

Review

Solid–Solid Interface Design for Hydrogen Production by Direct Seawater Electrolysis: Progress and Challenges

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Abstract: Using direct seawater electrolysis (DSE) for hydrogen production has garnered increasing scientific attention as a promising pathway toward sustainable energy solutions. Given the complex ionic environment of seawater, researchers have proposed a diverse range of strategies aimed at addressing the issue of enhancing the corrosion resistance of anodes, yet no optimal solution has been found so far. Among the emerging approaches, a design using multilayer electrode architecture offers notable advantages by introducing abundant active sites, diverse chemical environments, and robust physical structures. Crucially, these configurations enable the synergistic integration of distinct material properties across different layers, thereby enhancing both electrochemical activity and structural stability in harsh seawater environments. Despite these benefits, a limited understanding of the role played by solid–solid interfaces has hindered the rational design and practical application of such electrodes. This review focuses on the design principles and functional roles of solid–solid interfaces in multilayer anodes for the oxygen evolution reaction (OER) under DSE conditions. In addition, we systematically summarize and discuss the representative fabrication methods for constructing solid–solid interfaces in hierarchically structured electrodes. By screening recent advances in these techniques, we further highlight how engineered interfaces influence interfacial bonding, electron transfer, and mass transport during DSE processes, enhancing the intrinsic catalytic activity, as well as protecting the metallic electrode from corrosion. Finally, current challenges and future research directions to deepen the mechanistic understanding of interface phenomena are discussed, with the aim of accelerating the development of robust and scalable electrodes for direct seawater electrolysis.

Keywords: direct seawater electrolysis; hierarchical structure; solid–solid interface; hydrogen production



Academic Editor: Francis Verpoort

Received: 15 April 2025

Revised: 20 May 2025

Accepted: 27 May 2025

Published: 4 June 2025

Citation: Zhou, B.; Wu, T.; Dong, Y.; Zhan, Y.; Wei, F.; Zhang, D.; Long, X. Solid–Solid Interface Design for Hydrogen Production by Direct Seawater Electrolysis: Progress and Challenges. *Inorganics* **2025**, *13*, 183. <https://doi.org/10.3390/inorganics13060183>

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1. Introduction

Excessive reliance on fossil fuels has exacerbated the global energy crisis while intensifying environmental degradation. Therefore, there is an urgent need to develop cleaner and more sustainable alternatives to conventional energy sources [1]. Among these alternatives, hydrogen has emerged as a promising energy carrier due to its high energy density, carbon-free nature, and potential to facilitate a transition to a cleaner energy consumption system. As a result, hydrogen production technologies, particularly water electrolysis, have become a strategic research priority for many countries seeking to diversify their energy sources and reduce dependence on fossil fuels [2].

Over the past few decades, significant achievements have been made in water electrolysis, with much-improved energy efficiency, enhanced durability, and reduced production costs [3–5]. However, one key limitation of traditional water electrolysis is its reliance on purified water, which poses sustainability concerns due to the energy-intensive nature of water purification [6]. Given the vast availability and low cost of seawater, seawater electrolysis offers a compelling alternative to conventional freshwater electrolysis [7–9], which could be further divided into direct seawater electrolysis and indirect seawater electrolysis [10]. Compared with an indirect seawater electrolysis system that involves energy-intensive desalination processes and requires a large occupied area, DSE circumvents the desalination step, offering a more efficient and sustainable pathway for hydrogen production [11–13].

The primary distinction between the DSE system and the conventional freshwater electrolysis system lies in the use of alkaline seawater as the electrolyte. The presence of complex ionic species and suspended impurities in the seawater greatly compromises electrode stability, necessitating that the anode exhibits both strong corrosion resistance and high OER activity, while the cathode must be designed to effectively resist salt precipitation [14]. Though the Ca^{2+} and Mg^{2+} in seawater could easily be removed to circumvent the issue of cathode stability, the unavoidable chloride evolution reaction (CIER) on the anode competes with the OER and generates corrosive species, such as ClO^- , ClO_3^- , etc., which would seriously deteriorate the structure of the anode [15]. According to the Pourbaix diagram analysis, OER exhibits a pronounced thermodynamic advantage over CIER under alkaline conditions when the electrochemical potential remains below 1.71 V. The reduced OER overpotential facilitates the suppression of CIER and enhances electrolytic efficiency [16]. However, in practical applications, the operational overpotential is typically maintained above 480 mV to meet the requirements of industrial-scale, high-current-density electrolysis. Due to the more favorable kinetics of CIER, thermodynamic competition between the CIER and OER becomes inevitable during DSE processes [11]. Nevertheless, with a rational electrode design and material optimization, the oxygen purity in DSE systems can reach as high as 90% to 99%. This is primarily determined by the OER selectivity and corrosion resistance of the anode catalysts. Beyond anodic corrosion, well-documented failure mechanisms in DSE anodes primarily include catalyst layer delamination, surface blockages, and stress-mediated structural degradation. In particular, insufficient interlayer adhesion between the catalyst layer and substrate can lead to delamination under bubble-induced shear forces, representing a critical failure mechanism governed by mechanical–electrochemical coupling. Concurrently, biofouling from marine organisms and particulate sedimentation, as quantitatively demonstrated by Lu et al., induces up to 30% of performance decay through macroscopic surface blockages [17]. Under dynamic operating conditions, such as an intermittent power supply or fluctuating electrolyte flow, the combined effects of mechanical stress and harsh electrochemical environments can further induce surface cracking or even detachment of the active layer, making structural instability another prevalent failure pathway in particular DSE applications [18]. Developing robust, corrosion-resistant anodes that are capable of withstanding the harsh electrochemical conditions in DSE is, therefore, essential for advancing this technology [19–21].

In order to solve the anode corrosion issue caused by CIER products in DSE systems, various innovative catalysts have been designed and applied, including single-atom catalysts, doped catalysts, high-entropy catalysts, etc. [22–27]. Currently, the catalysts for DSE anodes primarily encompass non-precious metal phosphides, nitrides, borides, selenides, oxides, and hydroxides [18]. Each material category demonstrates distinct advantages in terms of electrocatalytic applications. For instance, phosphide-based catalysts are widely implemented in DSE anode design, due to their high catalytic activity and robust stabil-

ity [28]. Nitride catalysts, characterized by exceptional electrical conductivity and corrosion resistance, are frequently used as strategic materials for anode modification [29]. Additionally, borides, selenides, and hydroxides are also renowned as conventional catalytic materials, owing to their superior catalytic performance and elevated electrochemical activity [30–32]. Although these advanced catalysts have demonstrated promising performance by improving catalytic selectivity for the OER while inhibiting the CIER, they still face several challenges such as limited catalytic activity, slow electron transfer rate, ion leaching after prolonged operation, and poor mechanical stability under high current densities [33]. Beyond improving the catalytic activity and selectivity of catalysts toward OER, the rational design and construction of hierarchical electrode structures comprising multi-functional layers have emerged as effective strategies to enhance the overall performance of direct seawater electrolysis systems. These hierarchical electrodes have recently attracted increasing research attention, due to their potential to address the limitations associated with catalyst degradation and electrode corrosion.

In such hierarchical structures, the bonding strength and physicochemical properties of the solid–solid interface between adjacent layers play critical roles in determining the activity, mechanistic stability, and long-term durability of the electrodes used in DSE. Recently, significant achievements have been made in leveraging solid–solid interfaces to enhance interlayer adhesion and promote synergistic interactions, thereby improving the efficiency, stability, and lifespan of seawater electrolysis systems. Nevertheless, despite the growing body of research on DSE, there remains a notable gap in the literature. While several review articles have comprehensively summarized advancements in efficient catalysts [34–36], multilayer electrodes [37–39], and the dynamic evolution of catalysts during the electrochemical progress of seawater electrolysis systems [40], a systematic summary focusing on the design, fabrication, and optimization of hierarchical electrodes from the perspective of the solid–solid interface is still lacking.

This review aims to fill this gap by providing a comprehensive overview of recent progress in the development of hierarchically structured anodes with multi-functional layers for DSE. Firstly, the methods used for intentionally constructing hierarchically structured electrodes with different types of solid–solid interfaces will be reviewed. Then, a detailed discussion will be presented, focusing on the critical roles of solid–solid interface between the adjacent layers in enhancing interlayer stability, promoting synergistic effects, and improving overall electrode performance. Key design principles for next-generation anodes that are capable of sustaining long-term operation under the harsh conditions of DSE will be proposed. Finally, the remaining challenges and future opportunities will be thoroughly examined, aiming to provide valuable insights to accelerate the large-scale deployment of DSE for sustainable hydrogen production.

2. Fabrication Strategies for Constructing Solid–Solid Interfaces in Hierarchically Structured Anodes

Heterostructured electrodes have been widely investigated and well-developed in photoelectrochemical systems [41,42], which are attracting increasing attention from researchers in the field of electrochemical energy conversion reactions [43–45]. In the context of direct seawater electrolysis, numerous hierarchical anodes featuring distinct solid–solid interfaces have been reported, each offering unique advantages in terms of catalytic activity, stability, and durability.

In this section, we will review the latest progress regarding the fabrication and formation processes of these hierarchical electrodes, with a specific focus on the design principles underlying the construction of solid–solid interfaces. By examining representative methods and analyzing their impact on interfacial structure and electrochemical performance, we

aim to provide insights into how rational interface engineering can unlock the full potential of seawater electrolysis systems.

2.1. In Situ Transformation Methods

In situ transformation refers to the spontaneous formation of surface layers during electrochemical reactions, typically triggered by component leaching or ionic interactions under operational conditions. These processes result in multilayer structures where the newly formed layer is tightly integrated with the underlying substrate, offering improved mechanical integrity and better catalytic performance [18,46].

A widely adopted strategy involves the introduction of oxygen-containing anions (e.g., SO_4^{2-} and PO_4^{3-}) into the electrolyte to promote the formation of protective surface species. While this enhances electrode stability by electrostatically repelling corrosive Cl^- ions [47,48], excess anion concentrations can lead to active site blockage and reduced OER activity [49]. Consequently, controlling the generation and distribution of these species is critical for optimizing performance [50].

For instance, Tan et al. developed a $\text{Ni}_2\text{Fe-LDH}/\text{FeNi}_2\text{S}_4$ catalyst supported on nickel foam (NF), which generated a protective sulfate layer via cyclic voltammetry. This SO_4^{2-} layer effectively repelled Cl^- ions, achieving enhanced stability in both simulated and natural seawater over 20 h, with minimal current density loss ($\sim 8\%$ and $\sim 11\%$, respectively) [51] (Figure 1a,b). Similarly, Liu et al. employed a dual-ion strategy using PO_4^{3-} and $\text{Fe}(\text{CN})_6^{3-}$ to modify a $\text{CoFePBA}/\text{Co}_2\text{P}$ catalyst. The synergistic effects between these anions—with PO_4^{3-} providing strong electrostatic repulsion and $\text{Fe}(\text{CN})_6^{3-}$ ensuring high surface coverage—enabled ampere-level current densities to be sustained for over 1000 h [52]. Molecular dynamics simulations confirmed the suppression of Cl^- penetration at the solid–solid interface, validating the effectiveness of this approach (Figure 1c). Inspired by the corrosion resistance mechanism of stainless steel, Shao et al. developed a NiMoFe/NM electrode that formed a chloride-repellent molybdate layer during the OER (Figure 1d), achieving DSE stability over 1500 h at $100 \text{ mA}/\text{cm}^2$, with a $20 \text{ } \mu\text{V}/\text{h}$ degradation rate [50].

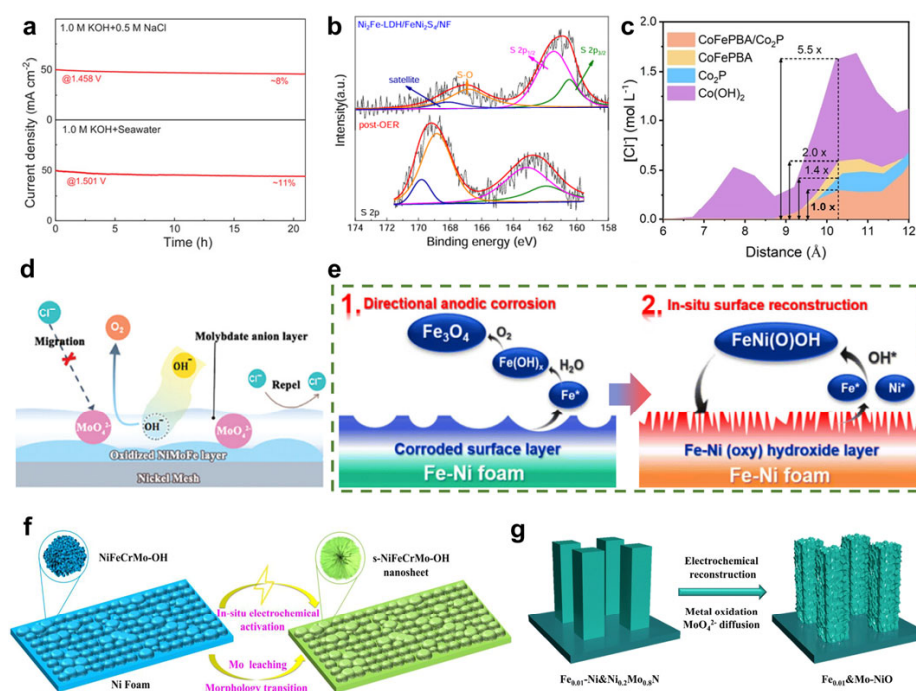


Figure 1. (a) Stability testing of $\text{Ni}_2\text{Fe-LDH}/\text{FeNi}_2\text{S}_4/\text{NF}$ in 1.0 M KOH with 0.5 M NaCl and 1.0 M KOH with seawater, respectively. Reprinted with permission from Ref. [51]. Copyright 2022 John

Wiley and Sons. (b) High-resolution XPS of S 2p of Ni₂Fe-LDH/FeNi₂S₄/NF before and after OER. Reprinted with permission from Ref. [51]. Copyright 2022 John Wiley and Sons. (c) In situ Raman spectra of CoFePBA/Co₂P at various potentials in 20 wt. % NaOH with saturated NaCl. Reprinted with permission from Ref. [52]. Copyright 2023 John Wiley and Sons. (d) Schematic illustration of the anti-corrosion strategy of NiMoFe/NM electrode. Reprinted with permission from Ref. [50]. Copyright 2023 John Wiley and Sons. (e) Schematic illustration of the in situ transformation process of the AC-FeNi(O)OH catalyst. Reprinted with permission from Ref. [53]. Copyright 2022 Royal Society of Chemistry. (f) Schematic illustration of the in situ transformation process of an s-NiFeCrMo-OH catalyst. Reprinted with permission from Ref. [54]. Copyright 2023 American Chemical Society. (g) Schematic illustration of the in situ transformation process of Fe_{0.01}&Mo-NiO catalyst. Reprinted with permission from Ref. [55]. Copyright 2022 Royal Society of Chemistry.

In contrast, Fan et al. leveraged Cl[−] to accelerate the in situ reconstruction of Fe-Ni foam, continuously generating a FeNi(O)OH layer on the electrode surface (Figure 1e) [53]. The fabricated AC-FeNi(O)OH electrode maintained its chemical composition and catalytic efficiency in alkaline seawater for 100 h. Similarly, Pan et al. achieved the partial leaching of Mo from a NiFeCrMo catalyst during electrochemical activation in alkaline seawater (Figure 1f), accompanied by the in situ transformation of NiOOH/FeOOH active layers [54]. The generated oxygen vacancies enabled the s-NiFeCrMo-OH catalyst to operate stably over 1000 h. Ning et al. further demonstrated a precursor catalyst (Fe_{0.01}-Ni&Ni_{0.2}Mo_{0.8}N) that transformed into an OER-active Fe_{0.01}&Mo-NiO phase via an in situ transformation (Figure 1g), sustaining alkaline DSE for 200 h [55].

2.2. Deposition Methods

Deposition-based methods offer precise control over surface composition and interfacial structure by forming active layers on pre-existing substrates through redox-mediated processes. Techniques such as electrochemical and chemical deposition enable the uniform growth of nanostructured coatings with strong interfacial bonding, thereby overcoming the limitations of weak van der Waals forces or electrostatic adhesion [56].

For example, Tran et al. fabricated a one-dimensional Cu@Co-CoO/Rh multilayer electrode using a multi-step deposition route. Co-CoO nanoflakes were first electrodeposited onto Cu nanowires to create a core-shell structure, followed by the chemical deposition of a Rh single-atom layer (Figure 2a,b) [57]. Density functional theory (DFT) calculations revealed that the interfacial interaction between Rh and Co-CoO enhanced charge transfer and generated new active sites, resulting in a low overpotential of 260 mV for 10 mA/cm² in simulated seawater. Then, to anchor catalytic active species onto specialized nanostructures, Ren et al. employed Ni₃S₂ nanopyramids as a robust support and electrodeposited a NiS@FeNi/NF multilayer electrode (Figure 2c,d) [58]. This method preserved the porous structure of the precursor while creating a chemically bonded solid–solid interface that significantly improved mass transport, electron distribution, and parasitic reaction suppression, enabling stable operation at 400 mA/cm² for over 70 h. To densify and roughen the precursor nanorods, Wang et al. electrodeposited NiFe-LDH on sulfide precursors [59]. The fabricated S-NiMoO₄@NiFe-LDH/NF electrode, with its enhanced roughness and porosity, required only 273 mV to reach 100 mA/cm² in alkaline seawater. In contrast to multi-step synthesis, Feng et al. developed a one-step electrodeposition strategy (Figure 2e) to fabricate Ni₃Se₂@MoO₃ catalysts on carbon fiber (CF) [60]. The synthesized Ni₃Se₂@MoO₃/CF heterointerfaces provided abundant active sites and boosted charge transfer via interlayer synergy, achieving 100 mA/cm² at 280 mV in alkaline seawater.

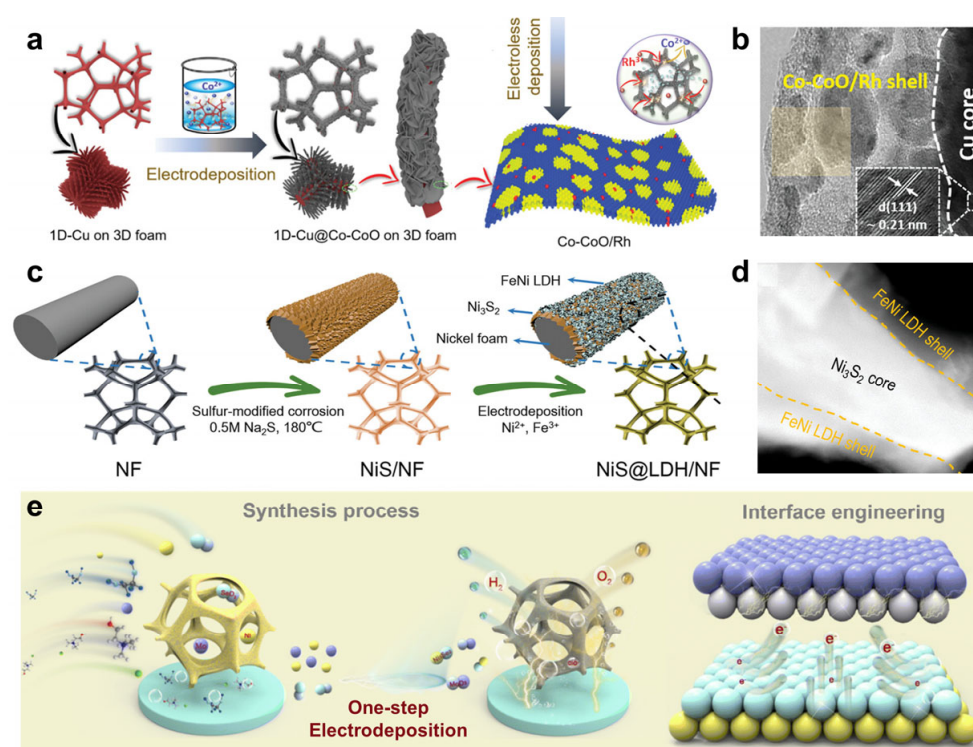


Figure 2. (a) Schematic diagram of the fabrication process of 1D-Cu@Co-CoO/Rh. Reprinted with permission from Ref. [57]. Copyright 2021 John Wiley and Sons. (b) High-resolution XPS of S 2p of Ni₂Fe-LDH/FeNi₂S₄/NF before and after OER. Reprinted with permission from Ref. [57]. Copyright 2021 John Wiley and Sons. (c) Schematic diagram of the fabrication process of NiS@FeNi/NF. Reprinted with permission from Ref. [58]. Copyright 2023 John Wiley and Sons. (d) Dark-field STEM image of NiS@LDH/NF after OER stability in seawater electrolyte. Reprinted with permission from Ref. [58]. Copyright 2023 John Wiley and Sons. (e) Schematic illustration of the synthesis process of Ni₃Se₂@MoO₃/CF. Reprinted with permission from Ref. [60]. Copyright 2023 Royal Society of Chemistry.

2.3. Thermal Synthesis Methods

Thermal synthesis methods are particularly effective for controlling the crystal structure, phase composition, and hierarchical morphology of materials. Conducted in a sealed container under carefully regulated conditions, including temperature, pressure, additives, and the gas/solution environment, these methods allow for the integration of nitrides, phosphides, and sulfides in direct seawater electrolysis anode designs [14,61–63].

For DSE electrodes, Yu et al. reported a NiMoN@NiFeN/NF bifunctional electrode created through hydrothermal growth, followed by thermal nitridation (Figure 3a,b) [64]. The resultant structure exhibited mesoporosity and hierarchical interfaces that were conducive to gas release and electrolyte infiltration, delivering 500 mA/cm² at a low overpotential of 369 mV in alkaline seawater. Similarly, Li et al. integrated bimetallic phosphides with an ultrathin carbon layer (schematic illustration shown in Figure 3c); these transition metal phosphides, which were prepared through thermal synthesis, are regarded as promising catalysts in seawater electrolysis due to their high electrocatalytic activity and corrosion resistance [65]. The C@CoP-FeP/FF multilayer electrode was fabricated by phosphidating a ZIF-67@CoFeO_x precursor on flexible fiber fabric (FF) [66]. The interfacial synergy between the carbon coating and the bimetallic phosphide layer yielded a 3D porous architecture that enhanced its durability, corrosion resistance, and catalytic performance, requiring only 297 mV for 100 mA/cm² in simulated seawater. Moreover, Bao et al. constructed a heterostructure with unique interfacial chemical bonds by coupling Ni-BDC and NM88B(Fe) layers via a two-step hydrothermal method (Figure 3d) [67]. The Ni-O-Fe electronic path-

ways at the interface enabled the electrode to achieve $100 \text{ mA}/\text{cm}^2$ at 299 mV in alkaline seawater. Following the same path, Vedanarayanan et al. sequentially synthesized NiCoS and ZnFe LDH through multi-step hydrothermal processes (Figure 3e), ultimately fabricating a ZnFe LDH@NiCoS catalyst that required only 284.8 mV to reach $10 \text{ mA}/\text{cm}^2$ in alkaline seawater [68].

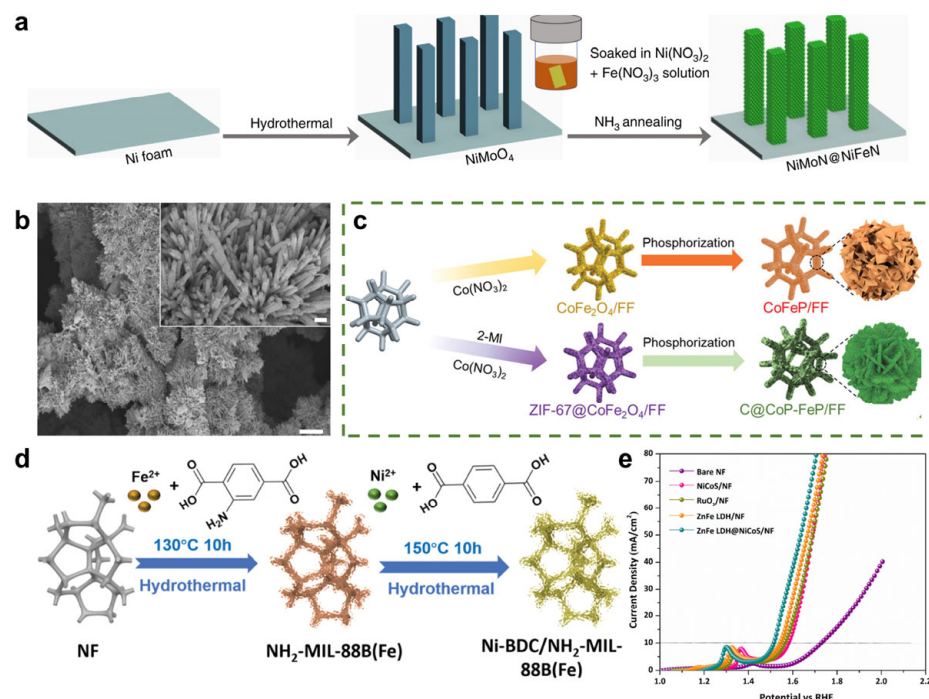


Figure 3. (a) Schematic diagram of the fabrication process of NiMoN@NiFeN/NF. Reprinted with permission from Ref. [64]. Copyright 2019 Springer Nature. (b) SEM image of NiMoN@NiFeN/NF. Reprinted with permission from Ref. [64]. Copyright 2019 Springer Nature. (c) Schematic diagram of the fabrication process of C@CoP-FeP/NF. Reprinted with permission from Ref. [66]. Copyright 2023 John Wiley and Sons. (d) Schematic illustration of the fabrication process of Ni-BDC/NH₂-MIL-88B(Fe). Reprinted with permission from Ref. [67]. Copyright 2024 John Wiley and Sons. (e) LSV curves of ZnFe LDH@NiCoS/NF and other synthesized electrodes in alkaline seawater. Reprinted with permission from Ref. [68]. Copyright 2024 American Chemical Society.

In summary, three primary fabrication strategies, namely, in situ transformation, deposition, and thermal synthesis, have been extensively applied to construct solid–solid interfaces in hierarchical anodes for direct seawater electrolysis. Each method confers unique advantages while introducing inherent trade-offs, as follows: (1) in situ transformation enables the self-formation of protective anion layers, enhancing Cl[−] resistance but potentially compromising interface stability. (2) Deposition methods offer superior interlayer bonding and structural precision, although they may suffer from non-uniformity due to edge effects and surface heterogeneity. (3) Thermal synthesis produces highly porous, crystalline structures that are favorable for mass transport, but high temperatures may induce unintended phase transformations at the interface. To improve accuracy when constructing complex DSE anode structures, researchers have adopted advanced strategies such as electrochemical templating, multi-step deposition, the rational design of metal affinity sites, and the introduction of directional constraint layers to guide catalyst growth [69–71]. These approaches, combined with in situ transformation and controlled deposition techniques, enable the formation of well-defined and uniform solid–solid interfaces, significantly enhancing the stability and activity of the anode architecture. To further evaluate the potential practical applications of these fabrication methods, the costs of the typical prepared electrodes were estimated and are shown in Table 1. This in situ

transformation process, with its mild reaction conditions, was clearly demonstrated to be the most economical option. However, the optimal preparation method should be selected based on the specific application scenarios and requirements. In addition to the chemical composition, electrodes fabricated via different methods often exhibit distinct performance standards, even when they share identical or similar compositions (Table 2). Generally, electrodes prepared by the deposition method have the advantage of low overpotential, but their high Tafel slopes reflect their poor reaction kinetics. This phenomenon is proposed to be related to the additional internal resistance introduced by the deposition method. The electrodes prepared by the thermal synthesis method have the advantage of good reaction kinetics, but the overpotential is generally high. This phenomenon is related to the 3D porous structure formed by the thermal synthesis method. For the in situ transformation method, the resulting electrodes not only show good reaction kinetics but also have lower overpotential and high stability, demonstrating the promising applications of this process for fabricating efficient electrodes. To scale these techniques for economically viable industrial production, two critical technical barriers remain regarding their practical application in cost-effective industrial production. First, laboratory-scale synthesis processes must be optimized for scalability, speed, and operational simplicity to meet industrial demands. This may involve adopting ambient-condition synthesis routes and integrating auxiliary techniques such as electromagnetic field assistance or ultrasonication to accelerate reaction kinetics and facilitate large-scale fabrication. Second, it is imperative to progressively scale up laboratory experiments and simulate realistic industrial operating environments to evaluate whether the electrochemical performance of the catalyst electrodes remains consistent and meets industrial benchmarks under large-scale manufacturing and application conditions. Moreover, further advancement requires a deeper mechanistic understanding and the rational design of solid–solid interfaces to balance structural integrity, catalytic activity, and operational durability. Innovations in characterization techniques, interfacial modeling, and AI-guided material discovery will be instrumental in guiding future research toward optimized multilayer electrode architectures for seawater electrolysis.

Table 1. The preparation cost of fabricating the DSE electrodes.

Sample		Preparation Cost (USD)
In situ transformation methods	Ni ₂ Fe-LDH/FeNi ₂ S ₄ /NF	1.2545
	CoFePBA/Co ₂ P	1.3402
	NiMoFe/NM	0.0401
Deposition methods	Cu@Co-CoO/Rh	5.6913
	NiS@FeNi/NF	0.1606
	S-NiMoO ₄ @NiFe-LDH/NF	0.4861
Thermal synthesis methods	NiMoN@NiFeN/NF	1.0064
	C@CoP-FeP/FF	0.9154
	ZnFe LDH@NiCoS	1.2967

Table 2. Comparison of the DSE performance of different electrodes fabricated using three methods.

Sample		Ref.	Overpotential (mV @ 100 mA/cm ²)	Tafel Slope (mV/dec)	Durability (h)
In situ transformation methods	Ni ₂ Fe-LDH/FeNi ₂ S ₄ /NF	[51]	261	55.9	>20 @ 50 mA/cm ²
	CoFePBA/Co ₂ P	[52]	297	43.5	>1000 @ 1000 mA/cm ²
	NiMoFe/NM	[50]	296	52	>1500 @ 100 mA/cm ²

Table 2. Cont.

	Sample	Ref.	Overpotential (mV @ 100 mA/cm ²)	Tafel Slope (mV/dec)	Durability (h)
Deposition methods	Cu@Co-CoO/Rh	[57]	~440	124.8	>12 @ 10 mA/cm ²
	NiS@FeNi/NF	[58]	258	Not mentioned	>100 @ 200 mA/cm ²
	S-NiMoO ₄ @NiFe-LDH/NF	[59]	273	90	>20 @ 60 mA/cm ²
	Ni ₃ Se ₂ @MoO ₃ /CF	[60]	280	74.7	>200 @ 100 mA/cm ²
Thermal synthesis methods	NiMoN@NiFeN/NF	[64]	286	58.6	>100 @ 500 mA/cm ²
	C@CoP-FeP/FF	[66]	297	59.09	>28 @ 100 mA/cm ²
	Ni-BDC/NH ₂ -MIL-888(Fe)	[67]	299	66.8	>28 @ 330 mA/cm ²
	ZnFe LDH@NiCoS	[68]	>460	85.7	>50 @ 10 mA/cm ²

3. The Critical Roles of Solid–Solid Interfaces in DSE Electrodes

Heterostructured electrodes usually exhibit significantly enhanced catalytic activity and stability regarding DSE, leading to greatly improved hydrogen production efficiency, with a reduced calculated hydrogen cost of as much as 24.4% [72]. Actually, the efficiency of the anodes greatly depends on the properties of the constructed solid–solid interfaces, which have been found to play critical roles in enhancing mass and electron transfer, facilitating interlayer synergistic effects, and strengthening the interface bonding force and anti-scaling effect, thereby improving the overall catalytic performance and long-term stability of the electrodes. In this subsection, we will fully discuss these roles, with representative examples.

3.1. Enhancing Electron Transfer

The most commonly used non-noble metal catalysts for DSE anodes, such as oxides, hydroxides, and sulfides, are mainly compounds with poor conductivity [73,74]. Although they are catalytically active for OER, their inherently low conductivity leads to sluggish reaction kinetics and substantial energy loss that limits the hydrogen production efficiency. Moreover, for DSE anodes with multiple solid–solid interfaces, the primary consideration should be the potential issues arising from the introduction of additional interfaces, which complicates electron transfer during the seawater splitting process. Therefore, many studies have been performed to couple poorly conductive OER catalysts with conductive materials, which improved the charge transfer of the electrodes [75,76].

Carbon materials often exhibit high conductivity and have been widely used in functional materials to improve their charge transfer [77–79]. This method has also been applied in direct seawater electrolysis systems. For example, Gao et al. reported a complex DSE electrode by introducing porous graphdiyne (GDY) interlayers on both sides of RhO_x. The fabricated GDY/RhO_x/GDY multilayer structure contains two solid–solid interfaces [80] with an sp-hybrid carbon-oxygen-rhodium (sp-C~O-Rh) configuration at the interface. The sp-C in GDY significantly enhanced charge transfer, endowing the GDY/RhO_x/GDY electrode with the lowest charge transfer resistance among all synthesized electrodes, as shown in Figure 4a. This interfacial optimization directly improved seawater electrolysis activity, requiring only 261 mV at 100 mA/cm².

Though carbon materials have high conductivity, the interactions between the adjacent layers would be relatively low, due to the chemically inert nature of carbon. Therefore, other compounds with high conductivity have been applied between the current collector and catalyst layer to enhance the charge transfer and robustness of the solid–solid interface. In 2021, Hung et al. introduced a Se layer between the NF and the catalyst of NiFe LDH. The much-reduced diameter of the Nyquist circle in EIS (Figure 4b) indicates the decreased

charge transfer resistance, confirming the enhancement of interlayer electron transfer with the introduction of the Se layer [81].

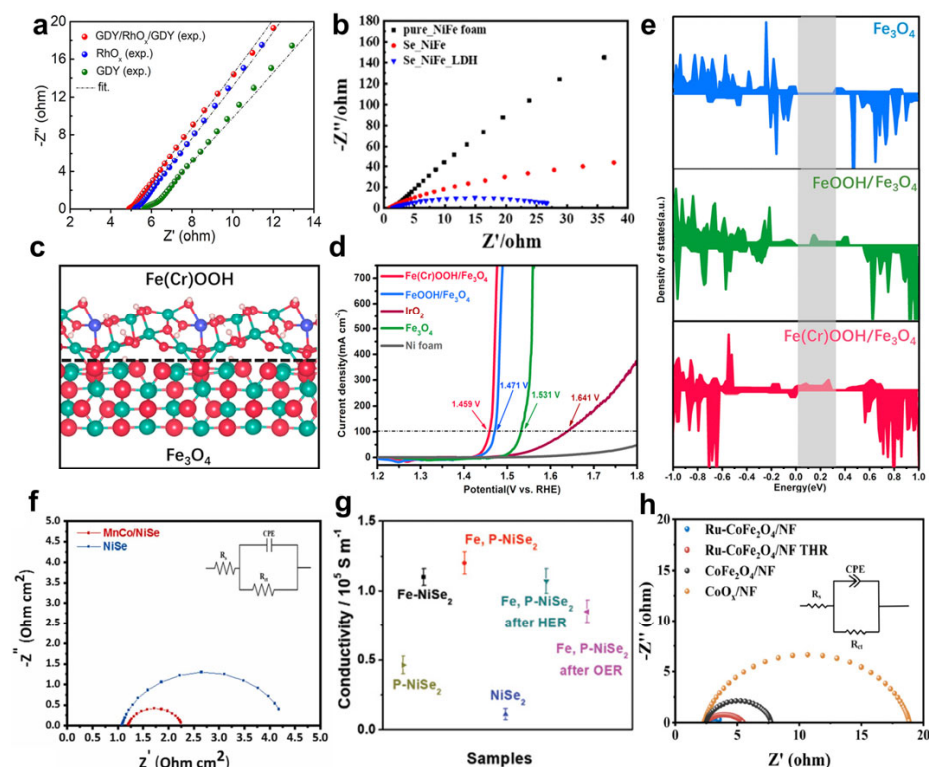


Figure 4. (a) EIS Nyquist plots of GDY/RhO_x/GDY and other synthesized electrodes. Reprinted with permission from Ref. [80]. Copyright 2022 National Academy of Sciences. (b) EIS Nyquist plots of Se_NiFe_LDH and other synthesized electrodes. Reprinted with permission from Ref. [81]. Copyright 2020 Elsevier. (c) The optimized structure of the Fe(Cr)OOH/Fe₃O₄ model. Reprinted with permission from Ref. [82]. Copyright 2022 Elsevier. (d) LSV curves of Fe(Cr)OOH/Fe₃O₄ and other synthesized electrodes at high current densities. Reprinted with permission from Ref. [82]. Copyright 2022 Elsevier. (e) Electronic density of the states of Fe(Cr)OOH/Fe₃O₄ and other synthesized catalysts. Reprinted with permission from Ref. [82]. Copyright 2022 Elsevier. (f) EIS Nyquist plots of NiSe and MnCo/NiSe. Reprinted with permission from Ref. [83]. Copyright 2023 Elsevier. (g) The conductivity of Fe, P-NiSe₂, and other synthesized catalysts. Reprinted with permission from Ref. [84]. Copyright 2021 John Wiley and Sons. (h) EIS Nyquist plots of Ru-CoFe₂O₄/NF and other synthesized electrodes. Reprinted with permission from Ref. [85]. Copyright 2023 Elsevier.

Besides the above-mentioned introduction of a conductive layer to form solid–solid interfaces for improving the charge transfer of the electrodes for DSE, the rationally designed interface interactions resulting from synergistic effects between the adjacent layers have also been found to enhance the conductivity of the heterostructured electrodes. For instance, Li et al. reported an Fe(Cr)OOH/Fe₃O₄ catalyst that exhibits a low overpotential of 229 mV at 100 mA/cm², which was 12 mV and 72 mV lower than that of FeOOH/Fe₃O₄ and Fe₃O₄, respectively (Figure 4c,d). The gray area of the density of states (DOS) analysis shows that FeOOH/Fe₃O₄ has new electronic states in the conduction band compared to Fe₃O₄, indicating that the newly formed solid–solid interaction with the introduction of the FeOOH layer has improved the conductivity of the electrode. Furthermore, Fe(Cr)OOH/Fe₃O₄ has further enhanced the DOS near the Fermi level (Figure 4e), suggesting strong interactions between Fe(Cr)OOH and Fe₃O₄. These results demonstrate that enhancing electron transfer by introducing specific solid–solid interfaces is able to significantly improve electrolysis efficiency [82]. In later studies, MnCo/NiSe (Figure 4f) [83], doped NiSe₂ with Fe/P (Figure 4g) [84], Ru-CoFe₂O₄ (Figure 4h) [85], and other composites have also been

reported. All of them exhibited a great reduction in charge transfer resistance compared to their single-component electrodes, indicating superior electron transfer efficiency with the incorporation of constructed solid–solid interfaces.

In the recent research cases discussed in this subsection, both strategies, namely, introducing conductive interlayers and reconstructing electronic states, fundamentally leverage the critical role of solid–solid interfaces in enhancing electron transfer. Although these designs of multilayer electrodes have significantly improved DSE efficiency, achieving ideal multilayer architectures still faces two key challenges: (1) the bottleneck of interfacial stability. The inherent chemical inertness difference between additional conductive layers and catalyst layers may lead to weak interfacial adhesion and compromised mechanical stability. (2) The trade-off between electron transport and catalytic activity. The conductive overlayers might block catalytic active sites, paradoxically reducing catalytic efficiency. Innovative in situ characterization techniques that reflect microscopic electronic behaviors, combined with a mechanistic understanding of how enhanced electron transfer improves OER performance, will be crucial for guiding the development of next-generation multilayer electrodes with coupled conductive layers.

3.2. Enhancing Mass Transport

Unlike single-layer electrodes, catalytic active sites in multilayer electrodes are not limited to locations on the outermost surface. This structural characteristic imposes requirements for electrolyte penetration depth and bubble detachment rates. The suboptimal design of solid–solid interfaces may induce weak mass transfer; for instance, dense passivation layers decrease OER active sites, while a gas-phobic interface may trigger oxygen bubble film formation, thereby inhibiting any subsequent reactions. Obviously, the bubbles generated during the OER process will accumulate over time, blocking the active sites and affecting the mass transfer process, thereby reducing the catalytic efficiency. Therefore, it is necessary to design the microstructure of the electrodes, especially the properties of solid–solid interfaces in DSE anodes, to improve the mass transfer performance [65].

Li et al. fabricated an NF/(CoMo)_{0.85}Se@FeOOH anode by integrating amorphous FeOOH onto NF/(CoMo)_{0.85}Se forming a 3D conductive scaffold. As revealed by droplet contact angle measurements (Figure 5a), the solid–solid interface between NF/(CoMo)_{0.85}Se and FeOOH conferred exceptional hydrophilicity (0° contact angle for water). This hydrophobic surface promoted efficient electrolyte infiltration and instantaneous bubble detachment, thereby optimizing mass transport kinetics and elevating electrocatalytic activity by reducing the 37 mV overpotential at 100 mA/cm², compared to an electrode made from NF/(CoMo)_{0.85}Se without a hierarchical structure (Figure 5b) [86]. Notably, Li et al. observed the modulated adsorption energetics of *OH intermediates (as verified by DFT calculation in Figure 5c) during OER processes on a NiTe–NiFeN multilayer electrode, which arose from the interfacial synergistic effect between NiTe and NiFeN layers. The optimized interface, with higher mass transfer, enabled the NiTe–NiFeN anode to achieve a Tafel slope of 39.9 mV/dec, outperforming its single-layer counterparts by more than 23% for DSE [87].

Beyond altering the surface physicochemical properties of catalysts, rationally designed solid–solid interfaces can generate a specific nanostructure that promotes oxygen bubble evolution. The MnO₂@NiFe LDH/NF designed by Tang et al. achieved rapid oxygen bubble release through the tip effect of MnO₂ nanoparticles and maintained consistent potential output capability in the gradient potential test (Figure 5d), indicating the excellent mass transfer ability of the multilayer electrode [88]. Guo et al. further engineered a multilayer NiMoO₄@NiFeP/NF electrode featuring a nanorod architecture, which exhibited hydrophilicity and oxygen-phobicity. This hierarchical structure provides abundant

3D channels for electrolyte penetration and promotes the generation and desorption of small-radius bubbles, enhancing the mass transfer of the electrode [89]. Figure 5e shows the changes of adhesion force and buoyant force in adsorption process (phase 1) and the desorption process (phase 2 and 3) of bubbles on the surface of $\text{NiMoO}_4\text{@NiFeP/NF}$. Compared with the initial adhesion force of bubbles on NF (57.9 μN), the initial adhesion force of $\text{NiMoO}_4\text{@NiFeP/NF}$ is close to 0 μN , indicating that it is more conducive to oxygen desorption and, hence, contributes to the fast reaction kinetics.

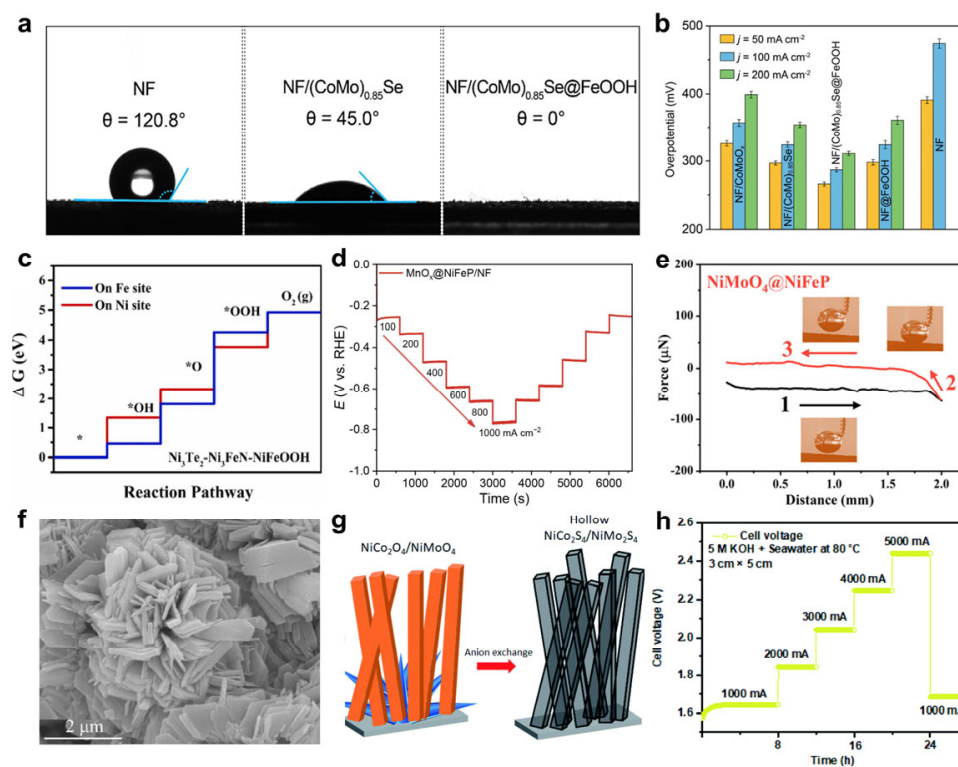


Figure 5. (a) The droplet contact angles of $\text{NF}/(\text{CoMo})_{0.85}\text{Se}$ and other synthesized electrodes. Reprinted with permission from Ref. [86]. Copyright 2023 American Chemical Society. (b) Comparison of the overpotential of $\text{NF}/(\text{CoMo})_{0.85}\text{Se@FeOOH}$ with other synthesized catalysts. Reprinted with permission from Ref. [86]. Copyright 2023 American Chemical Society. (c) Free energy diagrams of $\text{Ni}_3\text{Te}_2\text{-Ni}_3\text{FeN-NiFeOOH}$. Reprinted with permission from Ref. [87]. Copyright 2022 Elsevier. (d) Multistep CP curves of $\text{MnO}_x\text{@NiFeP/NF}$ in alkaline seawater. Reprinted with permission from Ref. [88]. Copyright 2025 Elsevier. (e) Gas-bubble adhesion force measurement during three bubble states. Reprinted with permission from Ref. [89]. Copyright 2023 American Chemical Society. (f) SEM image of $\text{FeCo}_2\text{O}_4\text{-FeCo}_2\text{S}_4/\text{NF}$. Reprinted with permission from Ref. [90]. Copyright 2024 Elsevier. (g) Schematic illustration of the reconstruction process of the $\text{NiCo}_2\text{S}_4/\text{NiMo}_2\text{S}_4$ catalyst. Reprinted with permission from Ref. [91]. Copyright 2022 Royal Society of Chemistry. (h) Multi-step chronopotentiometry test of $\text{NiCo}_2\text{S}_4/\text{NiMo}_2\text{S}_4$ in 5 M KOH with seawater. Reprinted with permission from Ref. [91]. Copyright 2022 Royal Society of Chemistry.

Furthermore, a nanoflower-structured $\text{FeCo}_2\text{O}_4\text{-FeCo}_2\text{S}_4/\text{NF}$ electrode was reported (Figure 5f), which has abundant interlaced petal-like channels providing accelerated gas diffusion pathways [90]. This structural advantage significantly enhanced OER mass transport kinetics, enabling the $\text{FeCo}_2\text{O}_4\text{-FeCo}_2\text{S}_4/\text{NF}$ electrode to achieve a low overpotential of 233 mV at 100 mA/cm^2 for DSE. In a parallel approach, Seenivasan et al. constructed a $\text{NiCo}_2\text{S}_4/\text{NiMo}_2\text{S}_4/\text{NiO}$ multilayer electrode with hollow rectangular prism morphology [91]. By precisely controlling the sulfidation time (8–10 h), they optimized the wall thickness of hollow channels to 15 nm (see the schematic plot in Figure 5g). This 3D structure boosted oxygen-bubble detachment efficiency, thereby improving mass transfer under

industrial-scale current densities, demonstrating exceptional stability at 5000 mA/cm², with 3% potential drift during 28-h multi-step chronopotentiometry tests (Figure 5h).

As shown in this subsection, the selected studies have recently demonstrated the critical role of solid–solid interfaces in enhancing mass transport. Among these works, some regulate interfacial hydrophilicity/hydrophobicity through material species, while others construct specific nanostructures via architecture design. Both strategies have effectively enhanced the mass transport capacity at electrode surfaces. However, future improvements in the mass transport capability of multilayer electrodes will require careful consideration of the following issues: (1) the trade-off between interface modification and catalytic activity. The introduction of surface modification layers should avoid excessive coverage that could lead to the blocking of active sites. (2) Quantitative descriptions should be created of the relevant structure–property relationships. Current research on improving mass transport predominantly relies on empirical structural designs, lacking the quantitative correlations between interfacial atomic arrangements and mass transport kinetics. Therefore, integrating machine learning to optimize multilayer structure design and developing in situ high-speed microscopic imaging characterization techniques will help quantify transport capabilities and guide future electrode engineering.

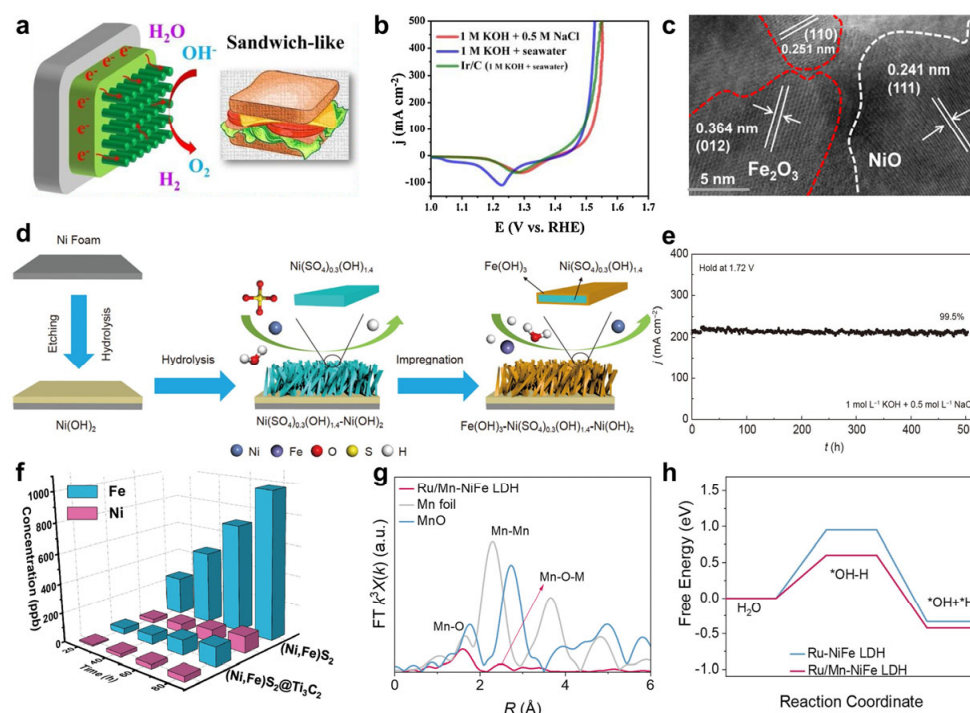
3.3. Strengthening Interface Bonding Force

During seawater electrolysis under high current densities, the substantial generation and detachment of gas bubbles induce strong catalyst–bubble adhesion forces. When these adhesion forces exceed the solid–solid interfacial bonding force, delamination of the electrocatalyst layer occurs [92–94]. Consequently, the mechanical stability of catalytic electrodes is fundamentally governed by the interfacial bonding force at solid–solid interfaces. Current multilayer electrode designs predominantly rely on relatively weak bonding mechanisms such as electrostatic adsorption, van der Waals forces, and mechanical interlocking at these interfaces, which results in inadequate mechanical stability [95]. Recent research advancements have demonstrated notable progress in strengthening the solid–solid interfacial bonding force, with this emerging as a critical direction for developing robust catalytic electrode architectures.

Chen et al. reported the creation of a sandwich-like bifunctional anode for DSE, consisting of a wood aerogel current collector, a NiMoP conductive corrosion-resistant layer, and an S, P-(Ni, Mo, Fe)OOH catalyst layer (Figure 6a). The fabrication process of electroplating and surface etching ensured that the NiMoP/S, P-(Ni, Mo, Fe)OOH interface had a strong interfacial bonding force, due to the presence of metallic bonds, chemical bonds, and van der Waals forces. Furthermore, the wood aerogel exhibited a rough surface morphology and hydroxyl-rich characteristics. Owing to the surface induction effect, the solid–solid interface bonding force between the wood aerogel and NiMoP was greatly enhanced. This electrode achieved a current density of 500 mA/cm² with an ultralow overpotential of 297 mV during the OER process of DSE (Figure 6b) [96]. Afterward, Li et al. synthesized the anode of Fe₂O₃/NiO/NF (FNE300) for DSE, which used NF as both the current collector and the nickel source [97]. During catalyst synthesis, an in situ-generated NiO layer is tightly connected to both the Fe₂O₃ catalyst layer and the NF current collector (Figure 6c).

The etching-hydrolysis strategy was also developed (see Figure 6d) to strengthen the bonding force of the solid–solid interfaces to improve the structural stability of the hierarchical electrodes for DSE. For example, Lu et al. synthesized an Fe(OH)₃-Ni(SO₄)_{0.3}(OH)_{1.4}-Ni(OH)₂ multilayer electrode, with the dendritic Fe(OH)₃ interacting with the catalyst layer and the substrate [98]. The synthesized electrode maintained 99.5% Faradaic efficiency after undergoing an accelerated durability test (ADT) of 500 h in simulated seawater (Figure 6e),

which indicated that the reinforced solid–solid interfacial bonding between the catalyst and substrate significantly enhanced its catalytic stability.



preventing the leaching of metal ions while reinforcing the solid–solid interface bonding force. Moreover, the results of the theoretical simulations shown in Figure 6h indicated that the Ru–O–Mn structure had the lowest formation energy, creating a stable Ru–Mn dual single-atom satellite system, which improved the OER efficiency and the stability of the anode [100].

In short, the solid–solid interfacial bonding force constitutes a critical factor determining the mechanical stability of multilayer electrodes. The recent case studies selected for this subsection demonstrate that through chemical bonding reinforcement and dynamic self-healing strategies, researchers have successfully addressed the delamination issues caused by bubble detachment and ion-leaching problems during long-term operation. However, these approaches still require further optimization: (1) there is a lack of quantitative analysis. A quantitative correlation model between interfacial bonding force and bubble detachment rate has yet to be established, hindering the availability of guidance for optimal solid–solid interface design. (2) Deviations in mechanical stability evaluation. Most current studies employ static tests using simulated seawater, neglecting the effects of real seawater flow conditions and collisions with suspended particulates. Future designs should focus on developing multiphysics coupling models that correlate interfacial bonding energy with stability, creating in situ characterization techniques for interfacial stress, and constructing bio-inspired interfaces for deeper exploration.

3.4. Enhancing Intrinsic Catalytic Performance

Generally, in addition to inheriting the characteristics of each material, heterostructured hybrids also demonstrate some unique properties arising from the constructed interfaces [86,102,103]. In recent years, DSE multilayer electrode designs leveraging the interlayer synergistic effects of such solid–solid interfaces have proliferated, with much-enhanced intrinsic catalytic activity toward OER.

Wang et al. reported a multilayer electrode $\text{CeO}_2/\text{D-NiFe-LDH}@Cu_W$, in which the CeO_2 nanoparticle layer and the cationic-defective D-NiFe-LDH layer synergistically form Ce–O–Ni units and facilitate electron transfer from Ni to Ce [104]. The DFT calculations shown in Figure 7a reveal that this synergistic effect optimizes the free energy adsorption barriers of reactive intermediates (OH^* , O^* , and OOH^*), serving as the primary mechanism for the enhanced OER activity seen in $\text{CeO}_2/\text{D-NiFe-LDH}@Cu_W$. A similar analysis result was reported by Hu et al. They designed a multilayer electrode of $\text{CeO}_{2-x}@\text{CoFe LDH}/\text{NF}$ and found that the presence of CeO_{2-x} induces the oxidation of Co species to form CoOOH , which is an active species of OER (Figure 7b). As shown in Figure 7c, the synergy between the CeO_{2-x} and CoFe LDH layers greatly increases the electrocatalytic activity and seawater electrolysis stability [105]. Zhou et al. fabricated a $\text{MoO}_3@\text{CoO}/\text{CC}$ electrode by sequentially coating first a CoO layer and then a MoO_3 layer on carbon cloth. While DFT confirms that MoO_3 has a chloride-blocking effect, its outstanding OER activity comes from the CoMo LDH phase generated by the interlayer synergistic effect. The surface dynamic reconstruction process is shown in Figure 7d. Remarkably, $\text{MoO}_3@\text{CoO}/\text{CC}$ exhibits minimal overpotential to achieve $200 \text{ mA}/\text{cm}^2$, compared to counterparts without an in situ-formed CoMo LDH phase, accompanied by a more than 20% enhancement in OER activity (Figure 7e) [106].

In the $\text{Fe}_2\text{P}/\text{Ni}_{1.5}\text{Co}_{1.5}\text{N}/\text{Ni}_2\text{P}$ multilayer anode reported by Zhang et al., the inner solid–solid interface generates synergistic effects, providing many multi-functional Fe active sites for OER. During seawater electrolysis, only 329 mV of overpotential is required to reach a current density of $1000 \text{ mA}/\text{cm}^2$ (Figure 7f) [107]. The $\text{GO}@\text{Fe}@\text{Ni-Co}@\text{NF}$ multilayer electrode designed by Amol R. Jadhav et al. (model shown in Figure 7g) demonstrates interlayer synergistic effects between the FeOOH and NiCe-LDH layers through oxygen-

bridged configurations of Fe-O-Co (model shown in Figure 7h), as confirmed by the high-resolution Co 2p XPS spectra [108]. This interfacial engineering induces pronounced synergistic catalytic effects on OER, with the Fe@Ni-Co@NF electrode exhibiting a ~130 mV reduction in overpotential at 1000 mA/cm² compared to their Ni-Co@NF counterpart (Figure 7i), while the GO layer does not directly contribute to enhanced OER performance.

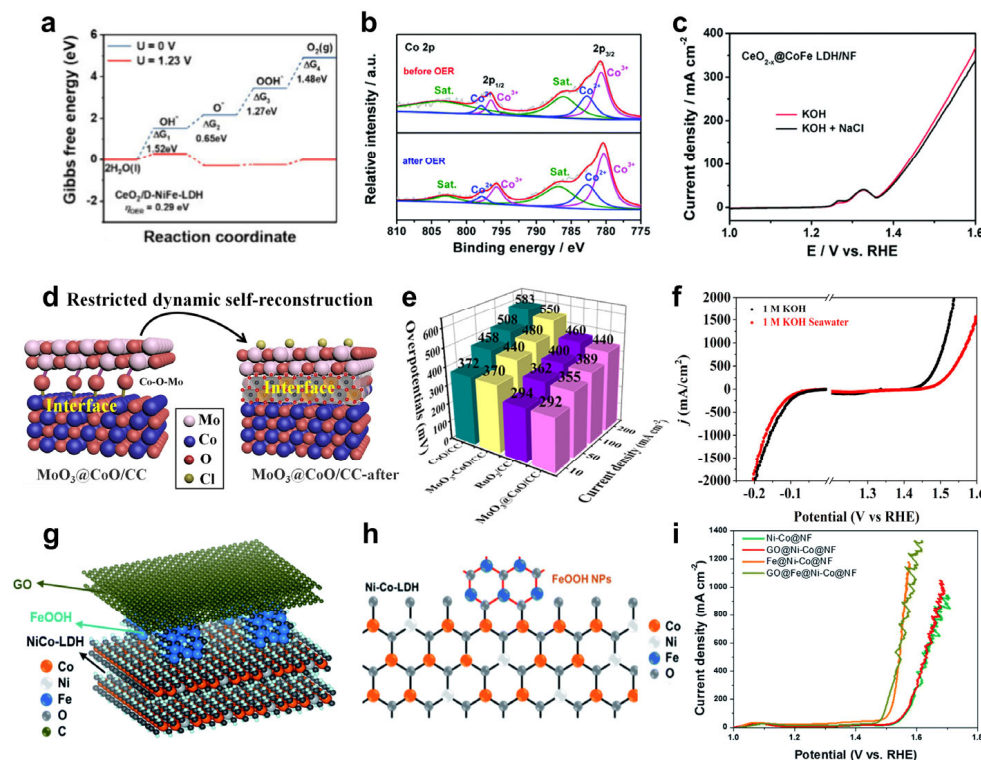


Figure 7. (a) ΔG chart of the OER steps and the density of states at $U = 1.23$ V and $U = 0$ V of $\text{CeO}_2/\text{D-NiFe-LDH}@Cu_W$. Reprinted with permission from Ref. [104]. Copyright 2024 American Chemical Society. (b) High-resolution XPS spectra of Co 2p of $\text{CeO}_{2-x}@CoFe$ LDH/NF. Reprinted with permission from Ref. [105]. Copyright 2020 Royal Society of Chemistry. (c) Polarization curves of $\text{CeO}_{2-x}@CoFe$ LDH/NF in 1 M KOH and 1 M KOH with 0.5 M NaCl. Reprinted with permission from Ref. [105]. Copyright 2020 Royal Society of Chemistry. (d) Schematic diagram of interface reconfiguration of $\text{MoO}_3@CoO/CC$. Reprinted with permission from Ref. [106]. Copyright 2024 Springer Nature. (e) The comparison of the overpotential of $\text{MoO}_3@CoO/CC$ with other synthesized catalysts. Reprinted with permission from Ref. [106]. Copyright 2024 Springer Nature. (f) The polarization curves of OER and HER of $\text{Fe}_2\text{P}/\text{Ni}_{1.5}\text{Co}_{1.5}\text{N}/\text{Ni}_2\text{P}$ in 1 M KOH and 1 M KOH with seawater. Reprinted with permission from Ref. [107]. Copyright 2023 American Chemical Society. (g) Model of $\text{GO}@Fe@Ni-Co@NF$ multilayer electrode. Reprinted with permission from Ref. [108]. Copyright 2020 Royal Society of Chemistry. (h) Model of the Fe-O-Co oxygen bridge. Reprinted with permission from Ref. [108]. Copyright 2020 Royal Society of Chemistry. (i) The LSV curves of $\text{GO}@Fe@Ni-Co@NF$ with other synthesized catalysts. Reprinted with permission from Ref. [108]. Copyright 2020 Royal Society of Chemistry.

In summary, the selected research cases in this subsection systematically demonstrate the role of solid–solid interfaces in enhancing intrinsic catalytic performance. The synergistic effects at solid–solid interfaces significantly improve the OER activity through mechanisms including electronic structure modulation, dynamic phase transition induction, and interfacial bonding reconstruction. Although these cases highlight the performance-enhancing potential of solid–solid interfaces for OER, their practical implementation remains constrained by two critical challenges: (1) a mechanical stability assessment of the reconstructed interfaces. Current research lacks systematic investiga-

tion into the mechanical durability of formed interfaces, hindering a reliable evaluation of their performance under industrial operating conditions. (2) Uncertainty in terms of reconstruction extent. The absence of in situ techniques for tracking interfacial reconstruction makes it difficult to quantify the degree of structural reorganization. Future industrial adoption of multilayer electrodes will require three key advancements: developing visualization-oriented interfacial dynamic characterization techniques, implementing machine learning-accelerated interfacial material screening, and establishing comprehensive synthesis–structure–property databases.

3.5. Chlorine Blocking Effects

In direct seawater electrolysis, the protection of the metallic electrodes from corrosion by chlorine-based species is critically important. To circumvent CLER interference during direct seawater electrolysis and enhance the overall OER selectivity, researchers have strategically leveraged the interlayer synergistic effects of multilayer electrodes, developing three strategic approaches: physical blocking, electrostatic repulsion, and dynamic equilibrium mechanisms (Figure 8a–c).

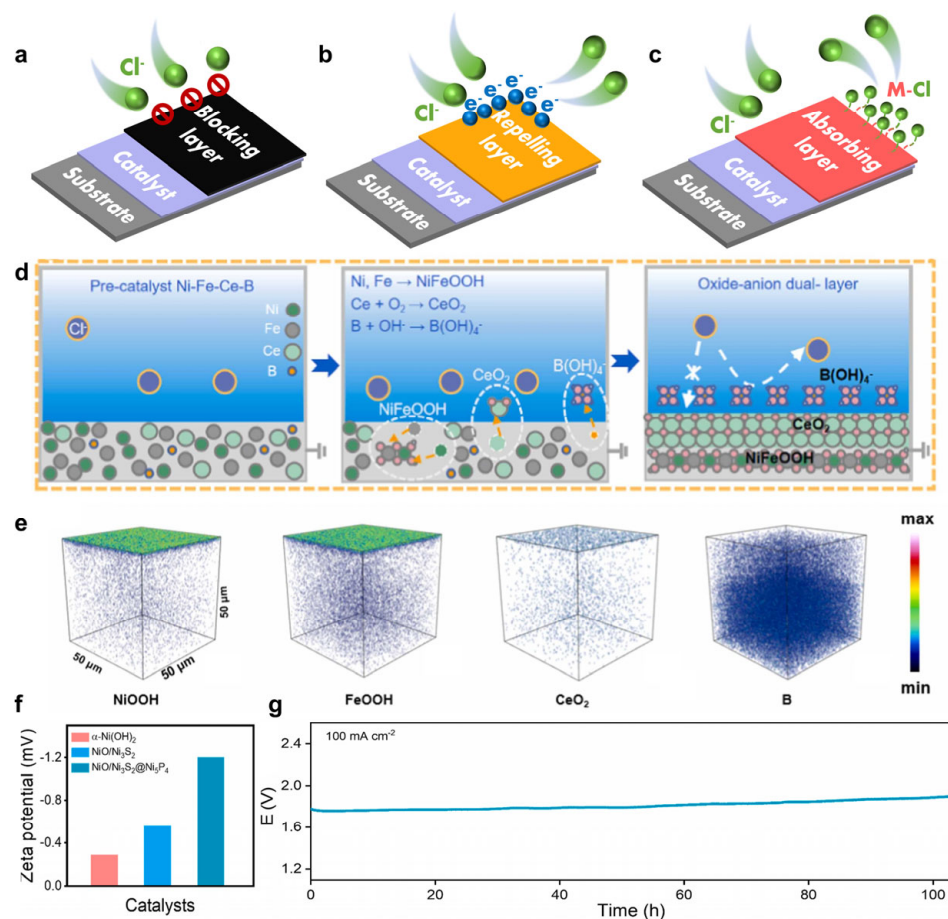


Figure 8. (a–c) Schematic diagram of physical blocking, electrostatic repulsion, and dynamic equilibrium strategies. (d) The in situ evolutionary formation process of $\text{CeO}_2\text{-B(OH)}_4^-$ dual-layer components during OER. Reprinted with permission from Ref. [109]. Copyright 2024 Elsevier. (e) TOF-SIMS images of the spatial distribution of different components in a Ni-Fe-Ce-B/MS electrode. Reprinted with permission from Ref. [109]. Copyright 2024 Elsevier. (f) Zeta potential of $\text{NiO/Ni}_3\text{S}_2\text{@Ni}_5\text{P}_4$ and other synthesized catalysts. Reprinted with permission from Ref. [110]. Copyright 2024 Elsevier. (g) A stability test of $\text{NiO/Ni}_3\text{S}_2\text{@Ni}_5\text{P}_4$ at 100 mA/cm^2 in seawater electrolyte. Reprinted with permission from Ref. [110]. Copyright 2024 Elsevier.

Bennett and Johannes G. Vos pioneered a MnO_x -based physical barrier layer strategy [111,112], which selectively screens Cl^- through interfacial gap dimensions at solid–solid interfaces, and maintains control at solid–solid interfaces, achieving 99% Faradaic efficiency in DSE. Inspired by this strategy, Liu et al. successfully developed a Ni-Fe-Ce-B/MS electrode with triple functional layers: a catalytic NiFeOOH layer, a CeO_2 barrier, and a $\text{B}(\text{OH})_4^-$ layer (Figure 8d) [109]. TOF-SIMS revealed that CeO_2 preferentially accumulates as a passivation layer after a long-term OER test (Figure 8e), synergistically confining the active layer and suppressing dissolution. This hierarchical design enabled stable alkaline seawater electrolysis for 100 h with only a 7% current decay. Following this principle of multilayer synergy, Yu et al. engineered a $\text{NiO}/\text{Ni}_3\text{S}_2@\text{Ni}_5\text{P}_4$ electrode that combined oxide/sulfide heterointerfaces and a Ni_5P_4 barrier [110]. Zeta potential measurements (Figure 8f) showed that its surface potential surpassed other synthesized electrodes by 2–5 times, correlating with enhanced corrosion resistance. The in situ-formed $\text{NiO}/\text{Ni}_3\text{S}_2$ barrier and phosphide passivation layer collectively extended the seawater stability beyond 100 h (Figure 8g).

While physical blocking layers mitigate chloride-ion contact with catalytic electrodes, they often compromise active site accessibility, bubble release, and electrolyte transport while increasing the resistance. To resolve this trade-off, electrostatic repulsion strategies leveraging the negative charge of chloride have emerged. For example, Fan et al. engineered a graphene quantum dot (GQD)-modified multilayer electrode (Figure 9a), where the negatively charged GQD layer simultaneously repels chloride ions by electrostatic forces and tightens interlayer spacing through strong GQD/ CoFe-C_i interactions (Figure 9b). This dual mechanism enhances OER selectivity while physically blocking chloride penetration via size exclusion, significantly improving corrosion resistance [113]. Similarly, the anti-corrosion layer of $\text{Fe-Ni}_3\text{S}_2$ has also been applied, meaning that the constructed NiFeS/NIF electrode exhibited advanced corrosion resistance in DSE (Figure 9c,d) [114].

Building on synergistic interfacial engineering, Zhang et al. developed an a- $\text{NiCoS}/\text{c-CeO}_x/\text{NF}$ multilayer electrode [115], where the electronic synergy between amorphous NiCoS and crystalline CeO_x accelerated SO_4^{2-} generation to suppress CIER while boosting OER selectivity. Post-OER characterization revealed near-complete sulfide leaching via attenuated Ni/Co-S vibrational signals in the Raman spectra, confirming in situ surface reconstruction as the origin of stability over 50 h (Figure 9e). This mechanistic insight aligns with the work of Song et al., who integrated CoFe-LDH with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene followed by phosphorization to create heterostructured $\text{CoFe-P-1000}@\text{Ti}_3\text{C}_2\text{T}_x/\text{CC}$ [116]. The synergy of heterostructure endows the composite with a maximized electrochemically active surface area (ECSA), which facilitates the in situ reconstruction of phosphate species, consequently inhibiting CIER (Figure 9f).

However, even with physical blocking and electrostatic repulsion strategies, complete avoidance of CIER under high-current conditions is difficult [35,120,121]. A paradigm-shifting approach now exploits chloride adsorption to establish dynamic equilibrium. For instance, Duan et al. engineered $\text{Ir}/\text{CoFe-LDH}$ to create unique $\text{Ir-OH}/\text{Cl}$ coordination by adsorbing Cl^- from seawater (Figure 9g). The designed interface simultaneously stabilizes OOH^* intermediates and prevents Cl^- coordination occurring with CoFe-LDH , achieving durable DSE [117]. Parallel innovations include Ag nanoparticle-mediated chloride immobilization (Figure 9h) [118] and $\text{Os-Ni}_4\text{Mo}/\text{MoO}_2$ [122]. This reverse thinking offers a new direction for designing DSE anodes. Beyond conventional strategies, synergistic solid–solid interfacial effects further optimize OER selectivity through reaction mechanism modulation. Feng et al. engineered a heterostructured $\text{RuO}_2@\text{Nb}_2\text{O}_5$ electrode that maintains 100 h at $100 \text{ mA}/\text{cm}^2$ [119]. EXAFS analysis (Figure 9i) revealed that interfacial electron transfer decreases the oxidation state of Ru to weaken Cl^- adsorption and enhance corro-

sion resistance. Crucially, the DFT calculations demonstrated that the Nb_2O_5 interlayer shifts the reaction mechanism from unstable lattice oxygen oxidation to a stable adsorbate evolution mechanism.

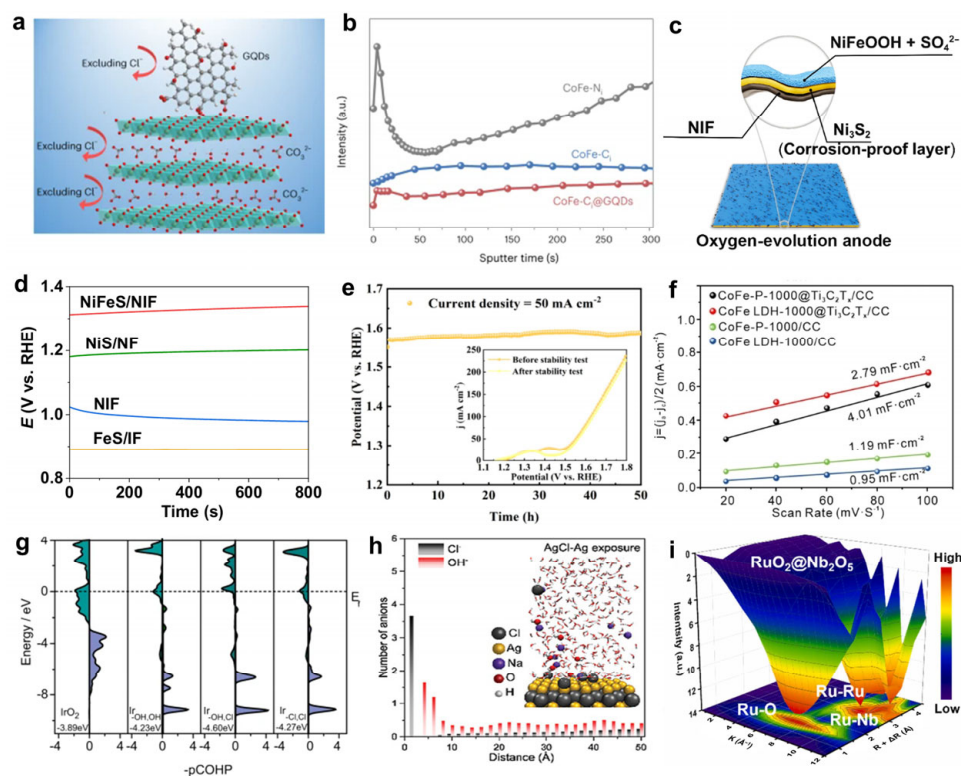


Figure 9. (a) Model of $\text{CoFe-C}_1\text{@GQDs/NF}$. Reprinted with permission from Ref. [113]. Copyright 2024 Springer Nature. (b) TOF-SIMS depth profiles of Cl species in $\text{CoFe-C}_1\text{@GQDs}$. Reprinted with permission from Ref. [113]. Copyright 2024 Springer Nature. (c) Schematic illustration of NiFeS/NIF . Reprinted with permission from Ref. [114]. Copyright 2024 Springer Nature. (d) The open circuit potential of NiFeS/NIF and other synthesized catalysts. Reprinted with permission from Ref. [114]. Copyright 2024 Springer Nature. (e) The stability test of a- $\text{NiCoS/c-CeO}_x\text{/NF}$ at 50 mA/cm^2 in alkaline seawater. Reprinted with permission from Ref. [115]. Copyright 2024 Elsevier. (f) The ECSA of $\text{CoFe-P-1000@Ti}_3\text{C}_2\text{T}_x\text{/CC}$ and other synthesized catalysts. Reprinted with permission from Ref. [116]. Copyright 2025 John Wiley and Sons. (g) The projected crystal orbital Hamiltonian population between the Ir center and the O atom in $^*\text{OOH}$. Reprinted with permission from Ref. [117]. Copyright 2024 Springer Nature. (h) The number of Cl^- and OH^- molecules versus distance above the AgCl-Ag exposure surface, as taken from the classical molecular dynamics simulation result. Reprinted with permission from Ref. [118]. Copyright 2023 John Wiley and Sons. (i) WT-EXAFS plot at the Ru K-edge $\text{RuO}_2\text{@Nb}_2\text{O}_5$. Reprinted with permission from Ref. [119]. Copyright 2025 Elsevier.

In summary, this subsection draws on recent research advances to discuss the role of solid–solid interfaces in chlorine-blocking effects. Three strategies—physical blocking, electrostatic repulsion, and dynamic equilibrium—have been implemented in multilayer electrode designs and demonstrated promising anti-corrosion performance. However, these approaches still exhibit notable limitations: (1) high current density constraints. Existing physical blocking and electrostatic repulsion strategies suffer from diminished chloride-blocking capability under high current density conditions. (2) Maintenance of dynamic equilibrium. The chloride adsorption equilibrium shows sensitivity to electrolyte composition, and natural seawater fluctuations pose the risk of disrupting the designed equilibrium. Therefore, future developments incorporating cross-scale collaborative designs that synergistically combine physical blocking, electrostatic repulsion, and dynamic equilibrium mechanisms may provide solutions to these challenges.

3.6. Anti-Scaling Effects

While significant advances have been made in enhancing anode corrosion resistance, comparatively less research attention has been paid to cathodic anti-scaling strategies in near-neutral DSE systems. In alkaline electrolytes, Ca^{2+} and Mg^{2+} ions are typically removed via seawater alkalization pretreatment, as their hydroxide precipitation is thermodynamically favorable [123]. Conversely, in acidic conditions, the precipitation of $\text{Ca}^{2+}/\text{Mg}^{2+}$ hydroxides is suppressed. Therefore, cathodic salt deposition becomes a critical issue, predominantly in near-neutral environments, where neither the removal nor suppression of these ions is efficient.

To mitigate this challenge, two primary strategies have emerged—both relying heavily on the design of solid–solid interfaces to improve structural integrity and mass transport dynamics. One widely adopted approach involves constructing self-cleaning electrode architectures. For example, Liang et al. developed a 3D honeycomb-like porous composite electrode (NCP/PC) featuring aligned microchannels that facilitate the transportation of hydrogen microbubbles and $\text{Ca}^{2+}/\text{Mg}^{2+}$ precipitates (Figure 10a), enabling rapid detachment from the electrode surface through hydrodynamic forces [124]. The solid–solid interface in NCP/PC provides robust interfacial adhesion, allowing a denser and more uniform loading of needle-like NCP catalysts (Figure 10b). Notably, its superior electrical conductivity indicates effective electrical coupling between NCP and PC layers (Figure 10c), enhancing cathodic HER performance with 1000-h operational stability (Figure 10d).

In a similar study, Liang et al. fabricated CW-1000, a cathode material featuring uniform pore size distribution and low tortuosity (Figure 10e), which demonstrates remarkable anti-scaling capability [123]. When integrated with a Pt catalyst layer (Pt/CW-1000), the electrode demonstrated significantly improved HER activity. The microbubbles generated during HER contribute to continuous surface cleaning, enabling stable operation over 180 h in untreated natural seawater (Figure 10f).

The second strategy to mitigate salt deposition focuses on preventing precipitate accumulation through the ionic repulsion mechanism. Liang et al. developed a positively charged organic superbases DMAN layer as a proton sponge on the cathode surface, effectively repelling the similarly charged $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions in seawater [123]. By precisely tuning the layer thickness in a DMAN/Pt/C multilayer electrode, this repulsive capability can be further optimized (Figure 10g). Similarly, Yi et al. utilized a high-surface-energy NiCu alloy to adsorb dense hydration layers; it excludes $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions and forces their nucleation in the electrolyte rather than on the electrode surface (Figure 10h), demonstrating solid-phobic anti-scaling characteristics [125]. Innovatively, Guo et al. introduced a Lewis acid layer on the cathode surface, significantly elevating the local pH value at the cathode–electrolyte interface (Figure 10i). This modification induces the precipitation of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in bulk seawater before their approach to the cathode (Figure 10j), achieving effective ion exclusion [126].

In conclusion, both strategies—which are rooted in solid–solid interface engineering—have shown considerable promise in enhancing cathodic durability in DSE systems. The self-cleaning approach effectively minimizes the accumulation of metal salts and other particulate contaminants, yet its intricate architecture may pose challenges in terms of manufacturing scalability and mechanical robustness. In contrast, the ionic repulsion strategy offers superior physicochemical stability but remains vulnerable to biofouling and particulate clogging, often necessitating seawater pretreatment in real-world applications. To date, research into cathode designs that systematically leverage solid–solid interfacial properties remains limited, indicating substantial opportunities for innovation and advancement in this emerging domain.

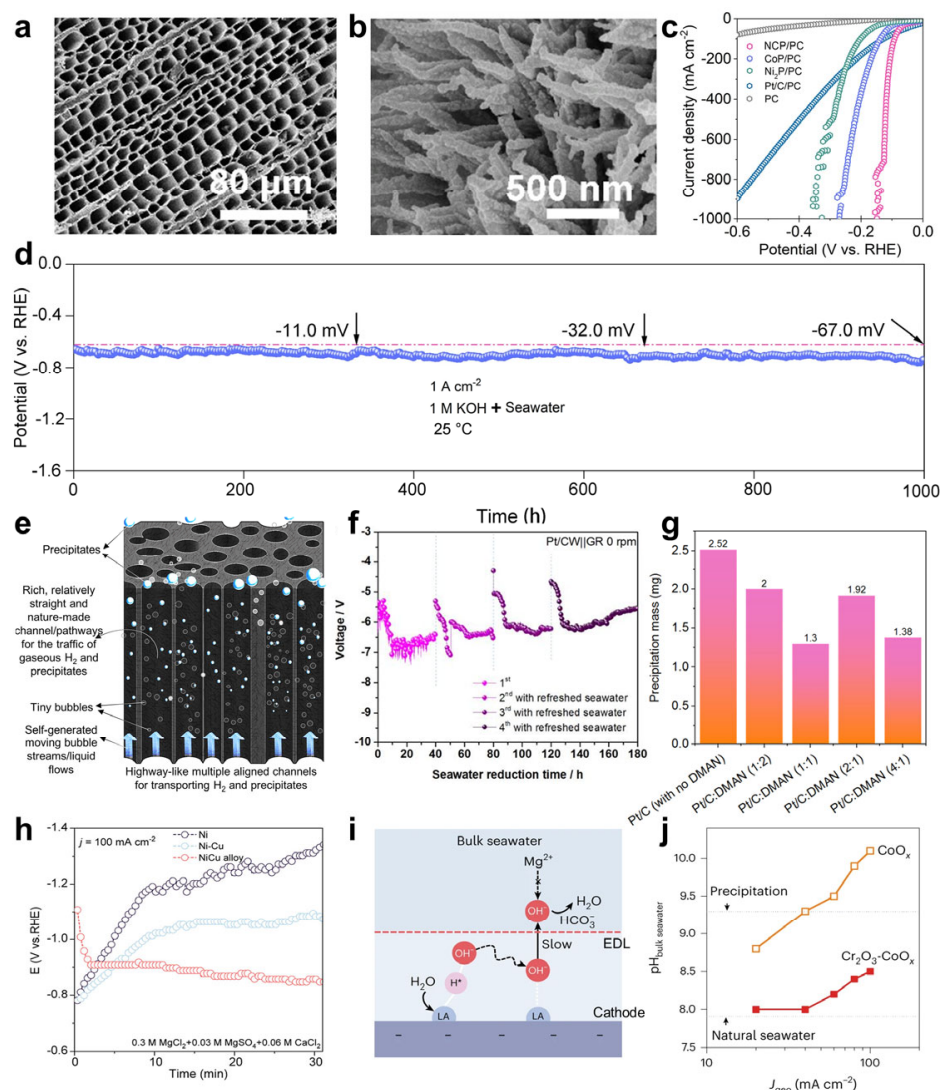


Figure 10. (a) SEM image of PC. Reprinted with permission from Ref. [124]. Copyright 2024 Springer Nature. (b) SEM image of NCP/PC. Reprinted with permission from Ref. [124]. Copyright 2024 Springer Nature. (c) LSV curves of NCP/PC and other synthesized electrodes. Reprinted with permission from Ref. [124]. Copyright 2024 Springer Nature. (d) Chronopotentiometry curve of NCP/PC at -1.0 A/cm^2 . Reprinted with permission from Ref. [124]. Copyright 2024 Springer Nature. (e) Schematic illustration of the CW cathode. Reprinted with permission from Ref. [123]. Copyright 2024 Elsevier. (f) Stability test for Pt/CW-1000 | GR. Reprinted with permission from Ref. [123]. Copyright 2024 Elsevier. (g) The amounts of precipitation, which increased on the electrodes after the test. Reprinted with permission from Ref. [123]. Copyright 2024 Elsevier. (h) Accelerated durability test of the NiCu alloy in simulated electrolyte ($0.3 \text{ M MgCl}_2 + 0.03 \text{ M MgSO}_4 + 0.06 \text{ M CaCl}_2$). Reprinted with permission from Ref. [125]. Copyright 2024 American Chemical Society. (i) Schematic diagram of local alkaline microenvironment generation on the $\text{Cr}_2\text{O}_3\text{-CoO}_x$ cathode. Reprinted with permission from Ref. [126]. Copyright 2023 Springer Nature. (j) The pH values of bulk seawater around the CoO_x cathode and $\text{Cr}_2\text{O}_3\text{-CoO}_x$ cathode. Reprinted with permission from Ref. [126]. Copyright 2023 Springer Nature.

4. Summary and Outlook

This review systematically highlights the critical challenges in the design of DSE electrodes and summarizes recent progress in the fabrication of hierarchically structured multilayer electrodes. Emphasis is placed on electrode architectures that achieve a balance between catalytic activity, long-term stability, corrosion resistance, and cost-effectiveness. In particular, this review offers a comprehensive analysis of the previously underexplored

roles of solid–solid interfaces within these multilayer structures, which are pivotal to the performance and durability of DSE electrodes.

Generally, the hierarchically structured electrodes used for DSE have been prepared via in situ transformation, deposition, and thermal synthesis methods. The existence of rationally designed solid–solid interfaces for use in these electrodes could greatly improve the charge and mass transfer and enhance the intrinsic catalytic activity toward OER, as well as protect the metallic electrode by blocking chlorine-based species. Furthermore, reinforcing the interfacial bonding through strong chemical interactions and abundant functional groups is essential for improving the mechanical robustness of multilayer configurations. Such interfacial engineering not only enhances structural integrity but also contributes positively to OER activity, thereby improving hydrogen production efficiency in real seawater environments. For the DSE cathode, the anti-scaling effect at the solid–solid interface significantly reduces the cathode failure problem caused by the deposition of the metal salts found in seawater, thereby synergically improving the system stability of the DSE process. Based on the multifunctional roles of solid–solid interfaces, integrating materials with specific interfacial functions—provided that no chemical incompatibilities occur—represents a promising strategy for constructing high-performance multilayer DSE anodes. This approach enables the electrode to simultaneously satisfy multiple requirements, such as enhanced electron/mass transport, catalytic activity, and chlorine resistance. However, increasing the number of layers indiscriminately may lead to reduced mechanical integrity and increased interfacial resistance, ultimately compromising electrode performance. Therefore, in designing the next generation of multilayer electrodes, it is essential to make informed material selections and optimize stacking sequences. These decisions should be grounded in a comprehensive understanding of the interfacial properties of each layer, supported by experimental validation, to achieve a practical balance between functional integration and structural stability.

Despite these advancements, the deeper understanding and systematic exploitation of solid–solid interfaces in multilayer electrodes remain at a nascent stage. To address these challenges and unlock the full potential of solid–solid interface engineering, the following future research directions are proposed:

- (1) Mechanistic insights and strategies for multi-ion corrosion resistance. While most current studies on DSE anodes focus on mitigating electrode corrosion by Cl^- , recent reports indicate that bromide ions (Br^-) may induce even more severe and mechanistically distinct degradation [127]. Cl^- often corrodes to form narrow and deep pits, due to its own rapid diffusion kinetics, while Br^- corrodes to form wide and shallow pits, due to its lower reaction energy. The experimental results prove that the corrosion induced by Br^- will cause the catalyst layer to peel off from the substrate over a large area, resulting in the rapid deactivation of the anode. Recently, some researchers have proposed solutions to this problem. For example, Fan et al. utilized the electrostatic complexation of biomass-derived polysaccharides to form gradient negative-charge interfaces [128]. This interface achieves a stable operation of 1300 h in natural seawater electrolytes by repelling Br^- . Therefore, conventional interfacial designs optimized for Cl^- resistance may fall short under real seawater conditions, where multi-ion co-corrosion occurs. Future efforts should focus on developing interface structures that can resist complex ion interactions and on constructing a mechanistic framework for multi-ion corrosion processes [129,130].
- (2) Understanding interfacial stress responses in dynamic environments. The integration of seawater electrolysis with intermittent renewable energy sources such as wind or solar power induces dynamic operating conditions [131–133]. The fluctuating operating conditions of intermittent renewable energy sources can lead to frequent

fluctuations in electrode potential [134], triggering redox cyclic stress and damaging the electrode structure. Recently, Liu et al. placed the seawater electrolysis system on a floating seawater hydrogen production platform and added an energy storage device that achieved a stable energy supply [135]. Although this offers temporary solutions, it also introduces added system complexity and costs. Alternatively, the dynamic repair interface of NiCoP-Cr₂O₃ designed by Sha et al. can be transformed in situ to form a phosphate passivation layer when the DSE system is turned on, preventing insoluble precipitation in seawater from blocking the cathode. When the DSE system is shut down, the phosphate ions that are converted and adsorbed on the electrode surface electrostatically repel chloride ions in seawater, preventing the electrode from being corroded. Therefore, the synthesized electrode can work stably for 10,000 h under fluctuating working conditions [134]. Advanced interfacial designs that are capable of accommodating stress fluctuations without performance degradation are urgently needed.

- (3) Integration of advanced in situ/operando characterization techniques. A variety of in situ and operando tools have emerged as being indispensable for elucidating the dynamic behavior of solid–solid interfaces under DSE conditions. Techniques such as in situ X-ray absorption spectroscopy can track local structural and chemical changes, shedding light on interface formation and evolution. In situ X-ray photoelectron spectroscopy can reveal electronic structure shifts and compositional changes during operation, while in situ transmission electron microscopy and X-ray diffraction enable the visualization of morphological and phase changes in real time. Moreover, in situ Raman spectroscopy captures the dynamics of the surface intermediates involved in interface reconstruction, and in situ EIS quantifies changes in interfacial charge and mass transfer resistance. These complementary techniques provide a multi-dimensional understanding of how solid–solid interfaces function and degrade in realistic DSE environments. Such insights are critical for predicting long-term electrode durability and for guiding the design of more robust, efficient interface architectures in future DSE systems.
- (4) Machine learning-assisted interface design. Theoretical modeling and machine learning offer powerful tools for accelerating electrode development [18,136]. By encoding the interfacial properties and material combinations discussed in this review as descriptors, it is possible to construct comprehensive databases for data-driven screening. DFT-based pre-evaluation, such as the successful prediction of the Fe-Ni₂P_v/NF system [137], provides a promising pathway for rational electrode design. Integrating these computational approaches with experimental validation will significantly enhance the discovery and optimization of high-performance multilayer electrodes for DSE.

Author Contributions: Conceptualization, B.Z. and X.L.; writing—original draft preparation, B.Z.; writing—review and editing, T.W., Y.D., Y.Z., F.W., D.Z., and X.L.; supervision, X.L.; funding acquisition, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Shanghai (24ZR1434300) and Shanghai Jiao Tong University (No. WH220828001, ZXDF280001).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations in alphabetical order are used in this manuscript:

ADT	Accelerated durability test
CC	Carbon cloth
CF	Carbon fiber
CIER	Chloride evolution reaction
DFT	Density functional theory
DOS	Density of states
DSE	Direct seawater electrolysis
ECSA	Electrochemically active surface area
EIS	Electrochemical impedance spectroscopy
FT-EXAFS	Frontier-extended X-ray absorption fine structure
GDY	Graphdiyne
GO	Graphene oxide
GQD	Graphene quantum dot
LDH	Layered double hydroxide
LSV	Linear sweep voltammetry
MS	Melamine sponge
NF	Nickel foam
OER	Oxygen evolution reaction
SEM	Scanning electron microscope
STEM	Scanning transmission electron microscopy
TOF-SIMS	Time-of-flight secondary ion mass spectrometry
XPS	X-ray photoelectron spectroscopy

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