



The Key Role of Interface Water Regulation in Proton-Exchange-Membrane-Water-Electrolysis Cell Electrodes

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Abstract

Proton-exchange-membrane-water-electrolysis cell (PEMWE) is one of the core technologies for achieving large-scale preparation of green hydrogen, and its performance bottleneck is largely limited by the microenvironment of the electrode interface. Interface plays a key role in proton coupled electron transfer, determining the stability of intermediates, and affecting reaction kinetics. This article proposes that the structure, orientation, and dynamic behavior of interface water should be considered as equally important as the intrinsic activity of catalysts. The overpotential of electrode can be significantly decreased, and the stability can be increased at high current densities by systematically regulating the water molecule network at the electrode interface, including interface water density, orientation, hydrogen bond topology, and interaction with ionic polymers. Furthermore, at the molecular scale, combined with electrochemical interface theory, the necessity and feasibility of interface water regulation as a new way for PEMWE electrode design are demonstrated, and current challenges and future directions are pointed out.

Keywords: Interface water; Electrode regulation; Hydrogen bond network, Proton-exchange-membrane-water-electrolysis cell.

Introduction

Proton-exchange-membrane-water-electrolysis cells (PEMWE) are considered one of the optimal pathways for coupling renewable energy for hydrogen production due to their high current density, fast response, and unique structure [1,2]. However, its anodic oxygen evolution reaction (OER) involves four electron transfer, slow kinetics, high overpotential, and a strong acidic and oxidizing environment that poses a severe challenge to the stability of the catalyst [3,4]. Traditional research often focuses on the intrinsic activity of catalysts, such as alloying, defect engineering, or carrier effects, but often overlooks a fundamental fact that all electrochemical reactions occur at the electrode/

electrolyte interface, and the organization of water molecules at the interface directly determines the microscopic pathways of reactant supply, intermediate adsorption, and product desorption [5-7].

Currently, the structural features of interfacial water have gradually been revealed with the advancement of in-situ spectroscopic techniques and theoretical simulations. It is not a simple bulk water, but a unique network shaped by electric fields, surface charges, and ionic polymers. Therefore, here aims to demonstrate that interface water regulation should be elevated to a new level and become a core strategy in parallel with catalyst engineering in PEMWE electrode design.

Electrochemical Role of Interface Water

In PEMWEs, the electrode contacts the proton exchange membrane, forming a complex solid-liquid-ionic polymer three-phase interface [8-10]. Interface water molecules undergo orientation and arrangement under the action of an electric field, and their hydrogen bonding network is reconstructed [8-10]. Specifically, the surface of the anode electrode is positively charged at the oxidation potential, attracting water molecules towards the surface with the oxygen end, forming an ordered interfacial water layer. This structure directly affects the adsorption energy of OER intermediates (such as OH*, O*, OOH*) [11-13]. In this process, the interface water as a proton acceptor/donor, it participates in proton-coupled-electron transfer, reducing the reaction energy barrier [14-16]. Meanwhile, it can effectively stabilize the key intermediates through hydrogen bonding networks and regulating reaction selectivity [14-16]. Furthermore, it affects the nucleation and desorption of oxygen bubbles, avoiding the coverage of active sites [14-16]. Therefore, interface water is a reaction medium, and an importantly synergistic catalyst for the reaction.

The Regulation Mechanism of Interface Water

In the anodic OER process, taking the RuO₂ electrode as an example, the hydrogen bonding topology of interface water on the RuO₂ surface determines the formation pathway of OOH* intermediates [17]. If the interface water network is too rigid, the intermediate stabilization is insufficient, and the overpotential increases; If the network is too loose, the proton transfer efficiency decreases. By introducing hydrophilic/hydrophobic micro regions to regulate the orientation of water molecules, the adsorption free energy of OOH* can be optimized, resulting in a reduction of overpotential by tens of millivolts [18,19]. In addition, the concentration and distribution of hydrated protons in the interface water directly affect the local pH value, which in turn affects the OER kinetics [20,21].

Regulatory strategies

The properties of interface water-controlled electrode materials can be achieved through various means, such as introducing hydrophilic groups (such as -OH, -CH₃) or hydrophobic chains through catalyst surface engineering technology to change the orientation of water molecules [22,23]. For example, modifying perfluorinated sulfonic acid ionomers on the surface of IrOx can form an ordered water layer and enhance OER activity [24]. The second strategy is to use ionic polymer design, which affects the interfacial water density and hydrogen bond strength by adjusting the side chain length and acidity of the ionic polymer [25]. Furthermore, as a typical strategy, by using pulsed potential or light field, the interface water orientation can be dynamically changed to break the linear scaling relationship of reaction intermediates [26,27].

Challenges and Prospects

Although the prospect of interface water regulation is broad, it still faces challenges. firstly, the dynamic evolution of interface water structure under working conditions makes in-situ characterization difficult. Secondly, the coupling mechanism between regulatory strategies and intrinsic activity of catalysts is

not yet clear. Thirdly, it is difficult to ensure the uniformity of the interface water environment in large-scale preparation. Therefore, in the future, the research should focus on the integration of multi-scale simulation and in-situ/operando characterization, establish a quantitative correlation between interface water structure-reaction energy barrier-device properties, and develop scalable interface engineering methods.

Conclusion

In summary, interface water regulation is a key lever for improving the performance of PEMWEC electrodes. It surpasses the limitations of traditional catalyst design and reshapes the reaction microenvironment at the molecular scale, providing a new pathway for reducing overpotential and improving stability. Incorporating interface water as a dynamic catalyst into electrode is expected to drive PEMWEC towards higher efficiency and lower cost. Regarding carbon neutrality and green hydrogen economy, it not only has scientific value, but also contains enormous potential for application.

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Conflict of Interest

No conflict of interest.

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