

Surface coating accelerates cathode development for next-generation anion exchange membrane water electrolysis

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The conversion and storage of sustainable energy is essential in addressing the global energy and environmental crises. Hydrogen, a clean and abundant energy carrier, plays a pivotal role in decarbonizing energy sectors. Anion exchange membrane water electrolysis (AEMWE) has gained attention due to cost-effective membranes and non-precious-metal electrocatalysts at the anode. However, a significant challenge remains in the hydrogen evolution reaction (HER) under

alkaline conditions, as it has significantly lower activity compared to acidic environments. The electrode-electrolyte interface is crucial in overcoming this challenge. It directly impacts system efficiency, stability, and longevity.

As a result, recent studies have frequently underscored the importance of interfacial regulators, particularly the application of surface coatings, as an effective strategy to enhance HER activity.^{1–4} These coatings, which may

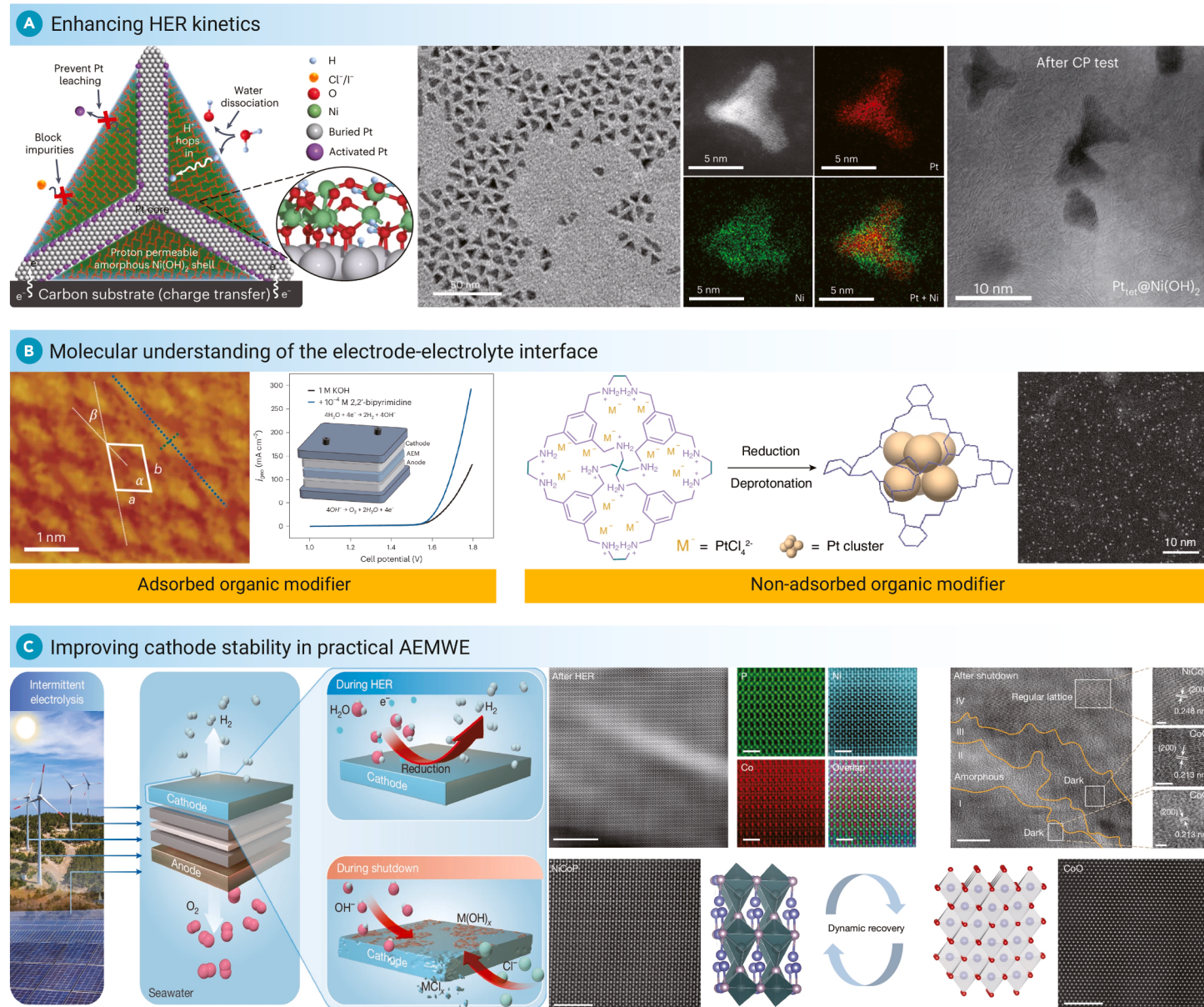


Figure 1. The recent representative progress of surface coatings in cathodes for AEMWE (A) Schematic of Ni(OH)₂-coated tetrahedral Pt nanoparticles and corresponding high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image before and after the HER. Reproduced with permission from Springer Nature,¹ copyright 2023. (B) Left: Scanning tunneling microscopy image of 2,2'-bipyrimidine-modified Pt(111) and corresponding polarization curves of the membrane electrode assembly. Reproduced with permission from Springer Nature,² copyright 2025. Right: synthesis process of porous amine-caged Pt clusters and the corresponding HAADF-STEM image. Reproduced with permission from Springer Nature,³ copyright 2025. (C) The phosphate passivation formation and recovery process for NiCoP–Cr₂O₃ during the HER. Reproduced with permission from Springer Nature,⁴ copyright 2025.

consist of diverse materials such as organic polymers, metal oxides, or phosphates, can improve the catalytic properties of the electrode by optimizing its interaction with H_2O , thus facilitating the reaction and reducing the energy barriers involved. Furthermore, surface coatings can play a vital role in mitigating undesirable effects, such as catalyst oxidation and poisoning, thereby enhancing the long-term stability and durability of the electrodes.

OVERCOMING THE SLUGGISH ALKALINE HER KINETICS

Unlike acidic environments, where hydrogen ions are readily available, the alkaline HER requires H_2O dissociation before hydrogen adsorption and recombination, introducing a substantial kinetic barrier. This step significantly reduces reaction rates, often resulting in performance that is several orders of magnitude lower than under acidic conditions. Consequently, optimizing the kinetics of H_2O dissociation and ensuring efficient proton supply to the active sites are paramount for enhancing cathode performance.

Surface coatings have emerged as powerful tools to address this kinetic bottleneck by tailoring the local chemical environment at the electrode-electrolyte interface. A landmark example is the design of Pt@Ni(OH)_2 core-shell nanoparticles.¹ As depicted in Figure 1A, this structure features a crystalline Pt tetrahedral core encapsulated within an amorphous Ni(OH)_2 shell. The amorphous Ni(OH)_2 shell serves a dual role, functioning as both a H_2O dissociation catalyst and a proton-conductive layer that ensures a continuous proton supply to the active Pt sites. This results in a proton-enriched local environment, which shifts the HER kinetics toward an acidic-like, Tafel-step-limited pathway. Furthermore, structural analysis confirms that the tetrahedral shape and core-shell structure of Pt@Ni(OH)_2 is well-maintained, while the Ni(OH)_2 shell effectively repels impurity ions and slows down the dissolution and diffusion of Pt atoms from the catalyst surface.

ESTABLISHING GUIDELINES FOR DESIGNING THE ELECTRODE-ELECTROLYTE INTERFACE

Accelerating H_2O dissociation necessitates precise manipulation of molecular and atomic interactions at the catalyst surface, particularly in optimizing the adsorption and activation of H_2O . However, a uniform and universally accepted guideline for this process has yet to be established. Recent studies have demonstrated that, in contrast to inorganic coatings, organic modifiers offer unique advantages in deciphering atomic-scale interactions between catalysts and their local environments.

Organic modifiers can be classified into two main categories, non-adsorbed and adsorbed modifiers, based on the nature of their interaction with the catalyst material. Adsorbed organic modifiers do not physically bind to the catalyst surface; rather, they are introduced into the electrolyte and interact with the interfacial H_2O during the HER. These modifiers enhance proton diffusion across the Pt- H_2O interface by facilitating hydrogen bonding through the Grotthuss mechanism. To establish molecular design guidelines, a recent study investigated well-defined single-crystal Pt facets with adsorbates composed of specifically designed molecular building blocks. Specifically, the adsorption of 2,2'-bipyrimidine on the Pt (111) facet was achieved through multiple cyclic voltammetry scans in an electrolyte. As depicted in Figure 1B, electrochemical scanning tunneling microscopy images revealed that adsorbed 2,2'-bipyrimidine on the Pt (111) surface adopts a nearly flat configuration. Remarkably, the coverage of the Pt (111) surface by 2,2'-bipyrimidine results in a 6-fold increase in geometric current density. The primary factor contributing to this enhanced performance is the reduction in activation energy during the Volmer step. Furthermore, the study found that the enhancement of HER activity by organic adsorbates is correlated with their binding energies to Pt electrodes, and these binding energies can be modulated by altering the number of aromatic rings and the hydrophilicity of the adsorbates.

Adsorbed organic modifiers, on the other hand, physically adhere to the surface of the catalyst, forming a thin layer or coating that directly alters the properties of the catalyst. Adsorbed organic modifiers on the catalyst surface can affect several key characteristics of the catalyst, including its electronic structure, charge transfer kinetics, and stability. For instance, a porous, amine-functionalized organic cage that acts as a molecular modifier for Pt clusters in a confined configuration was investigated (Figure 1B), aiming to modulate the electrochemical interface during the

HER.³ This organic cage interacts with the interfacial H_2O by forming moderate hydrogen bonds between its $-\text{NH}-$ groups and H_2O , which helps facilitate the reorganization of H_2O during charge transfer. Additionally, the $-\text{NH}-$ groups of the cage act as a proton pump, continuously transporting protons into the system while expelling hydroxide ions through the electrical double layer. This proton transfer occurs via a similar Grotthuss mechanism like adsorbed modifiers.

ENHANCING CATHODE STABILITY IN PRACTICAL AEMWE OPERATIONS

The practical application of AEMWE encounters not only challenges related to efficiency but also significant stability issues that directly impact its viability for large-scale deployment. A key challenge arises from the intermittent power supply, which leads to fluctuating current densities and operating conditions that may compromise the stability of both the electrochemical process and the system components. For instance, recent research has revealed that integrating seawater AEMWE with intermittent renewable energy sources can lead to operational instability due to frequent startup and shutdown cycles. To solve this issue, the *in situ* formation of a phosphate-based passivation layer on $\text{NiCoP}-\text{Cr}_2\text{O}_3$ has been reported⁴ (Figure 1C). This phosphate passivation layer effectively shields the metal active sites from oxidation during repeated discharge cycles and prevents the adsorption of halide ions on the cathode during shutdown conditions. The passivation mechanism involves an oxidation process in which Co undergoes oxidation, resulting in the formation of CoO and a transition from the NiCoP phase to the CoO phase. Simultaneously, Ni and P species migrate to the inner layer and sublayer, respectively, leading to the development of a Ni-rich inner layer and a CoPO_x sublayer. Notably, this *in situ*-formed passivation layer exhibits a remarkable recovery process under reductive potential, whereby the catalyst can revert to its original hexagonal NiCoP lattice.

SUMMARY AND PROSPECTS

The strategic application of advanced surface coatings has emerged as a critical method for advancing cathode performance in next-generation AEMWE. To drive future breakthroughs, the following points need to be addressed. (1) For a mechanistic understanding of interfacial processes, *in situ/operando* characterization techniques (e.g., Raman and XAFS [X-ray adsorption fine structure]) must be prioritized to unravel the dynamic evolution of coating-electrolyte interfaces under operational conditions, particularly the role of local pH gradients and H_2O reorganization kinetics. (2) For next-generation coating design, hybrid coatings combining inorganic stabilizers (e.g., phosphates) with organic proton relays could bridge the gap between activity and stability. Machine learning-assisted screening of molecular modifiers may accelerate the discovery of tailored interfacial structures. (3) To address system-level integration challenges, scaling coating technologies requires addressing manufacturability (e.g., spray deposition vs. atomic layer deposition) and compatibility with industrial AEMWE stacks.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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