 cycles are vertically offset by 2, 4, 6, 8 and 10 Ω , respectively, along the positive $-Z''$ direction for clarity; the initial spectra are shown without offset. (k) Direct comparison of the MOX and PVDF Nyquist responses at the initial state and after 50 cycles. (l) DRT spectra of the MOX and PVDF electrodes at the initial state and after 50 cycles; the insets enlarge the regions marked by the dashed boxes.

Just Accepted

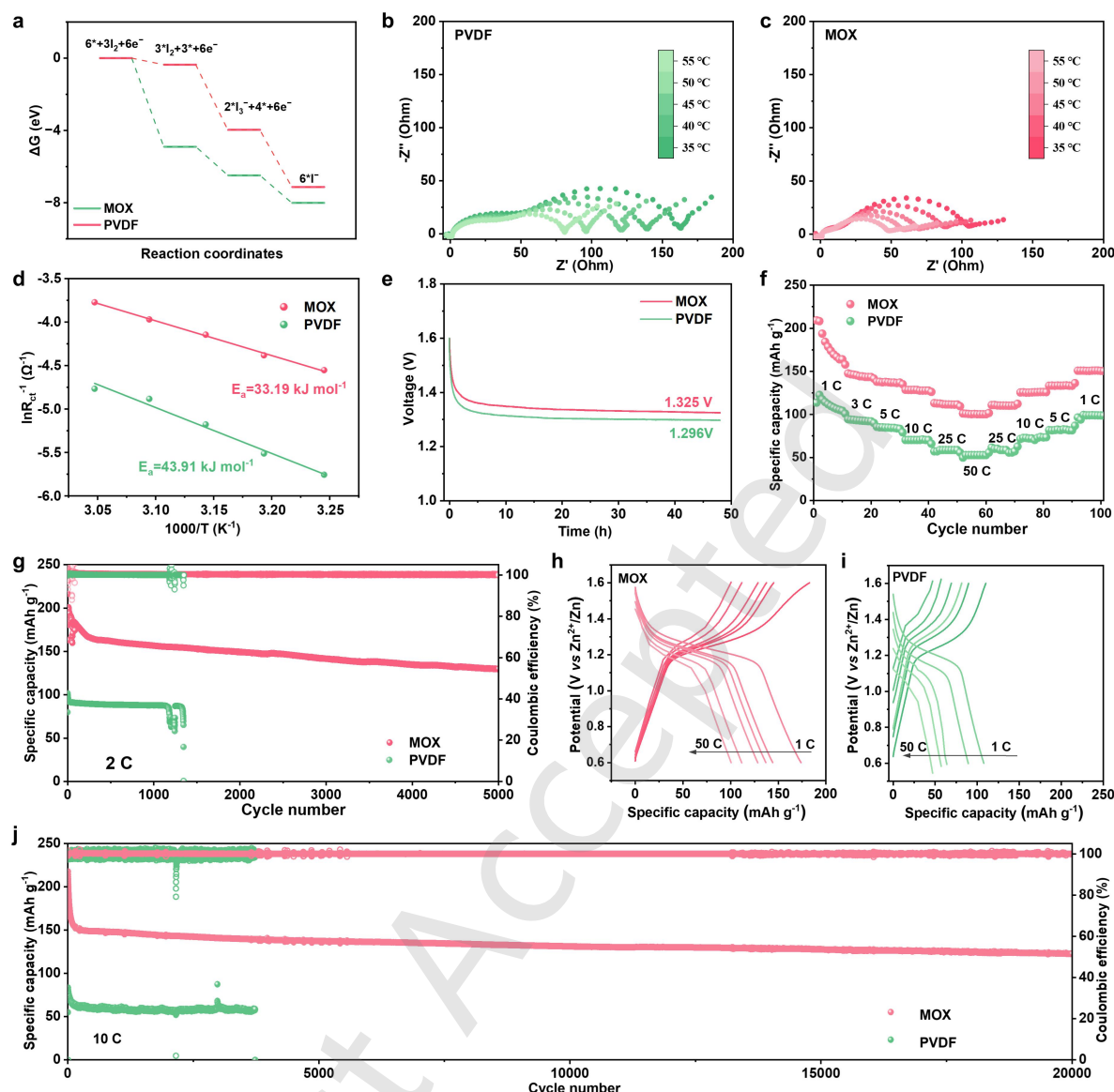


Figure 4. Reaction energetics and electrochemical performance of the MOX and PVDF cells. (a) Calculated stepwise free-energy profiles for the reduction of I_2 to I^- on the MOX and PVDF models. Temperature-dependent Nyquist plots of the (b) PVDF and (c) MOX electrodes measured from 35 to 55 °C. (d) Arrhenius plots derived from the temperature-dependent charge-transfer resistances and the corresponding apparent activation energies. (e) Open-circuit voltage profiles of fully charged MOX and PVDF cells during a 48 h rest. (f) Rate performance of the MOX and PVDF cells from 1 to 50 C. (g) Long-term cycling performance and corresponding Coulombic efficiencies of the MOX and PVDF cells at 2 C. Charge-discharge profiles of the (h) MOX and (i) PVDF cells at different rates. (j) Long-term cycling performance and corresponding Coulombic efficiencies of the MOX and PVDF cells at 10 C.

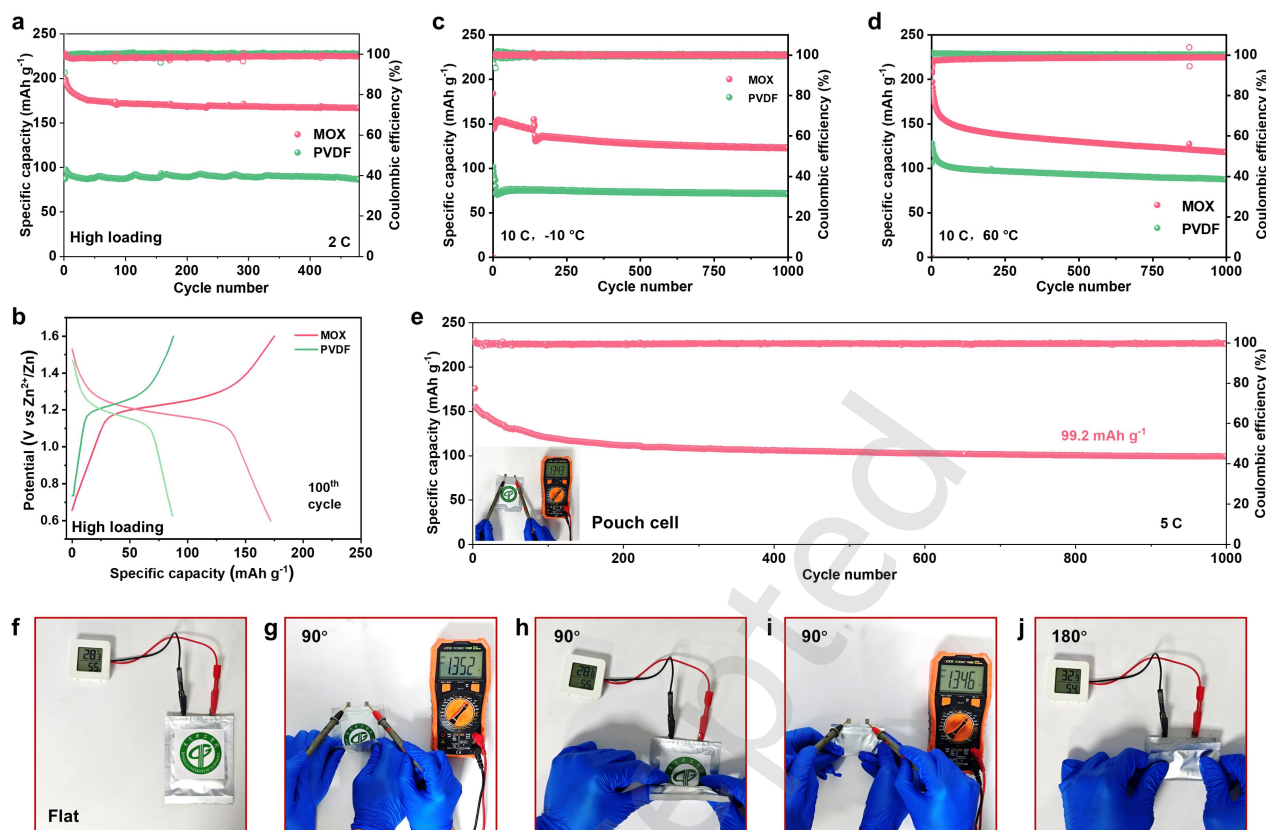


Figure 5. Electrochemical performance under increased iodine loading, temperature extremes, and pouch-cell conditions. (a) Cycling performance and Coulombic efficiencies of the MOX and PVDF cells at 2 C with an iodine loading of 7 mg cm^{-2} . (b) Charge-discharge profiles of the MOX and PVDF cells at the 100th cycle under the same loading condition. Long-term cycling performance and Coulombic efficiencies of the MOX and PVDF cells at 10 C under (c) -10°C and (d) 60°C conditions. (e) Cycling performance and Coulombic efficiency of the MOX pouch cell at 5 C. (f-j) Photographs of the pouch cell powering a hygrometer in flat, 90° -bent, and 180° -bent states, together with the corresponding voltage measurements.

Xinxin Han is pursuing her M.S. degree at the School of Materials Science and Engineering, Dongguan University of Technology, under the guidance of Associate Professor Min Chen. Her research interests lie primarily in the field of aqueous zinc-iodine batteries.



Dr. Min Chen received her Ph.D. degree in Materials Science and Engineering from Chongqing University in 2020. Currently a Distinguished Associate Researcher at Dongguan University of Technology, she focuses on aqueous zinc-iodine/zinc-sulfur batteries, lithium-sulfur/lithium-metal batteries, and biomass functional materials. Her publications appear in *Advanced Energy Materials*, *Advanced Functional Materials*, and *Energy Storage Materials*. Her research is supported by the National Natural Science Foundation of China and the Guangdong Basic and Applied Basic Research Foundation. She is a recipient of the Dongguan Municipal Special Talent (Category III) award.



Dr. Lu Chen received her Ph.D. degree in Materials Science and Engineering from Zhengzhou University in 2022. From 2023 to 2025, she conducted postdoctoral research at the University of Electronic Science and Technology of China and the Dongguan University of Technology. Currently,

she is an Assistant Researcher at the Dongguan University of Technology, focusing on the synthesis and application of metal-organic frameworks (MOFs) and metal-organic gels.



Dr. Yongqiang Yang received his Ph.D. degree in Central South University in 2023. Currently, he is a postdoctoral fellow in The Hong Kong Polytechnic University, focusing on Zn-halogen energy storage chemistry and the practical application of Zn-based energy storage devices.



Supporting Information

Metal-Organic Xerogel Binder Enables Strong Chemisorption and Fast Conversion Kinetics towards Shuttle-Suppressed Zn–I₂ Batteries

Xinxin Han ^a, Yicai Pan ^b, Min Chen ^{a, *}, Haoran Tu ^a, Wenlong Wang ^a, Lu Chen ^{a, *}, Yongqiang Yang ^{c, *}

^a School of Materials Science and Engineering, Dongguan University of Technology, Dongguan, 523808, China

^b Department of Materials Science and Engineering & Center of Super-Diamond and Advanced Films (COSDAF), City University of Hong Kong, Hong Kong 999077, China

^c Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hong Kong SAR 999077, China

* Corresponding authors email address: chenmin@dgut.edu.cn; chl2008051160@163.com; yong-qiang.yang@polyu.edu.hk

1. Experimental section

1.1 Materials

Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), trimesic acid (H_3BTC), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), iodine (I_2 , 99.8%), and zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Aladdin Reagent Co., Ltd. Ethanol was obtained from Shanghai Macklin Biochemical Co., Ltd. Poly(vinylidene fluoride) (PVDF) was purchased from Dongguan Canrd Laboratory Equipment Technology Co., Ltd. Activated carbon (AC; specific surface area $\approx 1800 \text{ m}^2 \text{ g}^{-1}$) was supplied by Jiangsu XFNANO Materials Tech Co., Ltd., and Ketjen Black (KB), used as the conductive additive, was obtained from Suzhou Shengernuo Technology Co., Ltd. Zinc foil, glass-fiber separators, and 400-mesh stainless-steel mesh were used for electrode preparation and cell assembly. Deionized water was used in all aqueous procedures. Unless otherwise specified, all chemicals and materials were used as received without further purification.

1.2 Synthesis of MOX

MOX was synthesized via a solvothermal coordination process. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1 mmol) and H_3BTC (1 mmol) were dissolved in 30 mL of DMF under magnetic stirring to form a homogeneous precursor solution. The solution was then transferred to a 100 mL Teflon-lined stainless-steel autoclave and heated at 150 °C for 16 h. After naturally cooling to room temperature, the resulting product was collected and washed three times each with DMF and ethanol to remove residual precursors and soluble impurities. The remaining DMF was subsequently replaced with ethanol by solvent exchange. Finally, the ethanol-exchanged product was vacuum-dried to yield the Fe–BTC metal–organic xerogel, denoted as MOX.

1.3 Preparation of the AC@I₂ Composite and Cathodes

The activated-carbon/iodine composite (AC@I₂) was prepared using a melt-infiltration method. AC and I₂ were mixed at a mass ratio of 1:1 and sealed in a glass vial. The mixture was heated at 120 °C for 6 h to allow molten iodine to infiltrate the porous carbon host. After naturally cooling to room temperature, the resulting black powder was collected and denoted as AC@I₂.

To prepare the iodine cathodes, AC@I₂, Ketjen Black, and MOX or PVDF binder were mixed at a mass ratio of 70:20:10 and thoroughly ground to obtain a homogeneous mixture. Deionized water and NMP were used as the slurry solvents for the MOX- and PVDF-based cathodes, respectively. Each slurry was evenly coated onto a 400-mesh stainless-steel current collector and dried overnight

to obtain the corresponding AC@I₂ cathode.

1.4 Sample Preparation for Polyiodide Adsorption Measurements

A fresh I₃[−] solution was prepared by dissolving I₂ and KI in deionized water at equal concentrations of 20 mM. For FTIR and XPS characterization, 10 mg of MOX or PVDF was dispersed in 3 mL of the I₃[−] solution and allowed to stand for 24 h. The solids were then recovered and dried prior to characterization. The resulting samples were denoted as MOX+I₃[−] and PVDF+I₃[−], respectively.

For the visual adsorption test and UV–Vis measurements, equal masses of MOX and PVDF were separately immersed in 5 mL of the freshly prepared I₃[−] solution for 24 h. An I₃[−] solution without adsorbent was maintained under identical conditions as the blank control. After adsorption, the supernatants were collected and diluted 30-fold with deionized water before UV–Vis analysis.

For Raman characterization, the MOX and PVDF solids were recovered after 24 h of exposure to the I₃[−] solution and dried prior to measurement. The resulting spectra were used to identify polyiodide species retained within the binder phases after adsorption.

1.5 Materials Characterization

Powder X-ray diffraction (XRD) patterns of MOX were recorded on a Rigaku D/max 2500 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) over a 2θ range of 5–40°. Fe K-edge X-ray absorption spectroscopy (XAS) was performed using a laboratory-based X-ray absorption spectrometer to probe the local coordination environment of the Fe centers. The extended X-ray absorption fine structure (EXAFS) spectra were Fourier transformed and fitted over a k range of 3.0–10.0 $\text{\AA}^{-1}$ and an R range of 1.0–3.0 $\text{\AA}$. The fit contained 8.7 independent points and six variables and gave an R -factor of 0.011. The detailed fitting parameters, including the coordination numbers, Fe–O bond lengths, Debye–Waller factors, energy shift, amplitude reduction factor, and available fitting uncertainties, are summarized in Table S1. Wavelet-transform EXAFS (WT-EXAFS) analysis was further conducted to differentiate the local Fe–O and Fe–Fe scattering contributions.

Table S1. Fe K-edge EXAFS fitting parameters for the Fe sites in MOX.

Parameter or path	Value	CN	$R(\text{\AA})$	$\sigma^2(\text{\AA}^2)$
k fitting range	3.0–10.0 $\text{\AA}^{-1}$	—	—	—
R fitting range	1.0–3.0 $\text{\AA}$	—	—	—

Independent points	8.7	—	—	—
Number of variables	6	—	—	—
R-factor	0.011	—	—	—
S_0^2	1.0	—	—	—
ΔE_0	−1.5 eV	—	—	—
Fe–O ₁	—	1.0	1.98 ± 0.02	0.0107 ± 0.0042
Fe–O ₂	—	1.0	2.05 ± 0.02	0.0086 ± 0.0026
Fe–O ₃	—	1.0	2.10 ± 0.06	0.0001
Fe–O ₄	—	1.0	2.13	0.0001

CN, coordination number; R , fitted bond distance; and σ^2 , Debye–Waller factor. Uncertainties are reported as provided in the original fitting output.

UV–Vis absorption spectra were recorded using a Hitachi UH4150 spectrophotometer. Raman spectra were collected on a HORIBA XploRA PLUS Raman microscope with a 532 nm excitation laser. Fourier-transform infrared (FTIR) spectra were acquired using a PerkinElmer Frontier FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCALAB Xi spectrometer, and all binding energies were calibrated against the C 1s peak at 284.8 eV. The Fe 2p spectra were fitted with Fe²⁺, Fe³⁺, and satellite components. For each ionic Fe doublet, the Fe 2p_{1/2}–Fe 2p_{3/2} separation was constrained to 12.8–13.8 eV, and the Fe 2p_{1/2} peak height was linked to 0.489 times that of the corresponding Fe 2p_{3/2} component. The peak-width and line-shape parameters were linked within each doublet, with the peak-width fitting parameter bounded between 0.5 and 5.0 eV. Satellite contributions were treated separately. The relative Fe²⁺ and Fe³⁺ fractions were normalized to their combined quantified contribution, excluding satellite components. The Fe⁰ contribution likely originates from the stainless-steel mesh current collector and was excluded from the relative Fe²⁺/Fe³⁺ quantification.

The surface morphologies of the cycled Zn anodes were examined using a Thermo Scientific Verios G4 UC scanning electron microscope (SEM), and the corresponding elemental compositions were analyzed by energy-dispersive X-ray spectroscopy (EDS). Prior to SEM and EDS characterization, the Zn anodes were retrieved from the disassembled cells, gently rinsed with deionized water, and naturally dried at room temperature.

1.6 Operando Raman and UV–Vis Measurements

Operando Raman measurements were performed using a custom-designed electrochemical cell equipped with an optical window. The cell was assembled with an AC@I₂ cathode containing either MOX or PVDF as the binder, a Zn foil anode, a glass-fiber separator, and 2 M ZnSO₄ aqueous electrolyte. During galvanostatic charge and discharge between 0.6 and 1.6 V, Raman spectra were continuously collected using a HORIBA XploRA PLUS Raman microscope with a 532 nm excitation laser. The electrochemical profiles and Raman spectra were recorded synchronously to track the evolution of polyiodide species under operating conditions.

Operando UV–Vis measurements were carried out using a custom spectroelectrochemical cell assembled in a quartz cuvette with an AC@I₂ cathode and a Zn foil anode. To ensure sufficient optical transmittance, 40 μ L of 2 M ZnSO₄ electrolyte was diluted with deionized water to a final volume of 1.20 mL, corresponding to a 30-fold dilution and a final ZnSO₄ concentration of approximately 0.067 M, before being introduced into the cuvette cell. The cell was continuously charged and discharged between 0.6 and 1.6 V, while UV–Vis spectra were collected at regular intervals using a Hitachi UH4150 spectrophotometer. The time-resolved spectra were correlated with the corresponding voltage profiles to monitor the dynamic accumulation and conversion of soluble polyiodides during electrochemical cycling.

Both operando Raman and operando UV–Vis measurements were conducted at 4 C (844 mA g⁻¹). The iodine loadings were 1.64 mg cm⁻² for the Raman measurements and 0.80 mg cm⁻² for the UV–Vis measurements. Raman and UV–Vis spectra were acquired at intervals of 1 min and 30 s, respectively. The intensity maps were constructed directly from the recorded spectral intensities without normalization. For each spectroscopic technique, the MOX and PVDF maps were plotted using the same intensity scale.

1.7 Electrochemical Measurements

Zn–I₂ coin cells were assembled using an AC@I₂ cathode, a Zn foil anode, a glass-fiber separator, and 2 M ZnSO₄ aqueous electrolyte. Unless otherwise specified, the conventional coin cells used for rate and long-term cycling measurements employed cathodes with a diameter of 12 mm and a typical iodine loading of approximately 1.5 mg cm⁻². The effective cathode area was approximately 1.13 cm², corresponding to approximately 1.70 mg of iodine per cathode. Each cell contained approximately 150 μ L of 2 M ZnSO₄ electrolyte, giving an electrolyte-to-iodine ratio of

approximately $88 \mu\text{L mg}^{-1}$. The Zn foil had a diameter of 12 mm and a thickness of 100 μm . Five cells were independently assembled and tested for each of the rate, 2 C long-term cycling, and 10 C long-term cycling measurements, and representative results are reported. For the high-loading measurements, circular cathodes with a diameter of 12 mm and an effective area of approximately 1.13 cm^2 were used. The iodine areal loading was 7 mg cm^{-2} , corresponding to approximately 7.9 mg of iodine per cathode. Each cell contained approximately 200 μL of 2 M ZnSO_4 electrolyte.

Three pouch cells were independently assembled using single-layer, single-side-coated cathodes with an effective coated area of $4.0 \times 4.0 \text{ cm}^2$. The iodine areal loading of the independently assembled pouch cells ranged from 1.2 to 1.7 mg cm^{-2} . The representative pouch cell used for the reported electrochemical measurements had an iodine loading of 1.6 mg cm^{-2} , corresponding to a total iodine mass of 25.6 mg, and contained 4.0 mL of 2 M ZnSO_4 electrolyte. A $4.2 \times 4.2 \text{ cm}^2$ Zn foil with a thickness of 100 μm was used as the anode.

Unless otherwise specified, all cells were tested at room temperature within a voltage window of 0.6–1.6 V. Galvanostatic charge–discharge, rate-capability, and long-term cycling measurements were conducted using a NEWARE battery-testing system (CT-4008Tn-5V10mA-164). Specific capacities and current densities were calculated based on the mass of active iodine in the AC@I₂ cathode. A rate of 1 C was defined as 211 mA g^{-1} based on the mass of I₂, corresponding to the theoretical two-electron capacity of iodine.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using a Bio-Logic VMP-3 electrochemical workstation. CV curves were recorded between 0.6 and 1.6 V at scan rates of 0.2–1.0 mV s^{-1} . EIS spectra were collected over a frequency range of 100 kHz to 10 mHz. For cycling-dependent impedance analysis, cells were measured in the initial state and after selected numbers of cycles. Temperature-dependent EIS measurements were conducted from 35 to 55 $^{\circ}\text{C}$, and the extracted charge-transfer resistances were used for Arrhenius analysis to determine the apparent activation energies. For self-discharge measurements, the cells were first fully charged and then rested under open-circuit conditions for 48 h, during which the open-circuit voltage was continuously recorded. Low- and high-temperature cycling tests were conducted at -10 and $60 \text{ }^{\circ}\text{C}$, respectively, using a temperature-controlled chamber. Pouch cells were assembled using enlarged AC@I₂ cathodes containing MOX as the binder, Zn foil anodes, glass-fiber separators, and 2 M ZnSO_4 aqueous electrolyte, followed by heat sealing in aluminum-laminated

pouches. The pouch cells were evaluated by galvanostatic cycling and were additionally tested in flat and mechanically bent configurations to assess their electrochemical output under deformation.

1.8 Computational Details

All DFT calculations were performed using ORCA 6.1.0.[1,2] Geometry optimizations and subsequent single-point energy calculations of all systems were carried out at the PBE0-D4/def2-TZVP level [3-5], together with the def2/J auxiliary basis set [6], RIJCOSX approximation [7,8], TightSCF convergence criterion, DefGrid3 numerical integration grid, and CPCM implicit solvation model [9,10] with water as the solvent. For Fe-containing MOX systems, unrestricted Kohn-Sham calculations were used, with the charge and spin multiplicity set to 0 and 16, respectively.

The single-point electronic energies were used for adsorption-energy calculations, according to:

$$\Delta E = E_{\text{complex}} - (E_{\text{fragment 1}} + E_{\text{fragment 2}})$$

where E_{complex} is the electronic energy of the optimized complex, and $E_{\text{fragment 1}}$, $E_{\text{fragment 2}}$ are the electronic energies of the corresponding isolated fragments. The calculated binding energies are summarized in **Table S2**. Electrostatic potential (ESP), independent gradient model based on Hirshfeld partition (IGMH) analysis and differential electron-density were analyzed using Multiwfn[11] and visualized using VMD.[12]

Table S2. Electronic energies of the adsorption complexes and isolated fragments, together with the calculated adsorption energies of iodine species on the MOX and PVDF models.

System	E_{complex} (eV)	$E_{\text{fragment 1}}$ (eV)	$E_{\text{fragment 2}}$ (eV)	ΔE (eV)
MOX-I ⁻	-221726.49858	-213619.78096	-8106.50401	-0.21361
MOX-I ₂	-229824.81874	-213619.78096	-16203.40681	-1.63097
MOX-I ₃ ⁻	-237931.8101	-213619.78096	-24310.63163	-1.39751
MOX-I ₅ ⁻	-254135.78708	-213619.78096	-40514.33474	-1.67138
PVDF-I ⁻	-17813.50677	-9706.9369	-8106.50401	-0.06587
PVDF-I ₂	-25910.46393	-9706.9369	-16203.40681	-0.12022
PVDF-I ₃ ⁻	-34017.7082	-9706.9369	-24310.63163	-0.13967
PVDF-I ₅ ⁻	-50221.645	-9706.9369	-40514.33474	-0.37336

The Gibbs free energy of each molecular species was obtained from ORCA thermochemistry

analysis, with the frequency calculations performed at the same level to verify the optimized structures and obtain thermodynamic corrections at 298.15 K:

$$G = E_{\text{elec}} + G_{\text{corr}}$$

$$G_{\text{corr}} = E_{\text{ZPE}} + \Delta H_{\text{thermal}} - TS$$

where E_{elec} is electronic energy, E_{ZPE} is the zero-point energy, $\Delta H_{\text{thermal}}$ is the thermal enthalpy correction, and S is the entropy from vibrational analysis.

The relative Gibbs free energy of each state was referenced to the initial state. The Gibbs free-energy change of each reaction step was calculated from the Gibbs free energies of the corresponding products and reactants according to the stoichiometric relation:

$$\Delta G = \sum_i \nu_i G_{\text{product},i} - \sum_j \nu_j G_{\text{reactant},j}$$

For electrochemical steps, the electron chemical potential was included through the corresponding electron term in the state free energy. Equivalently, the potential-dependent free-energy change can be expressed as:

$$\Delta G(U) = \Delta G(0) - neU [13]$$

where n is the number of transferred electrons, e is the elementary charge, and U is the applied electrode potential.

1.9 Kinetic and Electrochemical Analyses

The relationship between the absolute redox peak current ($|i_p|$) and scan rate (v) was analyzed using the following power-law equations:

$$|i_p| = av^b$$

$$\log|i_p| = \log(a) + b \log(v)$$

where a and b are adjustable parameters. The b value was obtained from the slope of the linear fit of $\log|i_p|$ versus $\log(v)$. A value approaching 0.5 indicates a predominantly diffusion-controlled response, whereas a value approaching 1.0 indicates predominantly capacitive or surface-controlled behavior.

The current response at a given potential was separated into capacitive-controlled and diffusion-controlled contributions according to:

$$i(V) = k_1 v + k_2 v^{1/2}$$

where $k_1 v$ and $k_2 v^{1/2}$ represent the capacitive-controlled and diffusion-controlled current contributions, respectively. The values of k_1 and k_2 were obtained from the linear relationship:

$$\frac{i(V)}{v^{1/2}} = k_1 v^{1/2} + k_2$$

In this analysis, the capacitive-controlled contribution refers to the current component that varies linearly with scan rate. This component may include electric-double-layer charging and fast surface or near-surface Faradaic reactions and should therefore not be interpreted exclusively as electric-double-layer capacitance. The $k_2 v^{1/2}$ term represents the current response associated with diffusion-coupled electrochemical processes.

The capacitive-controlled fraction at each scan rate was determined by integrating the absolute $k_1(V)v$ current over the investigated potential window and normalizing it to the integrated absolute total current. The remaining fraction was assigned to the diffusion-controlled contribution. The dependence of the redox peak current on the square root of the scan rate was further examined using the following empirical linear relationship:

$$i_p = k v^{1/2} + c$$

where i_p is the redox peak current, k is the fitted slope, and c is the intercept.

Apparent Tafel slopes were derived from the CV curves collected at 0.2 mV s^{-1} by fitting the linear regions of the electrode potential (E) against the logarithm of the absolute current density (j):

$$E = a + b \log|j|$$

where b is the apparent Tafel slope. The apparent activation energies were determined from the temperature-dependent charge-transfer resistances according to the Arrhenius relationship:

$$\frac{1}{R_{ct}} = A e^{-\frac{E_a}{RT}}$$

where R_{ct} is the charge-transfer resistance, A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. The E_a values were calculated from the slopes of the linear fits of $\ln(R_{ct}^{-1})$ versus $1000/T$. Accordingly, for a fitted slope m , the apparent activation energy was calculated according to $E_a = -1000 mR$.

Distribution of relaxation times (DRT) analysis was performed by transforming the EIS spectra into relaxation-time-dependent impedance distributions. The impedance response was represented as:

$$Z(\omega) = R_{\infty} + \int_{-\infty}^{\infty} \frac{\gamma(\ln\tau)}{1 + j\omega\tau} d(\ln\tau)$$

where R_{∞} is the high-frequency resistance, $\gamma(\ln\tau)$ is the DRT function, τ is the relaxation time, and ω is the angular frequency.

2. Supplementary figures and captions

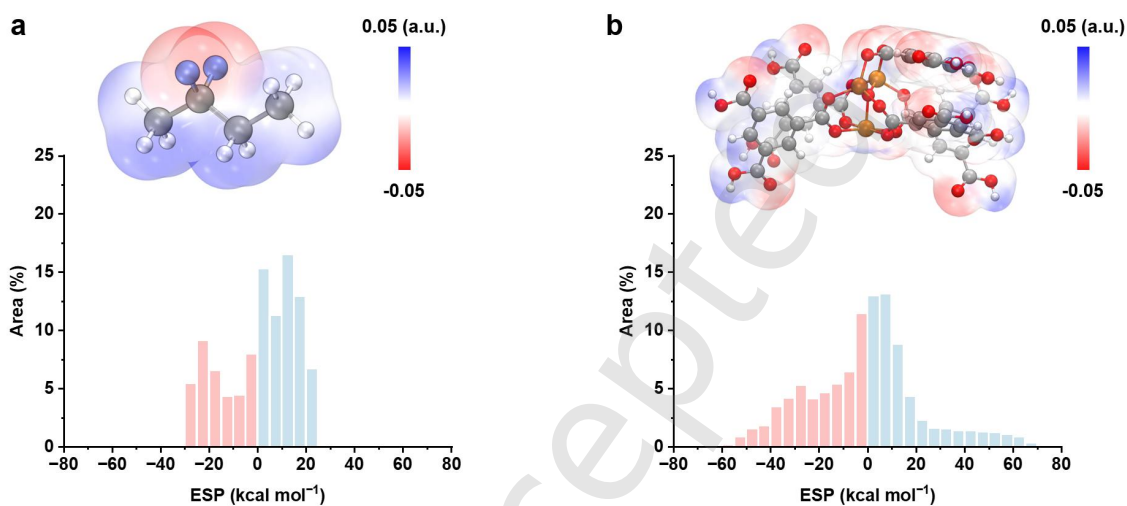


Figure S1. ESP maps and surface-area-weighted ESP distributions of (a) PVDF and (b) MOX.

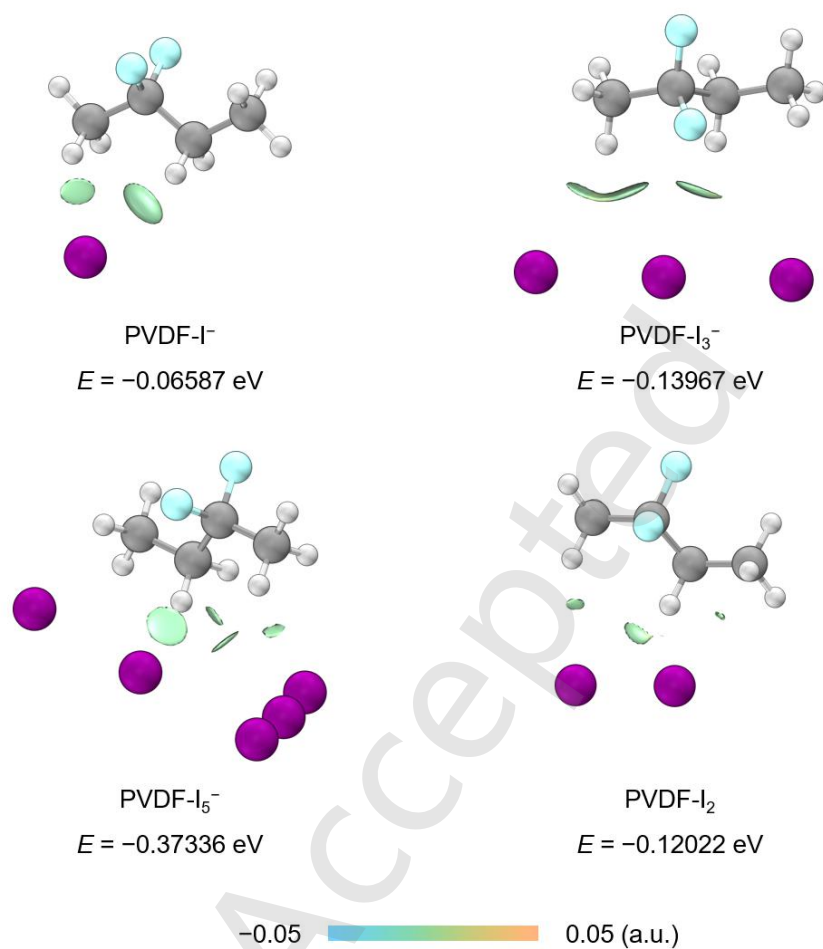


Figure S2. Calculated interaction energies and IGMH maps for PVDF with I⁻, I₂, I₃⁻ and I₅⁻.

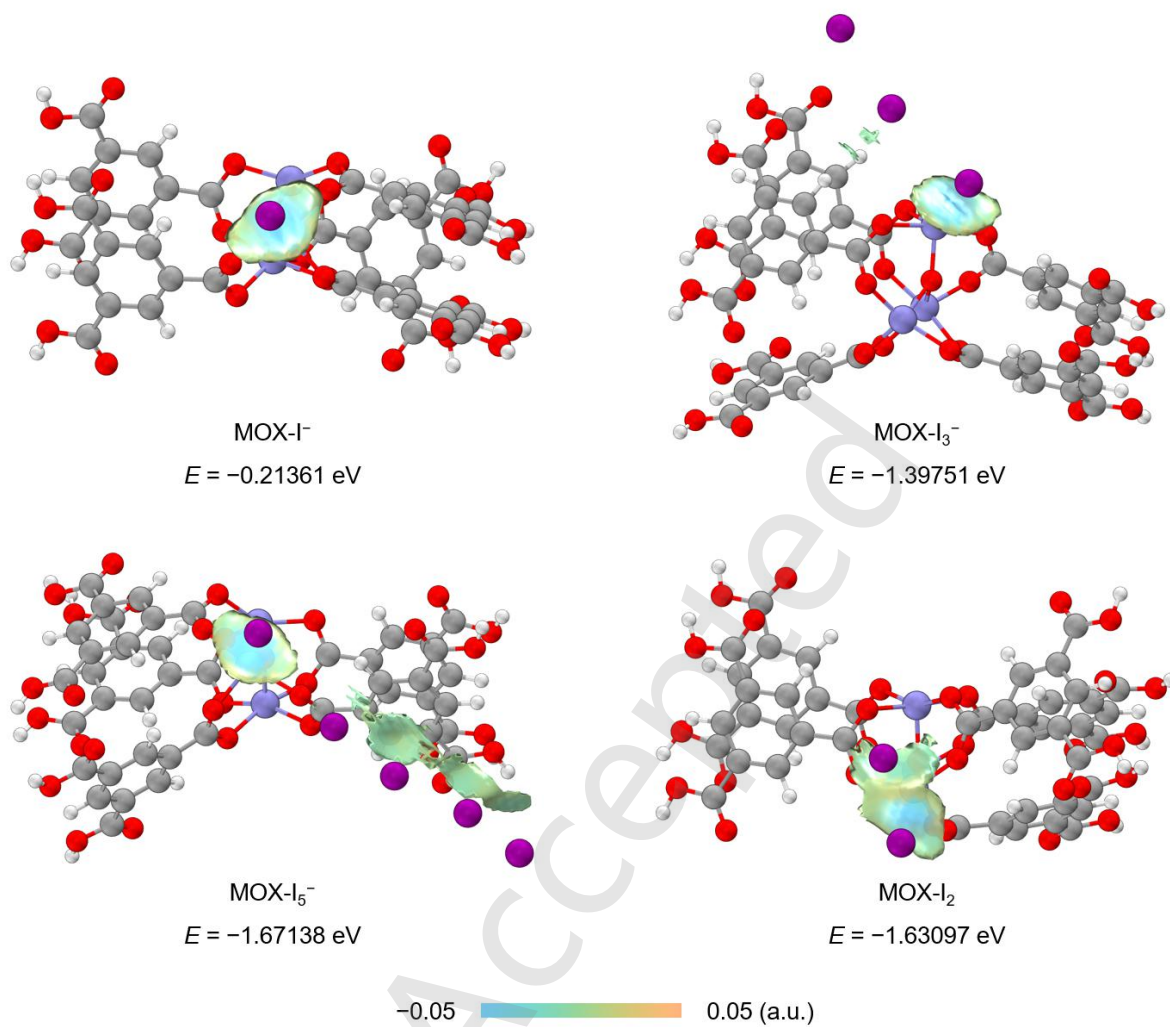


Figure S3. Calculated interaction energies and IGMH maps for MOX with I⁻, I₂, I₃⁻ and I₅⁻.

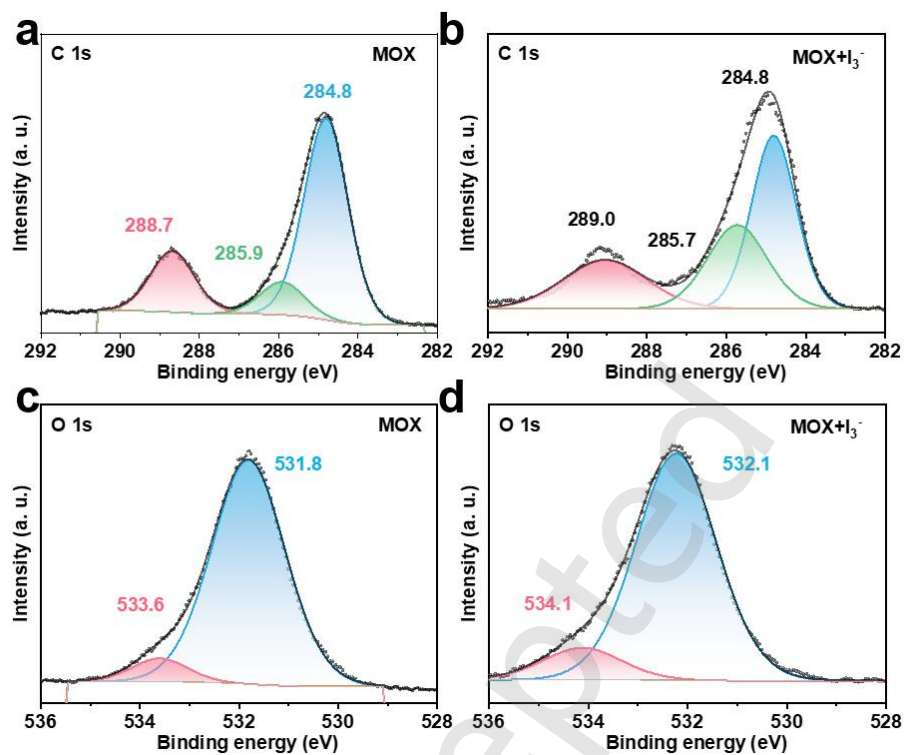


Figure S4. High-resolution C 1s XPS spectra of (a) pristine MOX and (b) MOX after exposure to I₃⁻, and high-resolution O 1s XPS spectra of (c) pristine MOX and (d) MOX after exposure to I₃⁻.

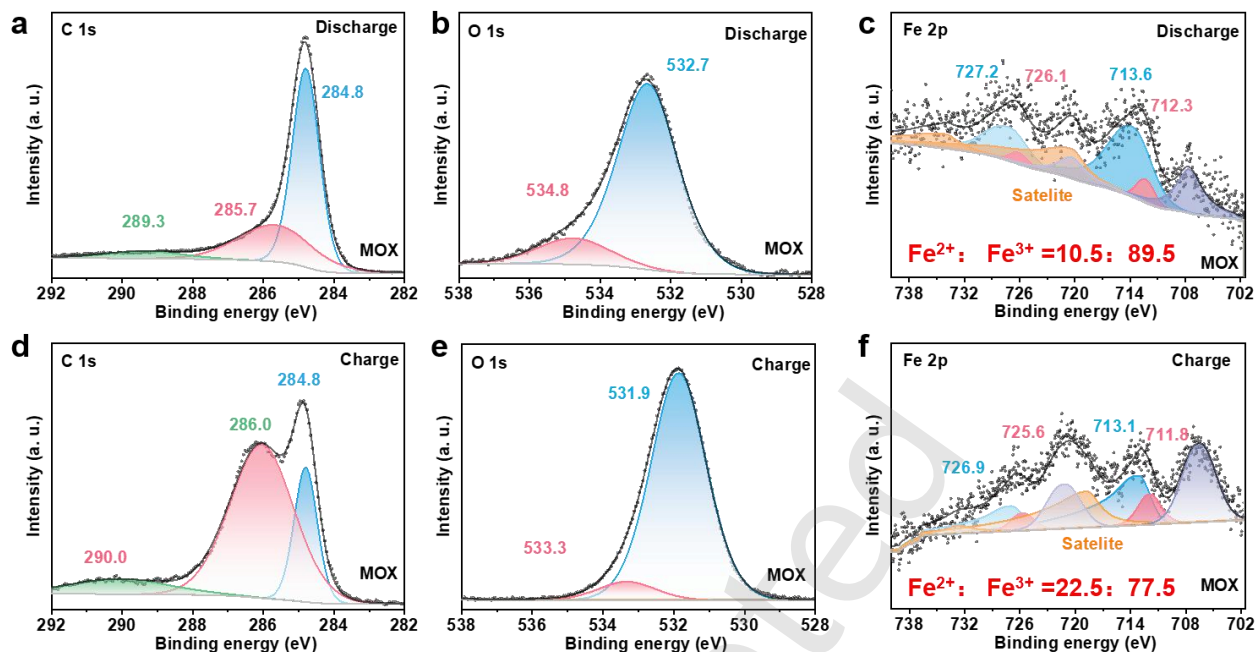


Figure S5. Ex situ high-resolution (a,d) C 1s, (b,e) O 1s, and (c,f) Fe 2p XPS spectra of MOX-containing cathodes collected after (a–c) discharge to 0.6 V and (d–f) subsequent recharge to 1.6 V. The Fe²⁺ and Fe³⁺ percentages represent their relative fractions normalized to the fitted ionic Fe contributions, excluding the Fe⁰ and satellite components.

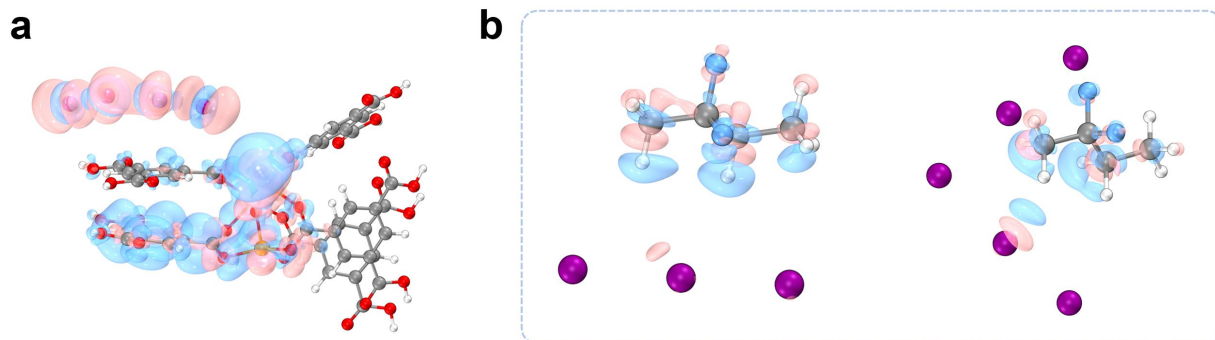


Figure S6. Charge-density differences of I_3^- adsorbed on the (a) MOX and (b) PVDF models. The pink and cyan regions represent electron accumulation and depletion, respectively.

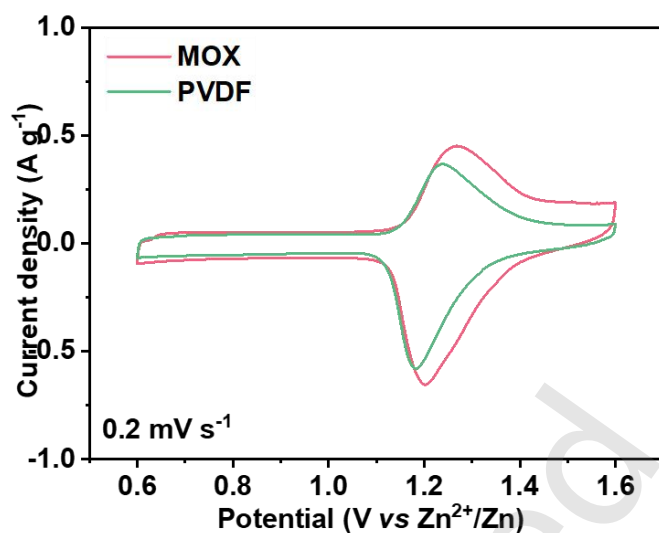


Figure S7. Comparative CV profiles of the MOX and PVDF electrodes at a scan rate of 0.2 mV s^{-1} .

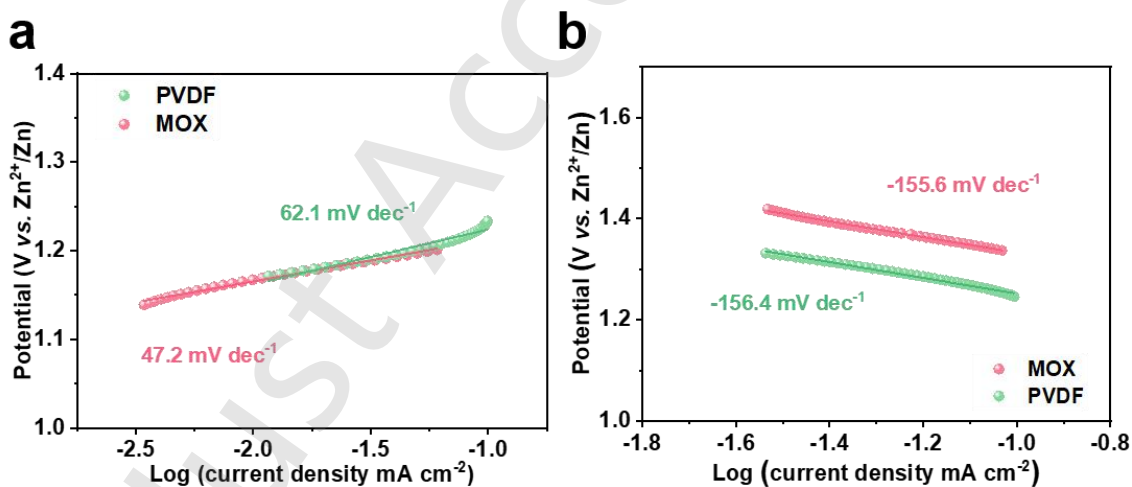


Figure S8. Apparent Tafel plots derived from the CV profiles of the MOX and PVDF electrodes at 0.2 mV s^{-1} for the (a) anodic and (b) cathodic reaction branches.

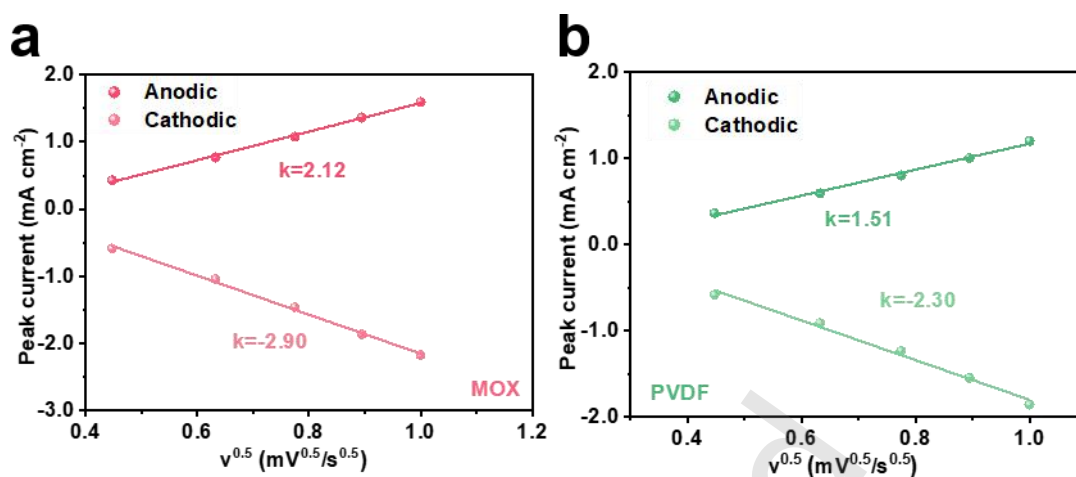


Figure S9. Linear relationships between the redox peak current and the square root of the scan rate for the (a) MOX and (b) PVDF electrodes.

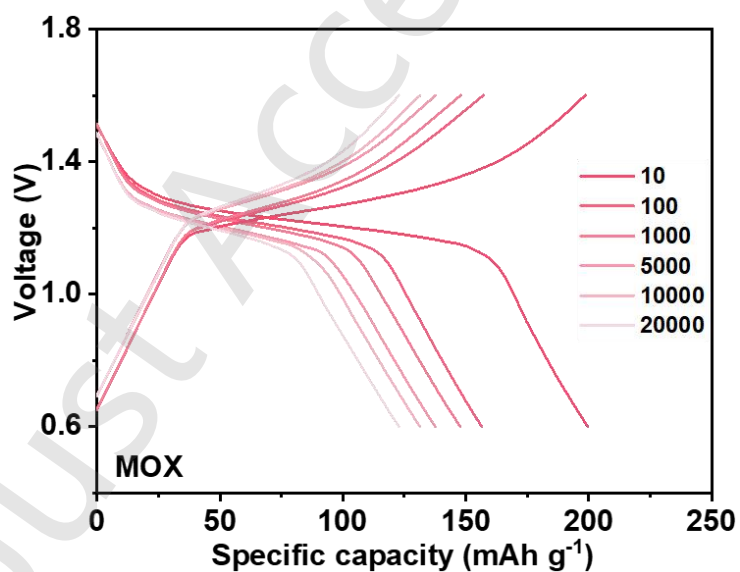


Figure S10. Charge-discharge profiles of the MOX cell at selected cycling stages of 10, 100, 1000, 5000, 10,000, and 20,000 cycles at 10 C.

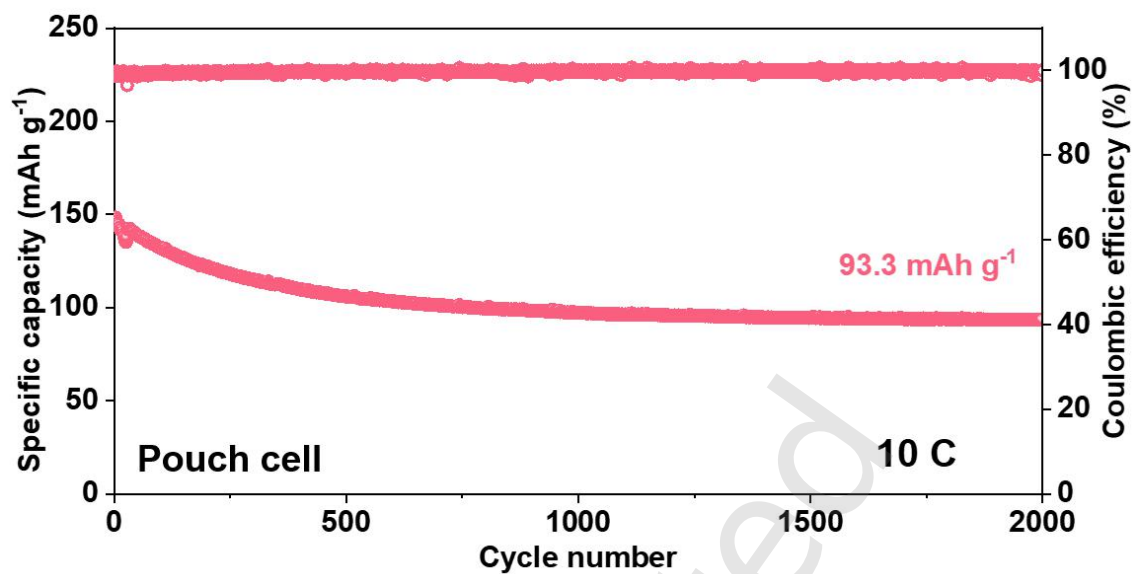


Figure S11. Long-term cycling performance and Coulombic efficiency of the Zn-I₂ pouch cell assembled using MOX as the binder at 10 C.

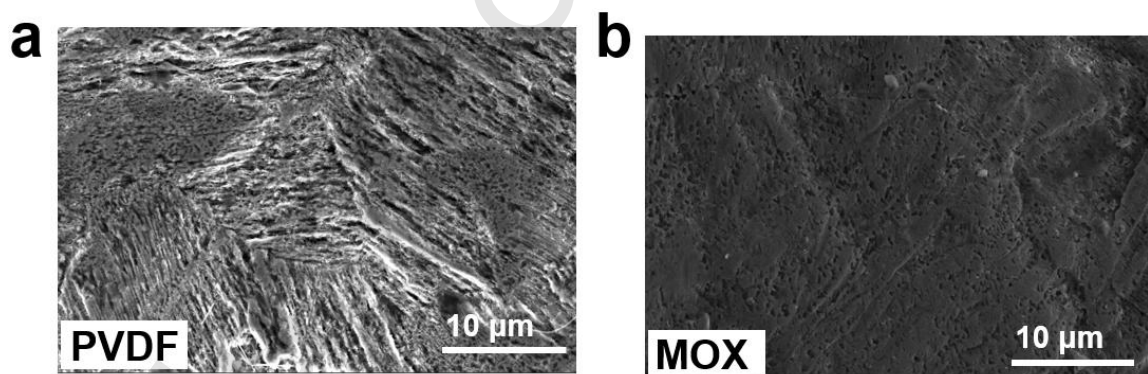


Figure S12. SEM images of Zn anodes recovered from the Zn-I₂ cells after 500 cycles at 10 C: (a) PVDF-based cell and (b) MOX-based cell. Scale bars: 10 μm.

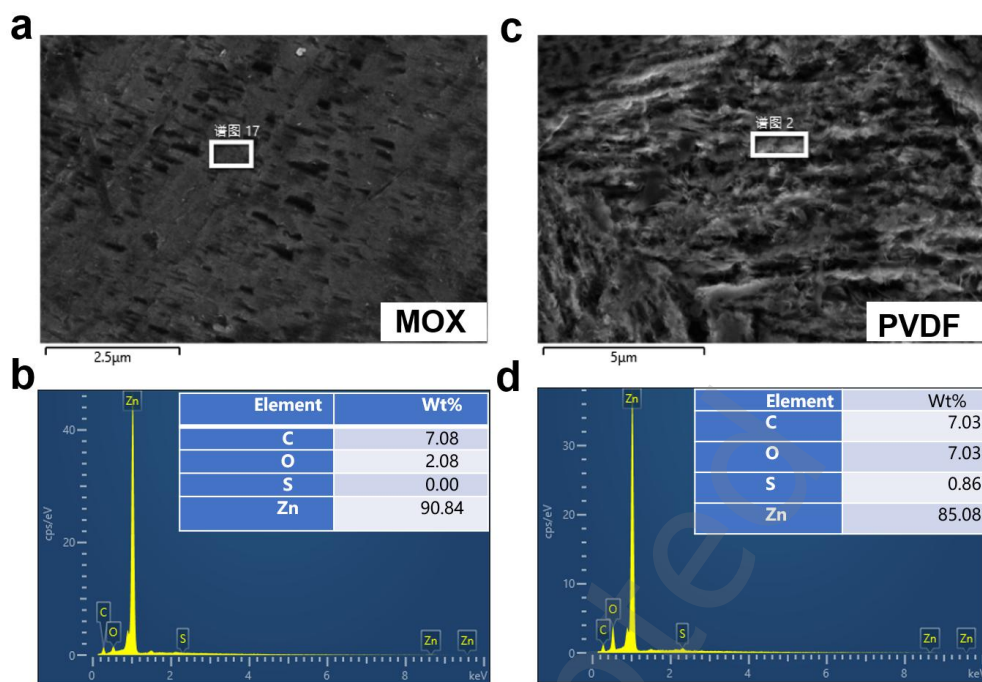


Figure S13. High-magnification SEM images and corresponding EDS spectra of Zn anodes recovered from the Zn–I₂ cells after 500 cycles at 10 C. (a,b) SEM image and corresponding EDS spectrum of the Zn anode from the MOX-based cell. (c,d) SEM image and corresponding EDS spectrum of the Zn anode from the PVDF-based cell. Scale bars: (a) 2.5 μm and (c) 5 μm.

References

- [1] Neese, F. Software Update: The ORCA Program System-Version 6.0. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2025, 15, e70019. DOI: 10.1002/wcms.70019.
- [2] Neese, F. The ORCA program system. Wiley Interdiscip. Rev. Comput. Mol. Sci. 2012, 2, 73-78. DOI: 10.1002/wcms.81.
- [3] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. J. Chem. Phys. 1999, 110, 6158-6170. DOI: 10.1063/1.478522.
- [4] Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A generally applicable atomic-charge dependent London dispersion correction. J. Chem. Phys. 2019, 150, 154122. DOI: 10.1063/1.5090222.
- [5] Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305. DOI: 10.1039/B508541A.
- [6] Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. Phys. Chem. Chem. Phys. 2006, 8, 1057-1065. DOI: 10.1039/B515623H.
- [7] Neese, F. An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. J. Comput. Chem. 2003, 24, 1740-1747. DOI: 10.1002/jcc.10318.
- [8] Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A chain-of-spheres algorithm for the Hartree-Fock exchange. Chem. Phys. 2009, 356, 98-109. DOI: 10.1016/j.chemphys.2008.10.036.
- [9] Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. J. Comput. Chem. 2003, 24, 669-681. DOI: 10.1002/jcc.10189.
- [10] Garcia-Rates, M.; Neese, F. Effect of the solute cavity on the solvation energy and its derivatives within the framework of the Gaussian charge scheme. J. Comput. Chem. 2020, 41, 922-939. DOI: 10.1002/jcc.26139.
- [11] Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. J. Comput. Chem. 2012, 33, 580-592. DOI: 10.1002/jcc.22885.
- [12] Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. J. Mol. Graph. 1996,

14, 33-38.

[13] Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* 2004, 108, 17886-17892. DOI: 10.1021/jp047349j.

Just Accepted