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Application of functional coatings in water electrolyzers and fuel cells

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Hydrogen, a sustainable energy carrier, plays a pivotal role in decarbonizing various industrial sectors. Key devices such as water electrolyzers and fuel cells enable a sustainable hydrogen cycle by producing hydrogen using renewable energies and converting hydrogen into electricity. The efficiency of these devices is primarily determined by electrocatalysts and other critical components like membranes, gas diffusion layers and bipolar plates. The dynamic and complex triple-phase reactions as well as the corrosive operational environments in these devices present significant challenges in achieving optimal performance and durability. This review not only summarizes recent advances in functional coatings but also elucidates the underlying mechanisms by which coatings modulate interfacial interactions and mitigate degradation. We further propose a roadmap for designing next-generation multifunctional coatings, emphasizing their potential to bridge the gap between laboratory research and industrial applications.

1. Introduction

Hydrogen is poised to redefine the global energy landscape as a clean, sustainable, and efficient energy carrier. With its high energy density (140 MJ kg^{-1}) and zero greenhouse gas emissions at the point of use, hydrogen has emerged as a promising alternative to conventional fossil fuels, addressing the growing global energy demand while mitigating climate change.[1,2] Unlike traditional hydrogen production methods such as coal gasification and steam reforming, which are heavily reliant on fossil fuels and associated with significant CO_2 emissions, water electrolysis presents a sustainable pathway for hydrogen generation.[3] By leveraging renewable energy sources such as wind and solar, water electrolysis enables the production of hydrogen and oxygen through the decomposition of water, contributing to carbon-neutral energy systems.[4]

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Water splitting, the foundational process in electrolysis, comprises two distinct reactions: the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode.[5] Depending on the electrolyte and operational conditions, water electrolysis technologies are classified into four main types: proton exchange membrane water electrolysis (PEMWE), alkaline water electrolysis (AWE), anion exchange membrane water electrolysis (AEMWE) and solid oxide electrolysis cells (SOEC).[6,7] Among these, PEMWE and AEMWE are recognized as the most efficient and scalable options for sustainable H_2 production due to their operational compatibility with intermittent renewable energy sources and superior electrochemical performance under high and low pH conditions, respectively.[8,9] PEMWE and AEMWE represent two distinct technological paradigms. PEMWE operates in highly acidic environments Using proton exchange membranes (PEMs), demanding coatings with exceptional resistance to acid corrosion. In contrast, AEMWE functions under alkaline conditions, utilizing hydroxide ion transport.[10]

The integration of hydrogen into energy systems extends beyond its production, with its storage and utilization playing pivotal roles. PEMFC and AEMFC exemplify the transformative potential of hydrogen in clean energy conversion.[11] These devices electrochemically convert stored hydrogen into electricity, offering high power density, excellent energy efficiency, and zero pollutant emissions at low operating temperatures.[12] Their versatility has made them indispensable for applications ranging from vehicular propulsion to stationary and portable power generation. As depicted in Fig. 1, PEMFCs and AEMFCs share structural similarities. The closed-loop system, where water produced by fuel cells can be reused in electrolysis, exemplifies the circularity and sustainability inherent in hydrogen energy systems.[13]

The core of both electrolyzers and fuel cells lies in the membrane electrode assembly (MEA), which integrates a catalyst layer (CL), a proton exchange membrane (PEM) or anion exchange membrane (AEM), and a gas diffusion layer (GDL).[14] The CL consists of catalyst nanoparticles embedded in an ionomer matrix, facilitating key electrochemical reactions and enhancing efficiency and performance.[15] The membrane serves as an electrolyte, selectively transporting ions while preventing the crossover of gases, ensuring efficient and safe operation.[16] GDLs and bipolar plates (BPs) further enhance performance by facilitating gas and heat management, maintaining mechanical stability, and reducing electrical resistance.[17] However, despite these advances, the reliance on rare and expensive metals such as iridium and platinum for catalytic activity and corrosion resistance presents significant cost and sustainability challenges.[18] Efforts to overcome these challenges have spurred the development of alternative catalysts that utilize abundant and cost-effective materials.

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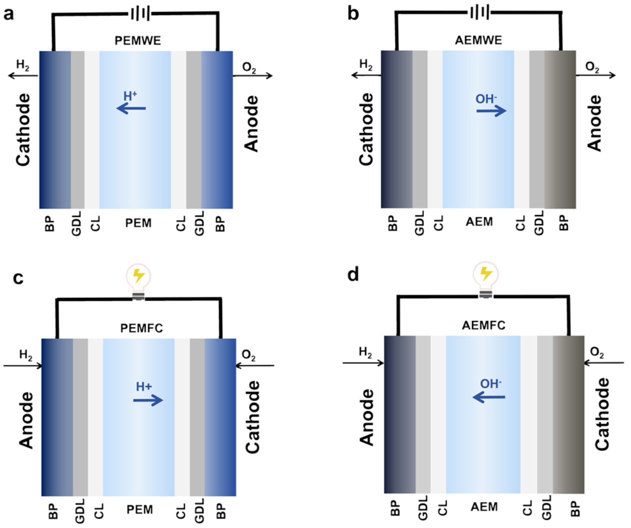

Fig. 1 Schematic illustration of (a) PEMWE, (b)AEMWE, (c) PEMFC and (d) AEMFC. BP: bipolar plate, GDL: gas diffusion layer, CL: catalyst layer, PEM: proton exchange membrane, AEM: anion exchange membrane.

Strategies include modifying the electronic structure of catalysts by doping with transition metals,[19] synthesizing non-precious metal compounds such as nitrides and sulfides,[20,21] and employing nanostructuring techniques to enhance surface area and catalytic activity.[22] While promising, these approaches are constrained by issues such as limited stability and susceptibility to corrosion during prolonged operation, highlighting the need for further innovation. Besides, membrane degradation also represents a major bottleneck in the performance and durability of water electrolysis systems. Perfluorosulfonic acid (PFSA) membranes like Nafion®, despite their chemical and thermal stability, often suffer from conductivity loss and structural degradation under practical conditions.[23,24] Similarly, AEMs face fouling challenges due to contamination by negatively charged organic species, which compromise their ionic conductivity and selectivity.[25] Additional factors such as the degradation of GDLs and the corrosion or passivation of BPs exacerbate system inefficiencies, emphasizing the need for improved materials and protective strategies.[26,27]

Surface coatings have emerged as a transformative approach to addressing these challenges. By modifying the surface properties of catalysts, membranes, GDLs, and BPs, coatings can enhance durability, reduce corrosion, and improve electrochemical performance. For instance, nanoscale coatings can increase the stability of non-precious metal catalysts by mitigating surface dissolution and optimizing electronic interactions. Similarly, protective layers on membranes and BPs can prevent fouling and oxidation, extending their operational lifespan. This review focuses on the latest advances in surface coatings for water electrolysis and fuel cell components, examining their impact on enhancing system efficiency, stability, and cost-effectiveness. More specifically, we discuss the role of coatings in improving catalyst performance for HER and OER, as well as their application in protecting BPs, GDLs and membranes. Finally, we highlight emerging research opportunities and propose future directions for developing innovative coating technologies that align with the global transition to a hydrogen-based energy system.

2. Coatings for water electrolysis catalysts

Electrocatalysts play a pivotal role in water electrolyzers, while HER is thermodynamically more favourable, its efficiency is limited by catalyst stability under highly dynamic electrochemical conditions. OER, on the other hand, is inherently sluggish due to its complex four-electron transfer mechanism and occurs in a highly oxidative environment, posing significant challenges for catalyst stability and performance.[26,27] The durability of catalysts in both HER and OER is crucial for the long-term efficiency and economic viability of water-splitting devices. However, HER catalysts often suffer from issues such as dissolution, hydride formation, and surface poisoning, particularly under acidic or alkaline conditions. OER catalysts face additional challenges, including phase instability, overoxidation, and mechanical degradation due to oxygen bubble evolution.[31] Despite significant advancements in catalyst design, these stability issues remain a major bottleneck. Surface coating technologies have emerged as transformative tools for optimizing electrocatalyst properties. By manipulating surface characteristics, coatings can enhance catalytic activity, stability, and resistance to harsh operating conditions. This section reviews recent research advancements in coatings for electrocatalysts in water electrolysis, with a particular emphasis on their role in improving catalytic performance and developing innovative coating strategies.

2.1 Coatings for OER electrocatalysts

Coatings play multiple critical roles in enhancing the performance of OER electrocatalysts. By rational composition and structure engineering, coatings can simultaneously provide protection, activation, and mass-transfer enhancement.

Protective passivation layers have demonstrated remarkable potential for enhancing the stability of OER electrocatalysts by mitigating corrosion and maintaining charge transfer at the electrode–electrolyte interface. The coating effectively increases the thermodynamic stability of the catalyst. Tran-Phu *et al.* highlighted the effectiveness of amorphous TiO_2 dielectric electrolysis for 80 h in near-zero pH environments. Interestingly, controlled pitting corrosion of the TiO_2 layer exposed catalytically active Co_3O_4 sites while preserving the overall structural integrity. Similarly, Ta *et al.* explored the impact of atomic layer deposition (ALD) on Co_3O_4 stability and activity by coating the material with a range of dielectric oxides, including Al_2O_3, SiO_2, TiO_2, SnO_2, and HfO_2 (Fig. 2a and b).[28] Among these, HfO_2 coatings demonstrated superior corrosion resistance and stability. An optimal HfO_2 thickness of 12 nm enhanced Co_3O_4 durability by over threefold, enabling sustained electrolysis at 10 mA cm^{-2} for more than 42 h in 1M H_2SO_4 electrolyte (Fig. 2c and d). The study revealed a performance hierarchy for coatings: $HfO_2 > SnO_2 > TiO_2 > Al_2O_3 > SiO_2$, underscoring the importance of material selection and thickness optimization in coating design. Wang *et al.* synthesized nitrogen-doped carbon-coated cobalt manganate particles, achieving a current density of 100 mA cm^{-2} at 1.56 V. The catalyst is covered with a graphitized carbon layer, which facilitates electron transport. Theoretical and electron density calculations revealed that the nitrogen-doped carbon layer significantly increases electron density around the surface Co^{3+} sites, reducing proton removal of intermediate products, promoting H_2O dissociation, and consequently enhancing the OER reaction.[35] The coating not only optimizes the electronic structure, but also provides more channels for electrolyte diffusion and bubble release, resulting in improved activity and mechanical stability. For instance, Liu *et al.* developed an FeOOH-coated WO_2-Na_xWO_3 catalyst (Fig. 2e), that achieved an ultra-low overpotential of 220 mV at 20 mA cm^{-2}.[29] Stability testing at 100 mA cm^{-2} in 1.0 M KOH demonstrated only an 18 mV increase in overpotential after 120 h, signifying excellent durability (Fig. 2f and g).

Besides, seawater electrolysis, as a sustainable approach, has garnered significant attention in recent years. However, it poses unique challenges due to the corrosive nature of chloride ions in seawater, which can degrade catalysts and reduce overall efficiency rapidly. Therefore, applying a corrosion-resistant coating on the catalyst has become an effective method. The coating selectively prevents the Cl^- anion from approaching the catalytic centre, effectively inhibiting Cl^- corrosion. Wang *et al.* addressed this issue by creating ultrathin MnO_x film-covered NiFe double hydroxide nanosheet arrays on nickel foam (MnO_x/NiFe-LDH/NF) through hydrothermal and electrodeposition techniques (Fig. 2h).[30] The MnO_x coating layer effectively blocked Cl^- ion penetration while allowing the water and O_2 molecules reach the catalyst surface, enhancing OER performance. It demonstrated that MnO_x/NiFe-LDH/NF exhibited a smaller corrosion current density (2.98 *versus* 4.26 μA cm^{-2} for NiFe-LDH/NF), indicating effective corrosion inhibition and catalytic enhancement (Fig. 2i and j).

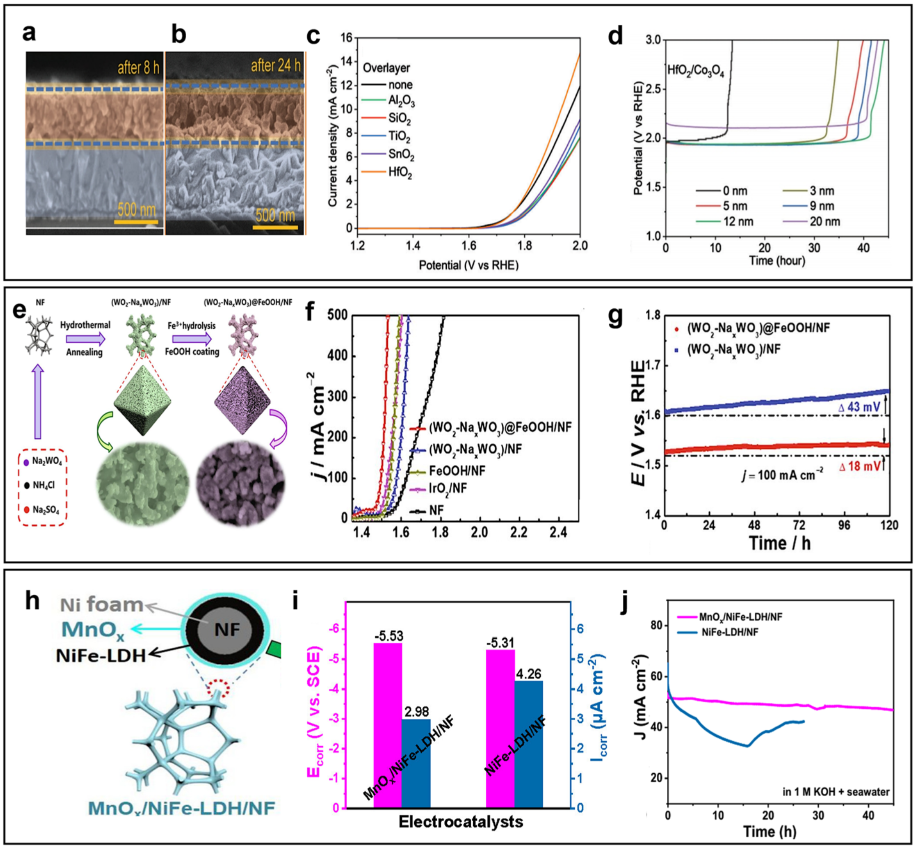

Fig. 2 (a) Cross-sectional SEM images of Co_3O_4/FTO anode coated with 3–4 nm thick HfO_2 after 8 h and (b) 24 h static flow OER tests at 10 mA cm^{-2} of 1 M H_2SO_4 (orange: Co_3O_4 electrocatalyst, blue: FTO, blue dashed lines: boundaries of pristine Co_3O_4 layer). (c) Linear voltametric curves of electrodes of Co_3O_4/FTO electrodes in the absence and at 3–4 nm thickness of different coatings (third scan) Scan rate 0.005 V s^{-1}. (d) Linear voltametric curves of electrodes with different thicknesses of hafnium oxide recorded at 10 mA cm^{-2} in 1 M H_2SO_4. Reproduced with permission from ref. 28 Copyright 2023 Wiley-VCH GmbH. (e) Preparation flow chart of $(WO_2\text{-}Na_xWO_3)@FeOOH/NF$. (f) Polarization curves of the samples for OER in 1.0 M KOH. (g) Chrono potentiometric of samples keep at 100 mA cm^{-2} for 120 h. Reproduced with permission from ref. 29 Copyright 2021 Elsevier. (h) The structure of MnO_x/NiFe-LDH/NF. (i) Corrosion potentials (red) and corrosion current densities (blue) of MnO_x/NiFe-LDH/NF and NiFe-LDH/NF in alkalized natural seawater. (j) Chronoamperometric measurements of MnO_x/NiFe-LDH/NF and NiFe-LDH/NF toward OER in 1 M KOH + seawater electrolytes. Reproduced with permission from ref. 30 Copyright 2022 American Chemical Society.

To summarize, coating OER catalyst surfaces with metal oxides or hydroxides, though not completely preventing the dissolution of the underlying catalyst, effectively mitigates the catalyst's corrosion rate, thereby enhancing stability. These studies offer new avenues and practical foundations for developing efficient and stable water electrolysis OER catalysts. Given the increasing demand for renewable energy sources, these achievements hold promise for significant technological breakthroughs and application prospects in the field of sustainable energy conversion and utilization.

2.2 Coatings for HER electrocatalyst

Efforts have been directed towards developing electrocatalysts for HER, primarily based on low-cost transition metals, aimed at cost reduction and enhanced adaptability to complex operational conditions. Coatings play crucial roles in enhancing the performance of HER electrocatalysts. They help mitigate the corrosion and modulate the electronic structure of heterogeneous interfaces, providing a conductive platform for efficient electron transfer. These functions are vital for the development of advanced HER catalysts. This section focuses on discussing electrocatalysts derived from surface coatings conducive to HER catalysis.

Coating HER catalysts with metal oxide layers contributes to enhancing the activity and stability of HER catalysts. Designing a defective coating can adsorb and dissociate water molecules, thereby significantly promoting the generation of active hydrogen in the Volmer step of the hydrogen conversion reaction.[36] For instance, Liu *et al.* deposited defective TiO_2 coatings on porous (Co, Ni)$_2$P nanosheets (Fig. 3a), providing abundant oxygen vacancies for the dissociative generation of active hydrogen atoms.[32] Additionally, the layered porous structure of the material demonstrates kinetic advantages by accelerating mass transport during HER. The porous (Co, Ni)$_2$P@0.1TiO_2 nanosheet array exhibits outstanding performance in alkaline HER, with a small overpotential of 92 mV at a current density of 10 mA cm^{-2}, a small Tafel slope of 49 mV dec^{-1}, and strong stability over 20 h (Fig. 3b and c).

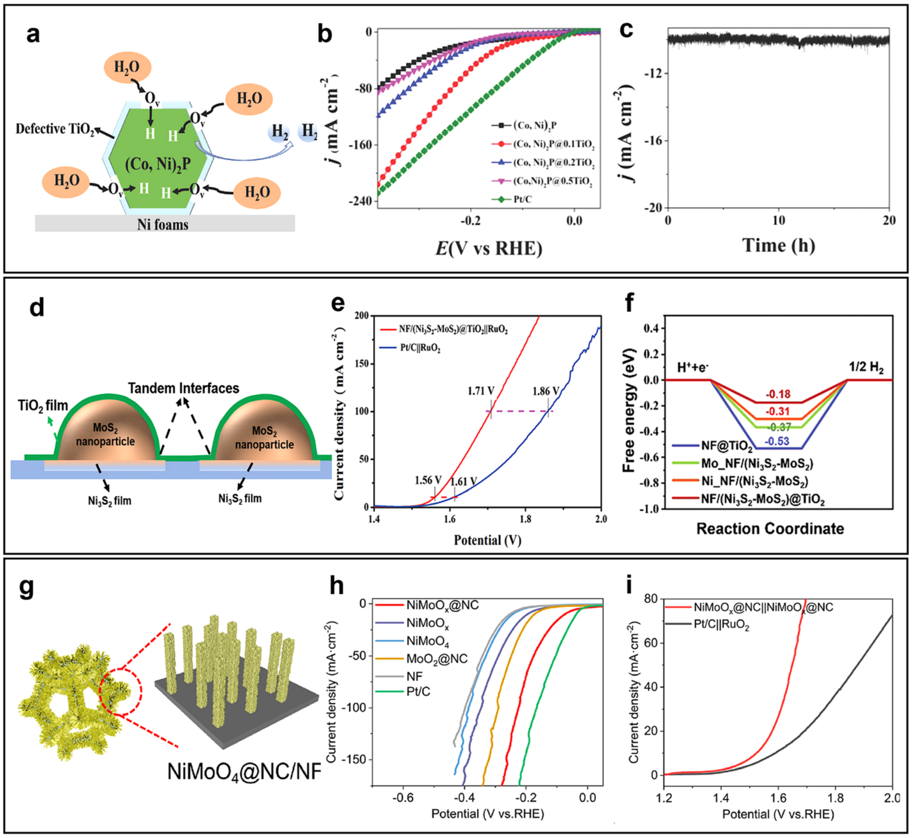

Fig. 3 (a) The possible reaction process on (Co,Ni)$_2$P@TiO$_2$ nanocomposite arrays for alkaline HER. (b) Steady-state polarization curves. (c) Current density *versus* time (*i*–*t*) curve of (Co,Ni)$_2$P@0.1TiO$_2$ arrays for HER at overpotential of 92 mV. Reproduced with permission from ref. 32 Copyright 2018 Wiley–VCH GmbH. (d) Composite material NF/(Ni$_3$S$_2$-MoS$_2$)@TiO$_2$ featuring tandem interfaces. (e) Polarization curves of overall water splitting at a scan rate of 10 mV s^{-1}. (f) Adsorption energy profiles of water molecule adsorption step catalyzed by active species of studied materials Reproduced with permission from ref. 33 Copyright 2022 Wiley–VCH GmbH. (g) Schematic representation of NiMoO$_x$@NC/NF electrocatalyst. (h) LSV curves. (i) LSV polarization curves of NiMoO$_x$@NC/NF and commercial catalysts in a two-electrode system. Reproduced with permission from ref. 34 Copyright 2024 Elsevier.

In addition, the coatings optimize the electronic structure of the composites/adsorbents/intermediates by modulating multiple heterogeneous interfaces. Guo *et al.* utilized ALD to deposit TiO_2 on Ni_3S_2-MoS_2 heterostructures.[33] They complementarily assembled nanostructured heterojunctions and ultrathin functional coatings on a conductive substrate to construct serial interfaces, achieving excellent HER performance (Fig. 3d). In neutral medium, the electrode of NF/(Ni_3S_2-MoS_2)@TiO_2||RuO_2 exhibits a lower potential at a current density of 10 mA cm^{-2} compared to commercial catalysts (Fig. 3e). The Gibbs free energy change (ΔG) for the representative reaction step was calculated, revealing that the ALD material NF/(Ni_3S_2-MoS_2)@TiO_2 exhibits a ΔG value of approximately −0.18 eV. This value is close to the optimal condition where $|\Delta G_{\mathrm{H}^*}| = 0$, indicating that this material has the smallest energy barrier, thus promoting the most favourable thermodynamic conditions for the adsorption and desorption of H* (Fig. 3f). The ALD oxide serial layer plays a crucial role in tuning various heterojunction interfaces and intermediate electronic structures.

Furthermore, the coating not only serves as an anti-degradation agent but also provides a conductive platform for efficient electron transfer. Ma *et al.* designed a nitrogen-doped carbon-coated $NiMoO_x$ rod (Fig. 3g), which exhibited remarkable superhydrophilic and super-oxygenophobic properties.[34] This unique structure significantly enhanced mass transfer and bubble removal, leading to accelerated reaction kinetics and improved stability. The $NiMoO_x$@NC/NF electrode demonstrated an overpotential of 126 mV at a current density of 25 mA cm^{-2} (Fig. 3h). Furthermore, the use of $NiMoO_x$@NC/NF as anode and cathode electrodes had lower cell voltages compared to commercial catalysts (Fig. 3i).

Surface coatings have emerged as a powerful strategy for enhancing the performance and stability of electrocatalysts in the HER. These coatings not only provide stability and prevent catalyst degradation but also serve to tune the electronic structure at multiple interfaces, enhancing overall catalytic efficiency. The collective advancements in coating technologies hold great promise for the development of cost-effective, high-performance electrocatalysts, offering significant improvements in HER efficiency and stability for sustainable hydrogen production. In summary, this section extensively investigates the research advancements in utilizing surface-coated electrocatalysts to promote the HER.

3. Components coatings

Water electrolyzers, especially PEMWE, face significant corrosion challenges due to prolonged interactions between the electrolyte and cell components. The corrosion and wear of key components compromise structural integrity and lifespan, thereby affecting the device's stability and overall performance. Therefore, applying coatings that effectively slow down the corrosion rate of BPs AND reduce the interfacial contact resistance (ICR) is essential for achieving more stable and efficient water electrolysis. This section discusses surface coatings designed to protect these components and enhance their performance.

3.1 BPs coatings

BPs are critical components in electrolyzers and fuel cells, responsible for conducting electricity, distributing fluids, separating gases and managing heat. However, commonly used metallic BPs (*e.g.*, titanium or stainless steel) are prone to corrosion and passivation under acidic and humid conditions,[37] leading to increased ICR and performance degradation. Functional coatings on these pates enhance their performance by providing corrosion resistance, reducing ICR, and improving durability under harsh operating conditions,[38] ultimately contributing to the longevity and efficiency of the devices.

Various types of coatings have been extensively researched and adopted to enhance the interface conductivity and corrosion resistance of BPs. Among these, metal/metal carbide coatings have excellent conductivity and corrosion resistance and are suitable as protective coatings for metal BPs. For instance, S. Stiber *et al.* utilized magnetron sputtering to deposit non-noble metal coatings of Ti and Nb/Ti on stainless steel (SS) BPs for PEMWE cells (Fig. 4a). These coatings increased current density by 13-fold while maintaining performance. Compared to uncoated Ti, the coated BP reduced

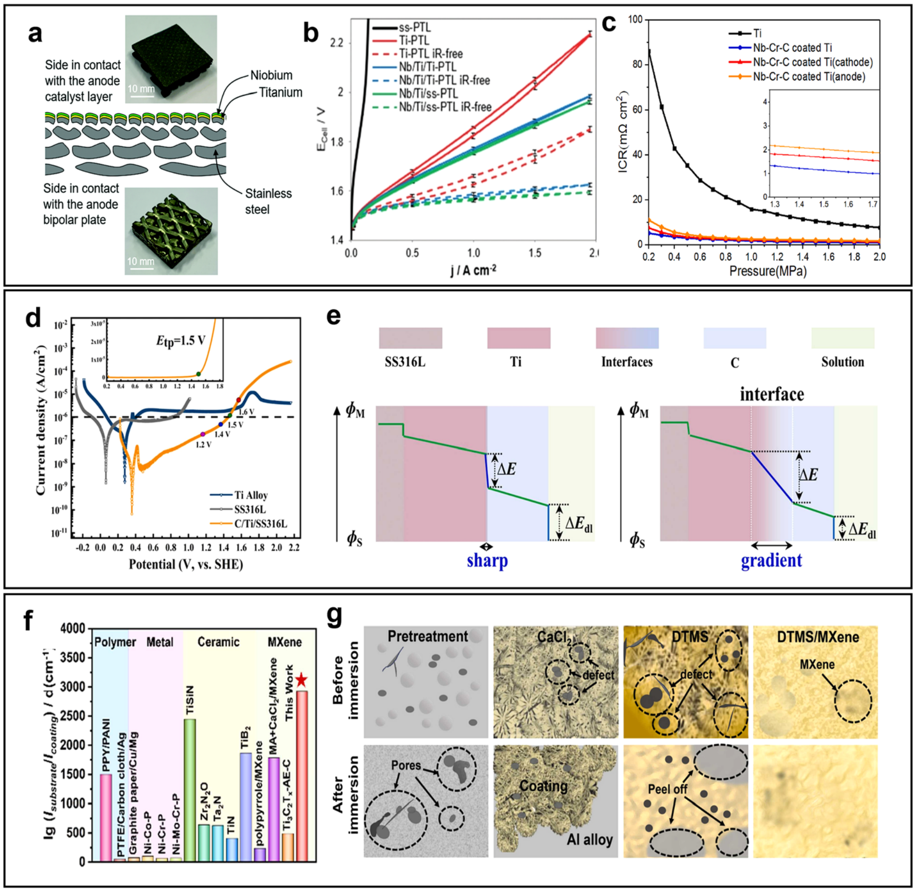

Fig. 4 (a) Scheme of the ss-mesh PTL with a plasma-sprayed Nb/Ti coating at the interface with the anode catalyst layer. (b) Polarization curves of PEMWE cells with the Ti-PTL, ss-PTL, Nb/Ti/Ti-PTL and Nb/Ti/ss-PTL. Reproduced with permission from ref. 39 Copyright 2022 The Royal Society of Chemistry. (c) ICR results of bare titanium and Nb–Cr–C coated titanium before and after potentiostatic polarization. Reproduced with permission from ref. 40 Copyright 2022 Elsevier. (d) Potentiodynamic polarization curves of C/Ti/SS, Ti alloy, and SS316L. (e) Schematic potential distribution across the interfaces of bilayer C/Ti coating without and with diffusional interfaces. The potential drop at the interface of C/Ti (ΔE) and coating/solution (ΔE_{dl}). Reproduced with permission from ref. 41 Copyright 2022 Elsevier. (f) Comparison of the ratio of the reduction of I_{corr} to the thickness of the coating with other samples reported in previous literatures. (g) Schematic illustration of surface changes of the various coatings before and after immersion tests. Reproduced with permission from ref. 42 Copyright 2024 Elsevier.

the cell voltage by over 300 mV at 2 A cm^2, translating to a 12% efficiency improvement with significant implications for hydrogen production costs (Fig. 4b).[39] Similarly, Gou *et al.* coated Ti BPs with a Nb–Cr–C thin film, achieving a reduction in ICR from 10.55 (bare Ti) to 1.15 mΩ cm^2. After 10 h of polarization testing, the ICR increased only slightly indicating excellent long-term stability (Fig. 4c).[40] In addition to metal-based coatings, carbon-based coatings remain a hot topic of research. Graphene materials are promising coatings for metal BPs due to their two-dimensional geometry, high conductivity, chemical inertness, and unique impermeability. Cui *et al.* developed a continuous liquid-phase coating method to construct highly oriented and densely packed graphene-based hybrid coatings, achieving excellent corrosion resistance (0.023 μA cm^{-2}) and high conductivity (9.94 Ω cm^2).[43] This method offers a practical alternative to vacuum deposition for corrosion-resistant coatings on SS BPs. Amorphous carbon (α-C) coatings are another promising approach due to their excellent conductivity and corrosion resistance. Yi *et al.* demonstrated the potential of multilayer Cr–C/α-C: Cr coatings, achieving a corrosion current density of 0.276 μA cm^{-2} at 0.6 V.[44] Additionally, nano-layered TiC_x/α-C coatings prepared using closed-field unbalanced magnetron sputtering achieved optimal performance with an ICR of 2.35 mΩ cm^2. However, further research is needed to improve the antioxidation properties of α-C coatings under high polarization potentials (>1 V), where SS BPs are susceptible to transpassive dissolution. To address oxidation issues, multi-layered C/Ti nanoscale coatings have been developed. Wang *et al.* fabricated such coatings on SS316L, achieving an ICR of 1.59 mΩ cm^2 and a corrosion current of 2×10^{-8} A cm^{-2} (Fig. 4d and e). The nanoscale C layer enhanced conductivity and stability by mitigating potential drop at the C/Ti interfaces.[41]

Emerging materials like MXene nanosheets also show promise for BP protection in PEMFCs due to their excellent conductivity and adjustable characteristics. Wang *et al.* utilized electro-deposition to construct thin dodecyl trimethoxy silane (DTMS)/TiCT MXene coatings on aluminum alloys (Fig. 4f).[42] These coatings achieved a corrosion current density as low as 9.284×10^{-7} A cm^{-2} and demonstrated extended delamination times during *in situ* corrosion tests, outperforming other protective coatings (metal, ceramic, and MXene coatings) (Fig. 4g). The incorporation of $Ti_3C_2T_x$ significantly improved the coating's adhesion, thickness, and porosity reduction, thereby enhancing its resistance to corrosive media. In corrosive environments, the DTMS/MXene coating could still completely cover the surface of the aluminum alloy, demonstrating its outstanding coverage and adhesion, which impart robust permeation resistance to corrosive media.

The performance of PEMWE and PEMFC heavily depends on the characteristics of BP materials. Ongoing exploration of coatings for these materials is crucial for advancing stack technology and its application in clean energy. While single-layer coatings have been extensively studied, challenges remain in designing multifunctional multilayer composite coatings and reducing production costs.

3.2 GDL coating

The primary functions of GDLs include redistributing reactants, expelling water, conducting electrons and heat, and providing mechanical support. GDL is also referred to as porous transport layer (PTL). The occurrence of deleterious passivation of titanium-based components is a major issue under real cell operating conditions, so coatings are needed to inhibit passivation of anode titanium-based GDLs. In PEMFC, coatings focus on mass transfer and water management issues at high current densities. In this section, we will primarily discuss research methods and advancements aimed at enhancing electrochemical performance through surface coatings on GDLs.

Liu *et al.* sputtered a thin layer of iridium on a titanium GDL by magnetron sputtering.[45] After assembling a PEM electrolyzer for testing, this GDL showed long-term stability within 4000 h (Fig. 5a and b) And they found that uncoated or poorly coated GDL will trigger severe degradation of the CL. Also, the interface between GDL and CL is a critical factor influencing fuel cell efficiency. Researchers have sought to improve the GDL/CL interface by applying platinum group metal (PGM) coatings onto GDLs. Liu *et al.* loaded Ir as a protective layer onto Ti GDLs and compared the performance of uncoated and coated GDLs with varying Ir loads.[46] Iridium-coated GDLs effectively reduce ICR and improve the cell performance compared to uncoated GDLs (Fig. 5c and d). For iridium-coated GDLs, the contact resistance decreases gradually with increasing Ir load, indicating that the amount of Ir, especially at low loads, has a significant effect on ICR. Additionally, Deng *et al.* developed a cost-effective TiC-coated GDL using a reverse-turn/vacuum sintering method (Fig. 5e).[47] The TiC microporous layers reduced contact resistance, improved electrochemical performance, and demonstrated long-term stability for 500 h at 2 A cm^{-2} and 80 °C (Fig. 5f and g). To enhance PEMFCs performance (under low relative humidity and high operating temperatures), researchers have focused on addressing mass transport and water management issues at high current densities. Hou *et al.* prepared self-humidifying MEAs by adding ultra-thin hydrophilic TiO_2 on GDLs (Fig. 5h).[48] They found that MEAs with TiO_2-coated GDLs exhibited significantly enhanced self-humidifying capabilities on the anode side of PEM fuel cells. With a TiO_2 loading of 0.3 mg cm^{-2}, the optimal performance was achieved, delivering a current density of 1190 mA cm^{-2} at a voltage of 0.6 V. Under conditions of 12% relative humidity and 65 °C, the current density remained at a high-level of 1140 mA cm^{-2} after continuous testing for up to 50 h, demonstrating the enormous potential of this coating technology in improving the stability and performance of fuel cells (Fig. 5i).

In summary, improving the coating surfaces has emerged as a superb strategy to enhance fuel cell performance. It can enhance mass transport rates, reduce internal resistance, enhance durability, and improve overall battery performance. It is worth noting that the preparation methods for GDL coatings involve complex processes and may be limited by higher

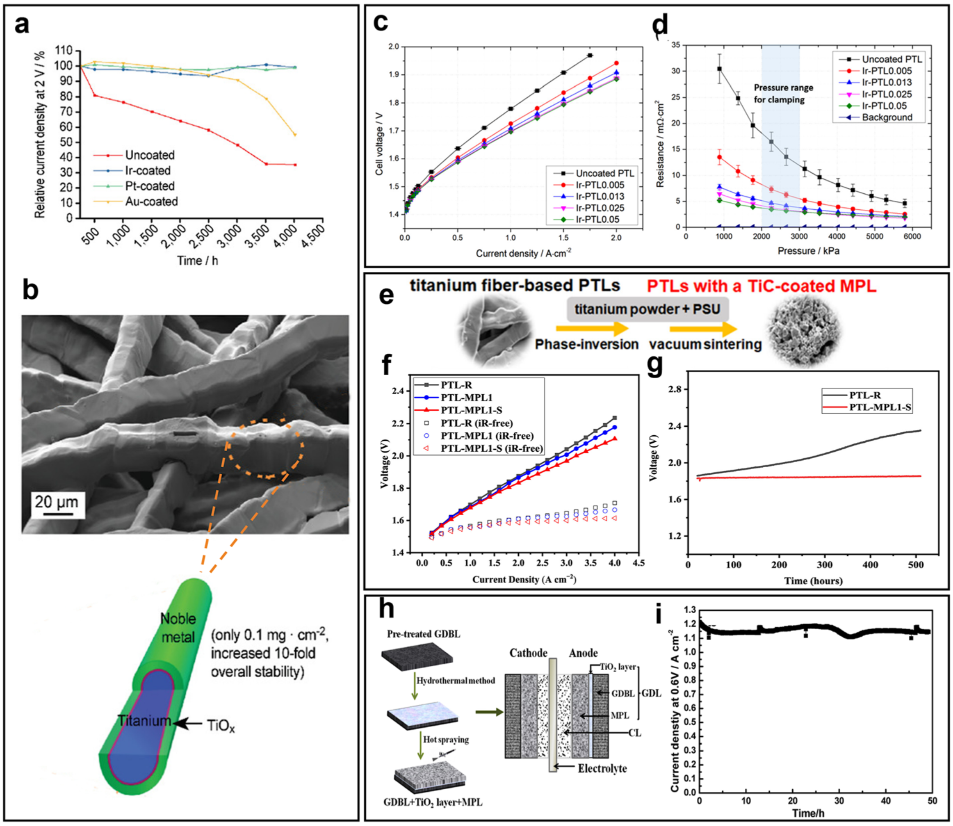

Fig. 5 (a) Relative current density at 2 V (the average value of current density between 200 and 250 h (conditioning) was determined to be 100%). (b) Focused ion beam-scanning electron microscope (FIB-SEM) image of an Ir-coated GDL. Reproduced with permission from ref. 45 Copyright 2021 Wiley–VCH GmbH. (c) Polarization curves of PEM water electrolyzer single cells assembled with GDL and uncoated GDL with different Ir loaded coatings. (d) Contact resistance of GDLs with different Ir content coatings and uncoated GDLs. Reproduced with permission from ref. 46 Copyright 2021 American Chemical Society. (e) Schematic diagram of the preparation process of GDLs with TiC-coated MPL. (f) Polarization curves of PEMWE cells with PTL-R, PTL-MPL1, and PTL-MPL1-S at 80 °C. (g) Stability test of PEMWE cells based on PTL-R and PTLMPL1-S at 80 °C and 2 A cm^{-2}. Reproduced with permission from ref. 47 Copyright 2023 American Chemical Society. (h) The preparation and structure of the prepared MEAs with a TiO_2 layer on the GDBL. (i) Continuous discharge curves of GDL3 with TiO_2 coated on the GDBL: 50 h test of GDL3 used as the anode. Reproduced with permission from ref. 48 Copyright 2020 Elsevier.

costs in practical applications. In the future, it will be necessary to optimize coating designs to achieve better stability and performance of fuel cells under high current densities.

3.3 Membrane coating

In the field of membrane materials research, the application of coating technology has attracted increasing attention. PEMs and AEMs serve as crucial ion transport media, playing vital roles in various applications such as fuel cells, electrolytic hydrogen production, and ion-selective separations. While PEMs and anion exchange membranes AEMs are vital in electrochemistry, they face common challenges. Stability is an issue for both PEMs and AEMs, especially during extended use and rapid cycling. Additionally, their production from costly materials like fluorocarbon polymers adds to their expense. Overcoming these hurdles is essential for broadening their practical applications in energy conversion and storage. Functional coatings effectively inhibit the formation of highly oxidizing free radicals while improving the mechanical and chemical durability of the films. In this section, we summarize the progress of research on membrane surface coatings. PEMs are renowned for their robust proton transport properties and high selectivity, making them one of the most favored materials in membrane-based energy conversion and storage devices. Polymeric membranes such as perfluorosulfonic acid (PFSA) membranes, including DuPont's Nafion® and those from 3M and Solvay, are widely used.[51] The formation of highly oxidative radical species (*e.g.*, *OH, *H, *OOH) radicals is a key factor leading to PEM degradation during fuel cell operation. To address this issue, Zhao *et al.* utilized the tunable and self-assembling feasibility of MXene and the cerium compound's ability to scavenge radicals and alleviate chemical corrosion in fuel cell MEAs.[49] They constructed a MXene-CeO_2 coating sprayed onto the cathode side of the proton exchange membrane, forming a mixed membrane with anti-radical properties. Meanwhile, the MXene-CeO_2 hybrid material established a two-dimensional long-range proton transfer pathway within the PFSA resin, counteracting the dilution effect of sulfonic acid salts in non-proton conductors. Applying MXene-CeO_2 to the cathode side of the membrane effectively removed radicals formed in the cathode region during operation, thereby prolonging the overall lifespan of the proton exchange membrane fuel cell (Fig. 6a). The comparison shows that the introduction of MXene carrier effectively enhances the durability of the membrane (Fig. 6b). In the PEMFC performance test, r-PEM/CeO_2-0.1 has the best battery performance and maximum power density (~1216.8 mW cm^{-2}) (Fig. 6c).

Furthermore, improving the mechanical and chemical durability of membranes as well as reducing electrical conductivity are critical issues. Kim *et al.* successfully constructed a well-distributed three-dimensional MWCNTs/CeO_2 network with a thickness of ~450 nm on a commercial NR211 membrane (Fig. 6d), which improved the mechanical and chemical durability of the membrane and reduced the loss of conductivity.[52] MWCNTs have a high aspect ratio and excellent mechanical properties, which increase the Young's modulus and membrane size stability. Compared with the original NR211 membrane (1.861 mV h^{-1}), the modified membrane with MWCNTs/CeO_2 functional layer showed a much lower decay rate of 0.931 mV h^{-1} and a peak power density (PPD) reduced by 28%. After OCV holding test for 72 h, due to the improved chemical durability of MWCNTs/CeO_2 functional layer, the modified membrane-based MEA showed higher PPD and current density at 0.6 V compared with the reference NR211, increasing by 17.9% and 36.9%, respectively (Fig. 6e). This newly developed ultrathin layer acts as an effective gas barrier on the outer surface of the membrane, showing reduced hydrogen crossover, slower OCV decay rate, and significantly reduced fluoride ion emission rate, indicating significantly improved chemical durability. Liu *et al.* obtained ZrO_2-coated ePTFE skeleton by surface sol–gel modification, through PDA hydrophilic modification and subsequent surface sol–gel process.[50] Then, ZrO_2-coated ePTFE skeleton-based reinforced composite membrane Z1-CM was prepared by solution coating method on various foamed PTFE skeleton (Fig. 6f). ZrO_2, as an antioxidant additive, anchored on the foamed PTFE reinforcement material, not only improved the interface bonding between the skeleton and PFSA resin but also inhibited the migration and loss of antioxidant additives.

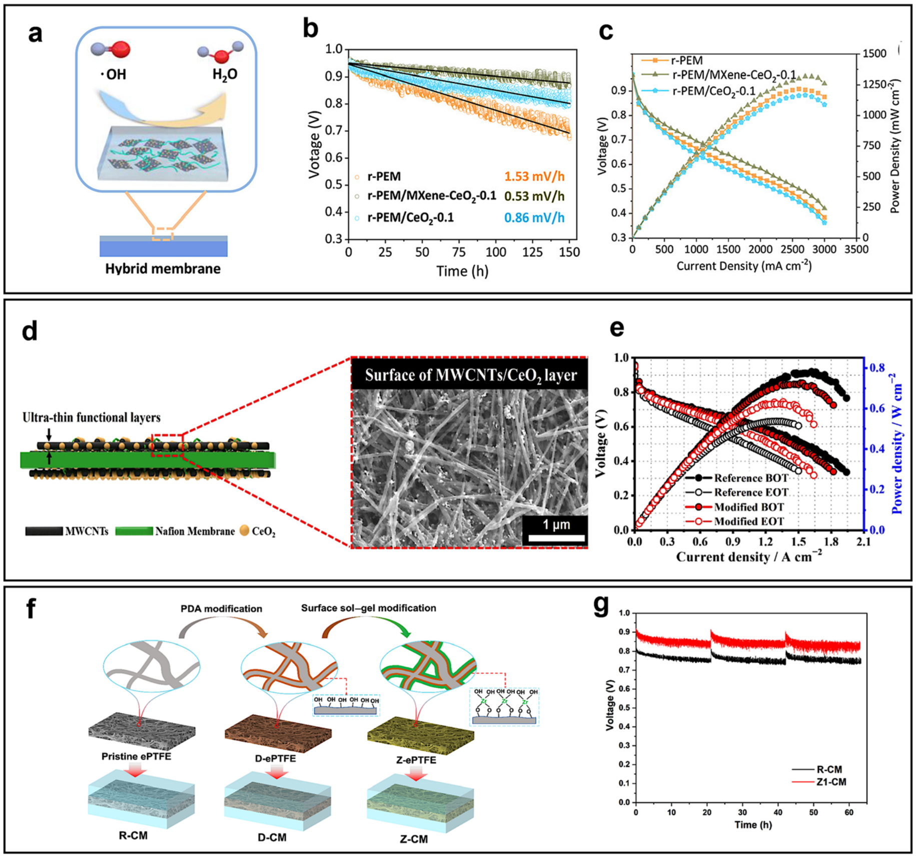

Fig. 6 (a) Schematic representation of water decomposition in Mxene-CeO_2. (b) OCV changes during the durability test of the pristine r-PEM, r-PEM/MXene-CeO_2-0.1, and r-PEM/CeO_2-0.1. (c) Polarization curves and power output of the r-PEM, r-PEM/MXene-CeO_2-0.1, and r-PEM/CeO_2-0.1 after ADT for 150 h. Reproduced with permission from ref. 49 Copyright 2022 American Chemical Society. (d) Schematic diagram and the SEM of the surface of MWCNTs/CeO_2 layer. (e) Polarization curves and power output of reference BOT, reference BOT, modified BOT, modified EOT. (f) Schematic diagram of modified ePTFE skeletons and corresponding reinforced composite membranes. (g) OCV curves vs time for R-CM and Z1-CM. Reproduced with permission from ref. 50 Copyright 2021 American Chemical Society.

At the same time, the hydrophilic and polar modification of ZrO_2 coating on ePTFE skeleton also contributes to the compatibility between ePTFE and PFSA resin. Z1-CM maintained a high OCV retention value throughout the entire test process. In addition, compared with R-CM ($3.51\ mV\ h^{-1}$), the average OCV decay rate of Z1-CM was lower, at $2.60\ mV\ h^{-1}$ (Fig. 6g).

In summary, the application of coating technology in the field of membrane materials research is undergoing rapid development, showing great potential in energy conversion, environmental protection, and chemical engineering. Currently, most research on membrane coatings for electrolytic water fuel cells is applied to PEMs, with fewer modifications on AEMs. Moreover, coating on PEMs/AEMs may face challenges such as compatibility, coating stability, preparation processes, and cost. Compatibility ensures that the coating is compatible with the membrane base material, avoiding delamination or performance degradation. Coating stability is crucial for the long-term performance of the membrane, preparation processes need to control the uniformity and adhesion of the coating and cost considerations should include the cost of preparation and coating materials. Addressing these issues requires comprehensive consideration of factors such as material selection, preparation processes and performance testing to ensure the successful application of coating technology on membrane materials. With ongoing innovation and improvement in coating technology, we can anticipate further diversification and functional enhancement of coating materials in the future. Additionally, there is a need for deeper research into the interaction mechanisms between coatings and substrates to further optimize coating.

4. Summary and outlook

The advancements in surface coating technologies reviewed above offer invaluable insights and a robust foundation for further exploration. However, the journey toward the development of high-performance, cost-effective, and sustainable coatings is far from complete. The following critical areas of investigation hold promise for transforming coating applications in energy systems and beyond.

4.1 Unravelling interface mechanisms

While coatings provide enhanced electrochemical performance primarily through their barrier properties and substrate adhesion, their inability to completely prevent substrate corrosion highlights the complexity of coating-substrate interactions. The mechanisms governing these interactions remain insufficiently understood, limiting the potential for targeted optimization. Advancing our knowledge of these processes requires integrating sophisticated *in situ* characterization techniques, such as X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES), X-ray diffraction (XRD), and infrared spectroscopy (IR), alongside theoretical tools like density functional theory (DFT). These approaches can reveal dynamic structural and chemical transformations during operation, providing the clarity needed to design next-generation coatings with unparalleled protective and functional capabilities.

4.2 Innovating multi-functional coatings

Current research has largely focused on single-layer coatings, yet their limitations suggest a pressing need for more versatile approaches. Layer-by-layer deposition and multi-layer coatings could offer tailored functionalities for catalysts, BPs, or GDLs, addressing specific challenges such as mass transport or thermal stability. Furthermore, the irreversible degradation of membranes underscores the potential of self-repairing coatings, capable of preserving performance over extended operational cycles. Inspiration drawn from biomimetic structures, such as those found in nature, may pave the way for coatings with unique properties, including superhydrophobicity, high thermal tolerance, and exceptional mechanical strength, thereby broadening their applicability in extreme environments.

4.3 Streamlining coating techniques

Despite remarkable progress, the fabrication of advanced coating often relies on intricate and resource-intensive methods. Simplifying these processes without compromising quality remains a priority. Techniques such as ALD, chemical vapor deposition (CVD), physical vapor deposition (PVD), and electrodeposition present opportunities to achieve scalable and efficient production. The challenge lies in fine-tuning these methods to achieve precise control over coating composition, thickness, and uniformity, ensuring compatibility with diverse substrates and applications.

4.4 Design principles of coatings

Effective coating design should consider the following critical aspects.

Barrier functionality. The primary role of coatings is to act as physical and chemical barriers, preventing corrosive species (*e.g.*, H^+, OH^-, Cl^-) from reaching the underlying materials. While for electrocatalysts coatings, in addition to anti-corrosion properties, ionic conductivity should be considered. Traditional dense coatings often suffer from limited ionic conductivity, while porous coatings might not effectively protect against corrosion, leading to a trade-off effect. Future research should focus on developing coatings with tuneable porosity and selective permeability to enhance barrier properties while maintaining ionic conductivity.

Interfacial optimization. Coatings must optimize electronic and ionic interactions at the material-electrolyte interface to enhance charge transfer and catalytic activity. This can be achieved through precise control of coating thickness, composition, and microstructure.

Durability under operational stress. Coatings must withstand mechanical, thermal, and chemical stresses during prolonged operation. Mechanical stability is critical for preventing delamination under high current densities, while thermal stability ensures performance under elevated temperatures.

Chemical stability, particularly in extreme pH conditions, is essential for long-term durability. Future research should prioritize the development of multifunctional coatings with self-healing capabilities, enabling sustainable and cost-effective energy conversion technologies.

By adhering to these principles, researchers can design coatings that not only protect catalysts but also enhance their performance. Future efforts should focus on integrating advanced characterization techniques to unravel the dynamic mechanisms of coating degradation and optimize material properties for specific applications. Additionally, the development of multifunctional coatings with self-healing capabilities could revolutionize the field, enabling sustainable and cost-effective energy conversion technologies. The strategic selection and refinement of coating materials are pivotal not only for advancing electrocatalysis and energy conversion but also for extending the performance and durability of electrochemical devices. This review underscores the transformative potential of coatings in addressing fundamental challenges in catalysis and energy storage, serving as a compass for future research. We envision a future where breakthroughs in coating science drive a new era of catalytic efficiency and stability, and sustainability, supported by innovative design and philosophies and scalable manufacturing techniques.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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