Journal of Electrochemistry

Volume 28
Issue 10 *Special Issue on Water Electrolysis for Hydrogen Production (II)*

2022-10-28

Alkaline Seawater Electrolysis at Industrial Level:Recent Progress and Perspective

Tao Zhang

Yi-Pu Liu

Qi-Tong Ye

Hong-Jin Fan
1. School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link,Singapore 637371, Singapore;, fanhj@ntu.edu.sg

Recommended Citation
Tao Zhang, Yi-Pu Liu, Qi-Tong Ye, Hong-Jin Fan. Alkaline Seawater Electrolysis at Industrial Level:Recent Progress and Perspective[J]. *Journal of Electrochemistry*, 2022 , 28(10): 2214006.
DOI: 10.13208/j.electrochem.2214006
Available at: https://jelectrochem.xmu.edu.cn/journal/vol28/iss10/5

电 化 学
J. Electrochem. 2022, 28(10), 2214006 (1 of 18)

[Perspective] DOI: 10.13208/j.electrochem.2214006 Http://electrochem.xmu.edu.cn

Alkaline Seawater Electrolysis at Industrial Level: Recent Progress and Perspective

Tao Zhang[1#], Yi-Pu Liu[2#], Qi-Tong Ye[2], Hong-Jin Fan[1*]
(*1. School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore; 2. State Key Laboratory of Marine Resource Utilization in South China Sea, School of Materials Science and Engineering, Hainan University, Haikou 570228 P. R. China*)

Abstract: Industrial hydrogen generation through water splitting, powered by renewable energy such as solar, wind and marine, paves a potential way for energy and environment sustainability. However, state-of-the-art electrolysis using high purity water as hydrogen source at an industrial level would bring about crisis of freshwater resource. Seawater splitting provides a practical path to solve potable water shortage, but still faces great challenges for large-scale industrial operation. Here we summarize recent developments in seawater splitting, covering general mechanisms, design criteria for electrodes, and industrial electrolyzer for direct seawater splitting. Multi-objective optimization methods to address the key challenges of active sites, reaction selectivity, corrosion resistance, and mass transfer ability will be discussed. The recent development in seawater electrolyzer and acquaint efficient strategies to design direct devices for long-time operation are also highlighted. Finally, we provide our own perspective to future opportunities and challenges towards direct seawater electrolysis.

Key words: Seawater electrolysis; anticorrosion; alkaline hydrogen generation; industrial electrolyser

1 Introduction

Large-scale electrochemical water splitting into hydrogen (H_2) by renewable electricity, characterized by high energy density (142 $MJ \cdot kg^{-1}$) and zero emission, has been regarded as one of the most promising strategies to handle the global energy crisis and environmental issues[1-4]. Nevertheless, the current electrolysis of high purity water at an industrial level would severely deplete freshwater resources. Seawater covers ca. 96.5% of the total water source on the planet and its typical salinity of 3.5wt% makes it a natural electrolyte[5,6]. Some renewable energy-conversion technologies are closely related to the ocean (solar, wind and wave energy), making it facile to link electrochemical seawater electrolysis to these environmental friendly technologies[7,8]. Additionally, the consumption of H_2 gas produced by seawater splitting can produce fresh potable water and afford electrical power via membrane exchange fell cells[9,10]. Direct electrolysis of seawater into highly pure H_2 is thus regarded extremely competitive to realize both sustainable energy and freshwater resource conservation (Figure 1).

For the purpose of industrial seawater splitting, the primary standard is high current density (> 500 $mA \cdot cm^{-2}$) and long-term durability (over 1000 h), especially at low overpotentials (< 490 mV)[11-15]. While seawater electrolysis is a promising technology, there

Cite as: Zhang T, Liu Y P, Ye Q T, Fan H J. Alkaline seawater electrolysis at industrial level: Recent progress and perspectives. *J. Electrochem.*, 2022, 28(10): 2214006.

Received: 2022-06-27, Revised: 2022-08-04. # Tao Zhang and Yipu Liu contributed equally to this work.* Corresponding author, Tel: +0065 65137408, E-mail: fanhj@ntu.edu.sg

are still grand challenges to meet the above standard. These challenges include:

1) *High cost of raw materials*. Pt-based nanoparticles are state-of-the-art hydrogen evolution reaction (HER) electrocatalysts, while Ir/Ru-based oxides are considered as commercial electrocatalysts for oxygen evolution reaction (OER). The scarcity and high cost of these noble-metal based materials restrict their large-scale industrial application[16,17].

2) *Insufficient performance of electrocatalysts*. The intrinsic catalytic activity is correlated to the energy barrier for surface chemisorption of intermediates, the density of effective active site (the key factor for high current-density), the electrical conductivity, and so on. Strategies such as phase/structure/atom engineering are being widely investigated to unlock the potential or enhance the existing active sites.

3) *Narrow thermodynamic potential window*. In a typical alkaline seawater system ($pH > 7.5$), the equilibrium potential of OER (E_{OER}^0) is more negative than that of chlorine evolution reaction (CER, E_{CER}^0). There is thus a thermodynamic potential window of around 480 mV ($E_{OER}^0 - E_{CER}^0$), where a 100% OER selectivity can be achieved[18-20]. However, the OER (four-electron transfer process) kinetic is more sluggish than that of two-electron CER. As a result, the real potential window for 100% OER is quite narrow. Thus, the OER-only potential window in the industrial seawater splitting should be widened as much as possible.

4) *Sluggish mass transfer process*. The industry level current densities would accelerate the consumption of reactant ions and accumulation of gaseous products on the electrode surface[21]. In this case, strategies are needed to manipulate the adsorption of electrolyte on the catalyst surface and desorption of gas bubbles by microstructure engineering.

5) *Corrosion and catalyst deterioration*. Besides the unavoidable corrosion of chloride (Cl^-) ions on both electrodes, the metal ions in seawater including magnesium (Mg^{2+}), calcium (Ca^{2+}), et al., and even bacteria, microbes, and small particles, will precipitate on the surface of electrode due to local pH increase or reduction reaction. These processes will poison the electrode materials and lead to catalytic performance degradation[22,23].

Although many excellent reviews are available on catalysts development for water electrolysis, few of them focuses on strategies for designing seawater splitting systems at industrial level, especially for seawater electrolysis devices. In this Review, we focus on three key characters of seawater electrolysis: general mechanism, design criteria for electrodes, and industrial electrolyzers for direct seawater split-

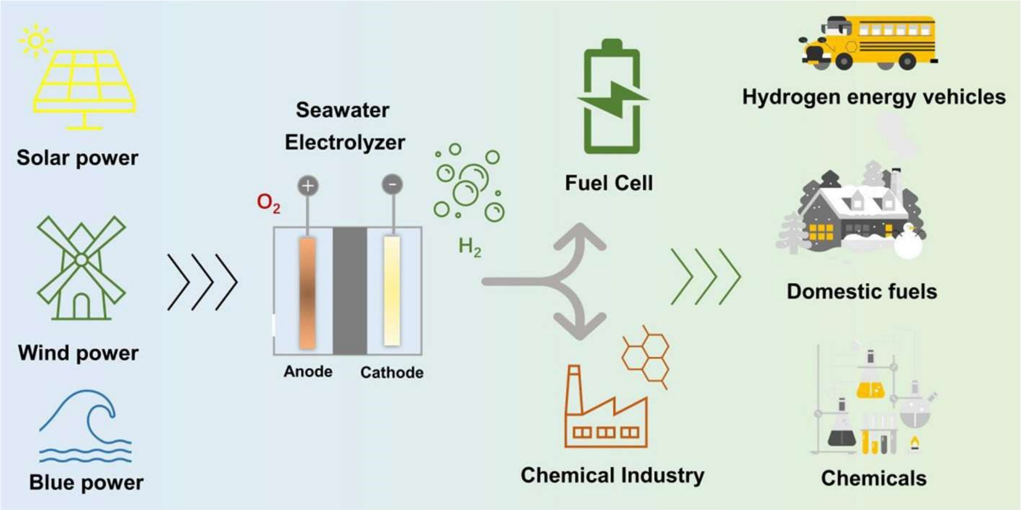

Figure 1 Schematic of seawater electrolysis industry based on renewable electrochemical energy-conversion technologies. (color on line)

ting. We first introduce the fundamental of seawater electrolysis, well-accepted descriptors, and anticorrosion ability for seawater oxidation , cathodic HER. Then, we highlight the design criteria of seawater electrolysis equipment, and the problems existing in current electrolytic cells and general solutions. Finally, we provide our perspective on future opportunities and challenges of direct seawater electrolysis industry.

2 General Mechanism of Seawater Splitting

Water electrolysis mainly contains two half-reactions: the anodic OER and cathodic HER. HER at a cathode is a typical two-electron transfer reaction with the production of H_2, while the OER at an anode is a four-electron transfer reaction, which removes four protons to produce each molecular oxygen. Moreover, the high concentration of chloride anions (~ 0.5 $mol \cdot L^{-1}$), which is mainly from sodium/potassium chloride, would lead to severe CER at an anode and severe electrode corrosion. The OER is more kinetically sluggish than the two-electron involved CER, thus the CER in the seawater might compete with OER at the anode and lower the overall efficiency of seawater electrolysis. An in-depth understanding of the above four main reaction mechanisms (HER, OER, CER and electrode corrosion) is crucial for the design and preparation of efficient seawater electrocatalysts, as well as electrolyzers.

2.1 Oxidation of Seawater

In view of the sluggish thermal dynamics from four electron-proton transfer steps, the anodic OER process remains a bottleneck in water decomposition. Possible mechanisms for OER at an anode for either acid (eqns. (1)-(5)) or alkaline media (eqns. (6)-(10)) are proposed.

Reaction in acidic media:

$$M + H_2O \rightarrow MOH_{ads} + H^+ + e^- \quad (1)$$

$$MOH_{ads} \rightarrow MO_{ads} + H^+ + e^- \quad (2)$$

$$2MO_{ads} \rightarrow 2M + O_2 \quad (3)$$

$$MO_{ads} + H_2O \rightarrow MOOH_{ads} + H^+ + e^- \quad (4)$$

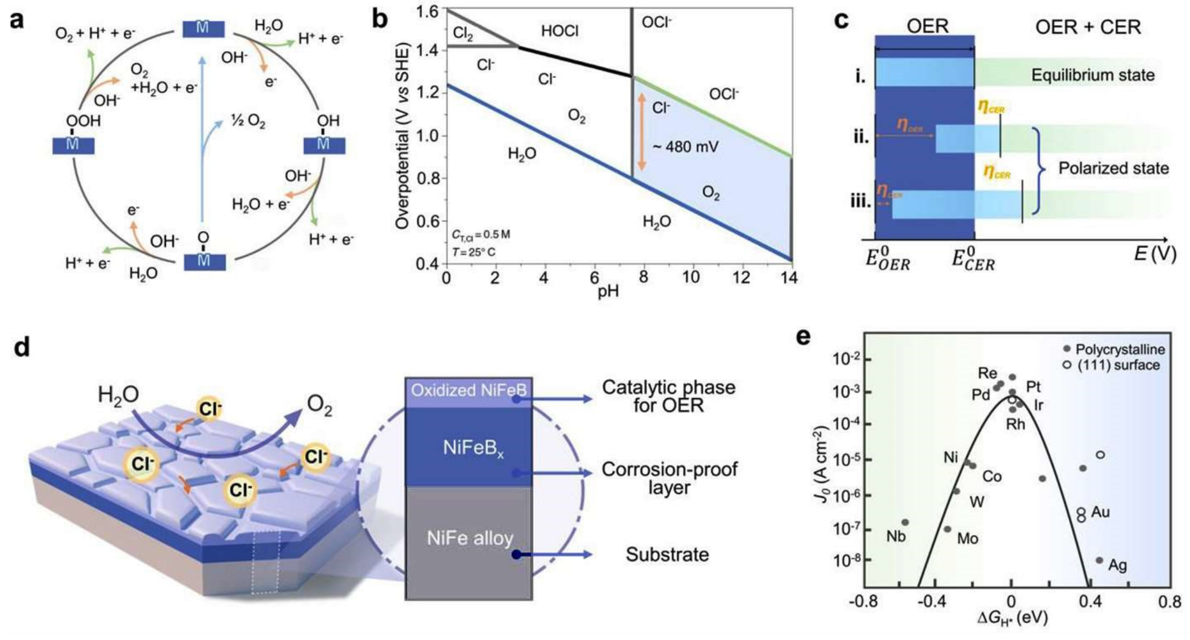

Figure 2 General mechanism for seawtaer elecreolysis. (a) The OER mechanism under acid (green line) and alkaline (yellow line) conditions. Reproduced with permission from ref[24]. Copyright 2017, Royal Chemical Society. (b) Pourbaix diagram of OER and CER. Reproduced with permission from ref[18]. Copyright 2016, Wiley-VCH. (c) General criterion for engineering the two reactions (OER and CER) for widenning potential window. (d) Structural illustration of a multilayered alloy electrode for seawater electrolysis. Panels c and d adapted with permission from ref[25]. Copyright 2021, Wiley-VCH. (e) ΔG_{H^*} volcano plot for metals based HER catalysts. Reproduced with permission from ref[26]. Copyright 2017, Science. (color on line)

$MOOH_{ads} + H_2O \rightarrow M + O_2 + H^+ + e^-$ (5)

Reaction in alkaline media:

$M + OH^- \rightarrow MOH_{ads} + e^-$ (6)

$MOH_{ads} + OH^- \rightarrow MO_{ads} + H_2O + e^-$ (7)

$2MO_{ads} \rightarrow 2M + O_2 + e^-$ (8)

$MO_{ads} + OH^- \rightarrow MOOH_{ads} + e^-$ (9)

$MOOH_{ads} + OH^- \rightarrow M + O_2 + H_2O + e^-$ (10)

Here M represents the active sites. It should be noted that two different approaches to form O_2 from MO intermediates would occur (Figure 2a)[24]. One route is via a direct combination of MO-MO to release O_2 (eqns. (3) and (8)), and the other refers to the generation of MOOH intermediates (eqns. (4) and (9)) which subsequently decompose into O_2.

Compared with the electrolysis of pure water, seawater splitting is more challenging in consideration of the diverse components, especially the high concentration of chloride anions, which would not only bring about the unwanted CER but also cause severe corrosion to many metallic electrodes. The competition mechanism has been explored for many decades. In 1980, Bennet pioneered the selective OER in seawater by a porous manganese-based electrode, but only using acidic seawater as an electrolyte[27]. The electrolysis performed in unbuffered seawater displayed a priority of CER at higher current densities. The OER-only window was located only at lower current density or at very high one due to severe CER mass-transfer limitations. Considering the inferiority of acid media in industrial applications such as corrosion of equipment, starting in 1984, Trasatti conducted the reactivity of various electrode materials to the OER and CER in a wide pH range[28]. It was found that a parallel activity scaling relationship for both reactions in either acidic or alkaline medium was independent of the catalytic materials. This work systematically elaborated the anodic reaction behavior in both theory and experiment to meet the increasing demand in chlorine industry and water electrolyzer. However, with the development of industrial seawater electrolysis in high efficiency and current densities, it becomes one of key issues to suppress the CER and reduce the overpotential of OER. Inspired by the developed theoretical and experimental results, Dionigi et al. conducted an in-depth analysis of the competition between OER and CER (Figure 2b)[18]. A description of the construction of the Pourbaix diagram for chlorine species is available by the following equations.

Reaction in an acidic medium:

$2Cl^- \rightarrow Cl_2 + 2e^- \quad E^0 = 1.36$ V vs. SHE, pH = 0 (11)

Reaction in an alkaline medium:

$Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^-$

$E^0 = 0.89$ V vs. SHE, pH = 14 (12)

The thermodynamic potential window for OER and CER is only 130 mV at pH = 0 (the equilibrium state). However, under alkaline conditions, the equilibrium potential of CER does not rely on the pH range, and the thermodynamic potential window increases up to 480 mV (Figure 2b and 2c Case i). Thus, alkaline seawater electrolysis is usually used as a general design criterion. As mentioned above, OER at an anode is a four electron-proton transfer process and shows more sluggish reaction kinetics than CER which is a two electron-proton reaction. In this case, the range of the OER-only potential window shows a drastic drop (e.g., ≈ 200 mV for IrO_2), as illustrated in Figure 2c, Case ii[25]. However, the industrial application for seawater splitting should be that the OER-only potential window should be widened as much as possible for promoting the OER and suppressing the CER simultaneously (Figure 2c Case iii).

2.2 Cathodic Hydrogen Evolution Reaction

Despite the previous investigations mainly pursuing highly active OER selective catalyst for reducing the overall energy barrier and Faradic efficiency, cathodic HER seems more straightforward, because the lower thermodynamic two-electron transfer process and absence of unwanted competitive side reaction. Compared to acid or neutral condition, same as OER reaction condition, an alkaline electrolyte in HER has received a wide range of attention due to its actual operability. Generally, alkaline HER occurs through either the Volmer-Heyrovsky or Volmer-Tafel mechanism, which mainly based on the active sites and can be described as fellow equations[29, 30].

Volmer step:

$M + H_2O + e^- \rightarrow M\text{-}H_{ads} + OH^-$ (13)

Heyvrosky step:

$M\text{-}H_{ads} + H_2O + e^- \rightarrow H_2 + M + OH^-$ (14)

Tafel step:

$M\text{-}H_{ads} + M\text{-}H_{ads} \rightarrow H_2 + 2M$ (15)

M presents the active sites. However, there are two main challenges in seawater HER: (1) deposition of precipitates on electrode due to the presence of alkaline earth metallic ions, bacteria, microbes, and small particles in seawater; (2) electrode corrosion by anions (mainly from Cl^-).

The major problem is related to the precipitates from various dissolved metal cations such as Mg^{2+}, Ca^{2+}, Pb^{2+}, Cu^{2+}, et al., which suppresses the catalytic performance of the electrode materials[31]. The formation of hydroxide precipitates during HER can be inhibited through optimizing the operating parameters to obtain superior overall catalytic performance of electrode, including additives or buffer solution that induce pre-precipitation before electrolysis and stabilize the pH value during the electrolysis of seawater. Moreover, Kirk et al. showed that high fluid flow rate of electrolyte and large applied current density are favorable for inhibiting the precipitate formation at high solution concentration while the total precipitate is proportional to the ionic concentration in seawater[32]. Additionally, membrane technologies including ion exchange membrane and permselective membrane have also been approved effective ways to reduce the coverage of precipitates on the cathode[33].

2.3 Chlorine Corrosion

Due to the presence of Cl^- ions with high concentration, their engineered structures of electrocatalysts would be easily damaged or corroded by the metal chloride-hydroxide formation mechanisms (eqn. (13) – (15))[18].

Adsorption of Cl^- on metal site:

$M + Cl^- \rightarrow MCl_{ads} + e^-$ (16)

Dissolution process:

$MCl_{ads} + Cl^- \rightarrow MCl_x^-$ (17)

Hydroxide formation:

$MCl_x^- + OH^- \rightarrow M(OH)_x + Cl^-$ (18)

M refers to the metal active sites at the electrode. Moreover, the Cl^- ions may even incorporate into the crystal lattice, leading to lattice distortion, structure instability and active sites deactivation[34]. Thus, how to maintain the structure stability is another great challenge.

3 Design Criteria for Electrode

3.1 Activity of Catalysts for OER and HER

The noble-metal based oxides such as ruthenium dioxide (RuO_2) and iridium dioxide (IrO_2) have been considered as state-of-the-art electrocatalysts for water oxidation, but their high cost and scarcity severely impede their large-scale application[35]. In addition, the theoretical overpotential of OER (0.59 eV) surpasses that of CER (0.28 eV) for IrO_2, determining the limited access to seawater electrolysis[25]. As alternatives, transition metal compounds have been proved more suitable for seawater splitting[23, 36-39]. Currently, γ-NiOOH is the widely accepted real active phase for Ni-based OER catalysts after surface reconstruction. Density functional theory (DFT) calculations demonstrate that the weak Cl^- ions adsorption on γ-NiOOH (Fe-dopped γ-NiOOH) extremely hinders the potential-determining step of OER. However, Fe-dopped γ-NiOOH shows better intrinsic catalytic activity for OER, significantly enlarging the actual OER-only potential window. Inspired by doping strategies, Li et al. developed a multilayered oxygen-evolution electrode with metaborate-modified γ-(Ni,Fe)OOH as real active sites[25]. Due to the unique muti-layered design, the engineered γ-(Ni,Fe)OOH exhibits lower OER overpotential, higher CER reaction barrier, and long-term durability (Figure 2d). You et al. recently introduced 5d transitional metal Ir into $Ni(OH)_2$, forming a monolayer NiIr-layered double hydroxide (NiIr-LDH) as an electrocatalyst with boosted seawater OER performance[40]. The reconstructed NiOOH combined with surface Ir-O spices optimized the generation of *OOH step and needed only 361 mV overpotential to achieve 500 $mA \cdot cm^{-2}$ with nearly 100% O_2 Faradaic efficiency in alkaline seawater.

Pt-based electrocatalysts are by far considered as the most effective electrode materials for HER but still face many drawbacks including high price and low reserve, thus restricting their industrial application[41]. Even the electrolysis occurs in seawater, the HER mechanism is same as that in purity water. The well-established Volcano plot can still act as a quantitative illustration of Sabatier principle for screening electrode materials (Figure 2e)[26, 42]. Thus, an active site should have neither too strong nor too weak bind with H* ($\Delta G_{H^*} = 0$). Alloying Pt group species with transition metals (Fe, Co, Ni, Cu, and Ti) not only can drastically enhance the catalytic activity of Pt-based alloyed electrocatalysts via downshifting the Pt d-band center but also enhance the corrosion resistance[43,44]. As shown in the Volcano plot, compared with other transition metals, metallic Ni has a better affinity with H*. Hence, the development on Ni-based alloys is a preferred alternative way to reduce the use of Pt group materials. For instance, a NiMoN nanostructure catalyst can reach a high current density of 1000 mA·cm^{-2} at an overpotential of 170 mV in simulated seawater[20]. In addition to the cost reduction and intrinsic activity enhancement, the feasibility of introducing a third transition metal into a binary domain, such as PtAgCo[45], PtRhCo[46], and PtNiCo, endows the electrode superior structural stability[47].

Recent experimental and theoretical results illustrate that transition metal nitrides have moderate binding energy with reactant intermediates (water molecules, atomic hydrogen, or protons), endowing them with superior HER catalytic activity. As a model electrocatalyst, a heterogeneous Ni-MoN nanostructure was demonstrated by Ren's group (Figure 3a)[48]. The unique hierarchical crystal-amorphous structure and tremendous boundaries/defects provide abundant active sites for the electrode. Moreover, the hydrophilic surface contributes to accelerated water molecules mass-transfer and gas-release capabilities. Calculation reveals the combination of Ni and MoN boosts the water-dissociation kinetics at the metallic Mo sites. Accordingly, the Ni-MoN electrocatalyst can well maintain the catalytic activity and stability at a high constant current density of 500 mA·cm^{-2} in both alkaline natural seawater and alkaline saline electrolytes. Qiao's group put forward a nickel surface nitride electrocatalyst with unsaturated Ni-N bonds for alkaline seawater splitting (Figure 3b)[49]. Promisingly, a two-electrode electrolyzer system that coupled with hydrazine oxidation at the anode requires a cell voltage of only 0.7 V to achieve a high current density of 1000 mA·cm^{-2}. Caution should be taken if these transition metal compounds will be electrochemically oxidized on the surface under an alkaline condition, which has been shown to be more significant in OER process than in HER.

Unlike the traditional nanostructured electrocatalysts, the single-atom catalysts (SACs) exhibit maximum atom utilization and active site exposure, which are favorable for catalytic reaction. Transition metal SACs, such as Co[50], Ni[51], Mo[52], and W[53], have been widely investigated for HER in alkaline freshwater, but rarely used in seawater. For example, Zang et al. pioneered highly dispersed Ni atoms coordinated with triple nitrogen ($Ni-N_3$) as an effective HER electrode in seawater, which exhibited lower overpotential than $Ni-N_4$ in seawater electrolyte (Figure 3c)[54]. It is still a question if these transition metal SACs are competitive for industry-level current densities and if they can be stable under alkaline seawater condition.

3.2 Reaction Selectivity

A wide potential window for selective OER is one of the highest priorities in designing electrocatalysts for seawater splitting, which usually determines excellent OER activity, high overpotential of CER, and large current density. Electrocatalysts with inherent corrosion resistance are a direct and effective method to enhance the operating selectivity as well as durability.

In situ phase transformation during OER can form a new layer of active species, which usually occurs in transition metal selenides and sulfides. In seawater oxidation, metal ions in these catalysts will transform into MOOH (M here refers to transition metal), while anions will evolve into corresponding oxides. These

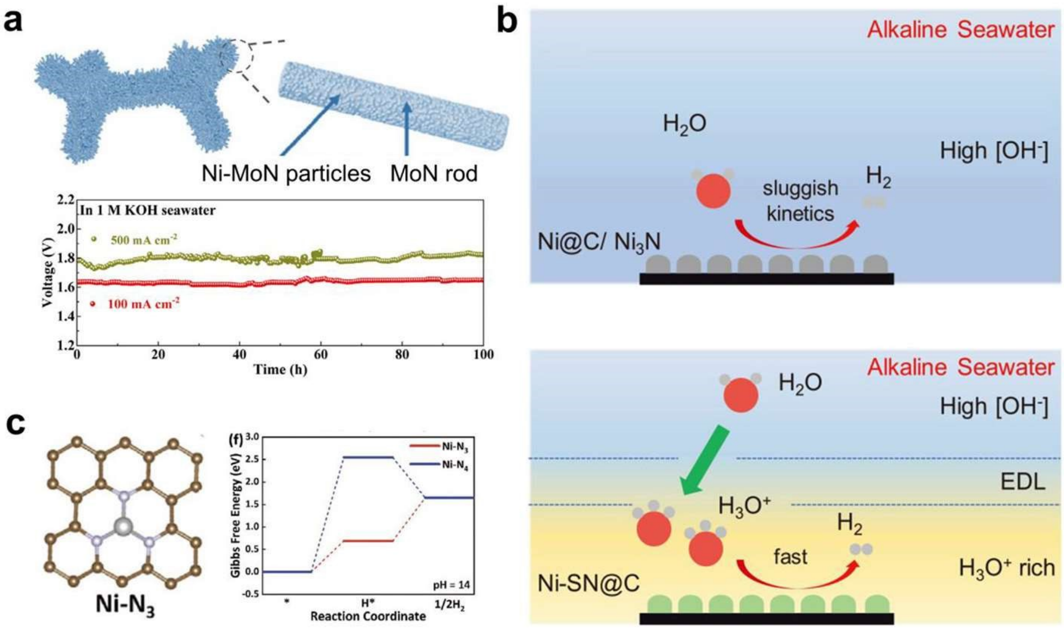

Figure 3 General strategies for boosting HER. (a) Structure of Ni-MoN and long-term durability for alkaline seawater electrolysis. Adapted with permission from ref[48]. Copyright 2022, Wiley-VCH. (b) Illustration of the hydronium ion generation mechanism on a nickel surface nitride catalyst (Ni-SN@C). EDL: electric double layer. Adapted with permission from ref[49]. Copyright 2021, Wiley-VCH. (c) Schematic of Ni-N_3 and the Gibbs free energy diagram of HER on the Ni-N_3 and Ni-N_4 configurations at pH = 14. Adapted with permission from ref[54]. Copyright 2021, Wiley-VCH. (color on line)

newly formed layers can be used not only as active center, but also as anticorrosion layers. Based on the perspective of protection layer, Kuang et al. demonstrated a multilayer electrode consisting of a NiFe layer and NiS_x layer deposited on the porous Ni foam. An amorphous oxygen-containing NiFe layer was in situ generated in alkaline seawater splitting, which is responsible for chloride repelling and high corrosion resistance (Figure 4a), leading to operation at the current density of 400 $mA \cdot cm^{-2}$ for 1000 h[10]. Similarly, when a Se layer was covered by an NiFe LDH layer, it exhibited extraordinary stability and activity in an aqueous sea-like solution (Figure 4b). During the operation, the Se layer *in situ* transformed into SeO_x^- species (SeO_3^- and SeO_4^-)[55], which have attributed to the stability and anticorrosion ability due to the repelling Cl^- ions. In our opinion, these *in situ* phase transformation method can be considered as passive protection strategies and more likely a kind of byproducts.

In contrast, an active protection provided by a thin layer of manganese oxide electrodeposited on IrO_x is proven useful in restraining the corrosion of Cl^- on IrO_x active sites (Figure 4c)[56]. In fact, coating conductive carbon-based materials (e.g., layered carbon, graphene, graphene oxide, and carbon nitride) on the catalyst surface have been an effective strategy to either boost the conductivity of electrode, or retain the performance of active sites under harsh conditions due to physical contact barrier[57-60]. In addition, the negatively charged surface can repulse the Cl^- ion, thus protect the active site from chloride corrosion[13]. Inspired by this protection strategy, Li and coworkers demonstrated that an outer graphene oxide (GO) lay er could effectively protect the FeOOH@NiCo LDH active material (Figure 4d)[61]. Due to the optimal energy barrier of the central core for intermediates and anticorrosion ability of the GO layer for Cl^- ions, this composite electrode delivered a current density of 1 $A \cdot cm^{-2}$ for 378 h.

Besides external protection layer, the internal structure stability of electrocatalysts should be equally considered. Previous work showed that alloying is a general approach to enhance the structural stability of electrodes, which can also be applied in anticorrosion of seawater[62-65]. For example, in a self-supported heterogeneous Ni_2P-Fe_2P electrode, alloying electron-negative P with transition metal Fe/Ni makes metal dissolution thermodynamically less favored, leading to enhanced corrosion resistance[66]. Most recently, an exciting achievement, reported by Xu's group, demonstrated a unique buffer structure to endow the $Co_2(OH)_3Cl$ with long-time durability and high Faraday efficiency of ca. 99.6% for seawater OER[67]. It is shown that the lattice Cl^- of $Co_2(OH)_3Cl$ can serve as the structural buffer, whose continuous leaching during OER can leave vacancies for seawater Cl^- invasion and thus avoid catalyst deactivation (Figure 4e). This structural buffer strategy may pave a new way to resist the corrosion and boost their OER performance in alkaline seawater.

Different from anodic OER, the primary concern for cathodic HER relates to the precipitates. As we all know, in addition to high concentrations of chloride ions, seawater contains high concentrations of undesirable cations, including Ca^{2+}, Mg^{2+}, and Pb^{2+}, which are easy to be deposited on cathode as $Mg(OH)_2$ and $Ca(OH)_2$ due to the increasing local pH or metallic precipitates such as (Pb) and copper (Cu) under reduction reactions[32,33]. The current density losses can approach ~50% after short periods of operation. Thus, the critical problems from HER are the corrosion by Cl^- ions of cathode material, deposition of the precipitates on active sites, and cathodic competing reduction reactions from the dissolved metal ions (Figure 5a). For the practical application of seawater

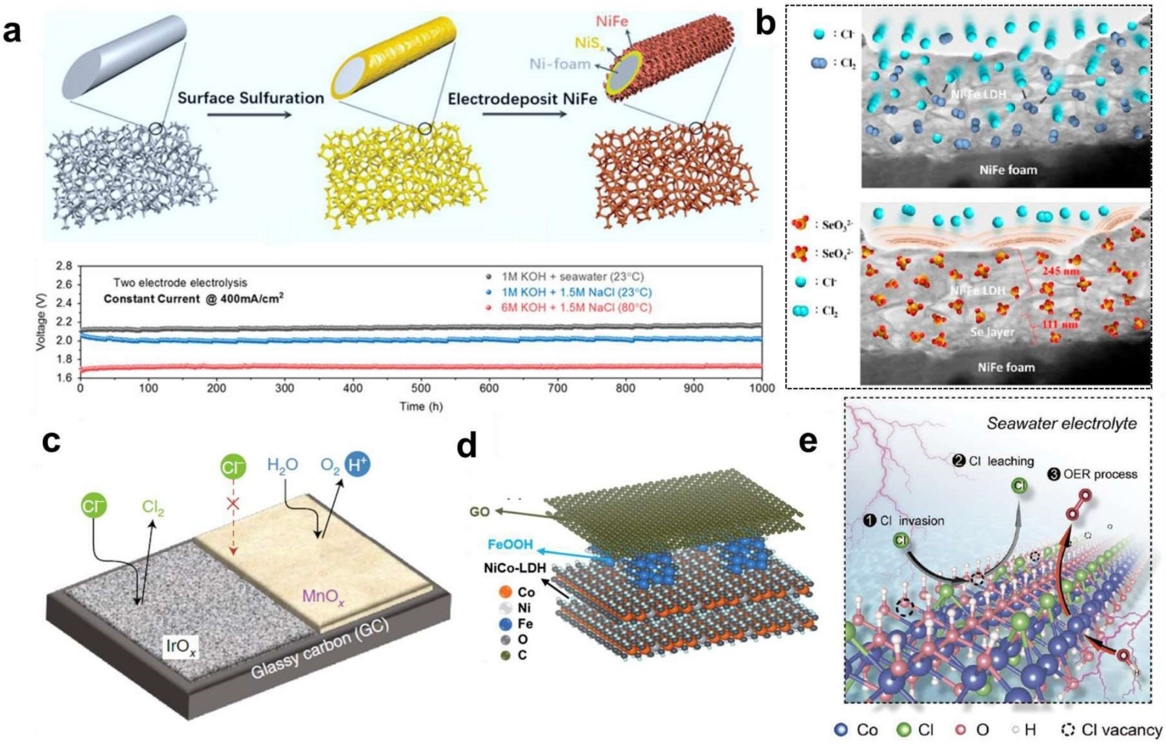

Figure 4 Strategies for anticorrosion. (a) Schematic of the fabrication of NiFe/NiS_x catalyst on Ni form, and durability tests recorded at high currents in the seawater. Adapted under the terms of the Creative Commons Attribution License[10]. (b) The mechanism of stability improvement for NiFe-LDH/Se composite catalyst on NiFe foam. Adapted with permission from ref[55]. Copyright 2021, Elsevier. (c) A thin MnO_x layer deposited on IrO_x surface provides protection for Cl^- corrosion. Adapted under the terms of the Creative Commons Attribution License[56]. (d) A surface graphene oxide layer protects the active material of FeOOH@NiCo LDH. Adapted with permission from ref[61]. Copyright 2021, Royal Chemical Society. (e) Reaction mechanism of lattice Cl^- for inhibiting Cl^- corrosion and deactivation. Reproduced with permission from ref[67]. Copyright 2021, Wiley-VCH. (color on line)

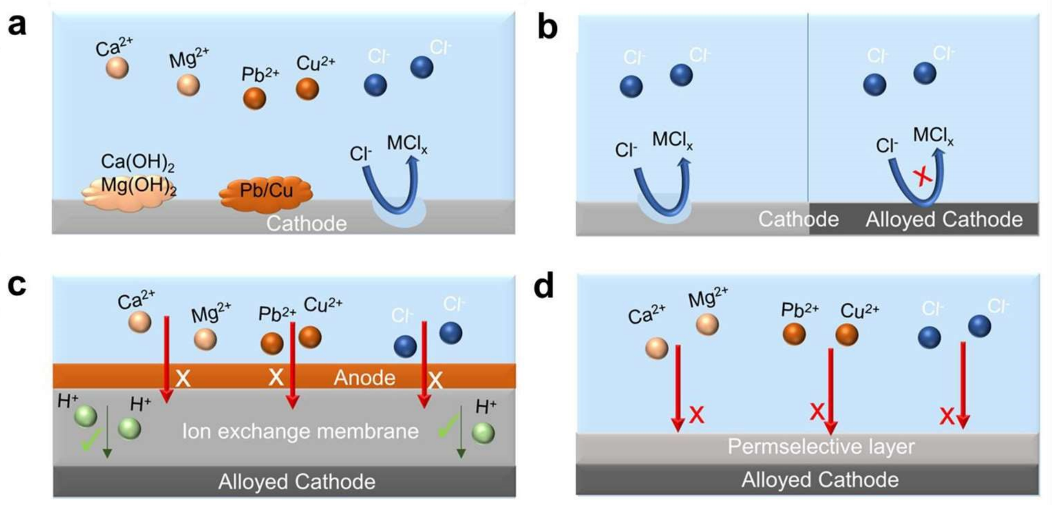

Figure 5 Challenges and potential solutions for promoting selectivity of HER in seawater. (a) Electrode corrosion by Cl^- ions and deposition of precipitates on active sites. (b) Electrode alloying engineering, (c) employment of ion exchange membrane, and (d) permselective layer for enhanced anti-corrosion and anti-poison. (color on line)

HER, it is necessary to inhibit the unfavorable electrochemical reaction. According to this design principle, developing alloyed electrocatalysts with an enhanced anticorrosion ability (Figure 5b), adopting suitable ion exchange membrane to protect the electrocatalyst from the corrosive seawater (Figure 5c), or using permselective barrier layers attached onto the cathode materials, blocking adverse reactions are considered effective methods to promote the long-time durability of seawater HER (Figure 5d).

3.3 Mass Transfer

Seawater electrolysis performance at high current densities is not only controlled by the reaction kinetics but also by the mass transfer rates[68-70]. The OER process at large current densities will lead to drastic depletion of electrolyte and intensive generation of O_2 bubbles, which requires an adequate resupply of electrolyte and fast release of bubbles. Morphology engineering of the electrocatalysts into hierarchical structures is proven a potent way for accelerating mass transfer process and increasing active sites, which greatly promotes the accessibility of molecules and catalytic performance[71-74]. Wen et al. developed a kind of ultrathin NiS nanosheets and NiFe LDH heterostructure, as a Schottky heterojunction, and tuned systematically the mass transfer and electronic configuration[75]. In these catalysts, the porous morphology of NiS nanosheets contributed to the efficient infiltration of electrolyte and the desorption of O_2 bubbles, guaranteeing the mass transport rates. Thus, such a NiFe LDH/NiS system delivered a current density of 1000 mA·cm^{-2} at the ultralow overpotential of 325 mV. Furthermore, Seenivasan et al. developed a more complicated $NiCo_2S_4$/$NiMo_2S_4$/NiO electrodewith two different interfaces[76]. The OER process actually occurs on the surface reconstructed MOOH and surface beneath the M-S sites. This catalyst showed superior mechanical strength and high density of active sites, and consequently, good industrial durability and reaction kinetics.

A low interfacial adhesion energy of the catalyst is conducive to promote the transfer processes of products and intermediates, especially at high current densities. As an example, for a new kind of Pt/Ni-Mo electrocatalyst proposed by Liu and coworkers, a rationally designed 3D rugged morphology makes the electrode surface super hydrophilic[12]. The nearly zero static contact angle (θ) and the small dynamic contact hysteresis (θh) of Pt/Ni-Mo (3°) indicate a low interfacial adhesion (Figure 6a-b). This will expectedly lead to high mass transfer kinetics of electrolytes and fast removal of hydrogen bubbles from the elec-

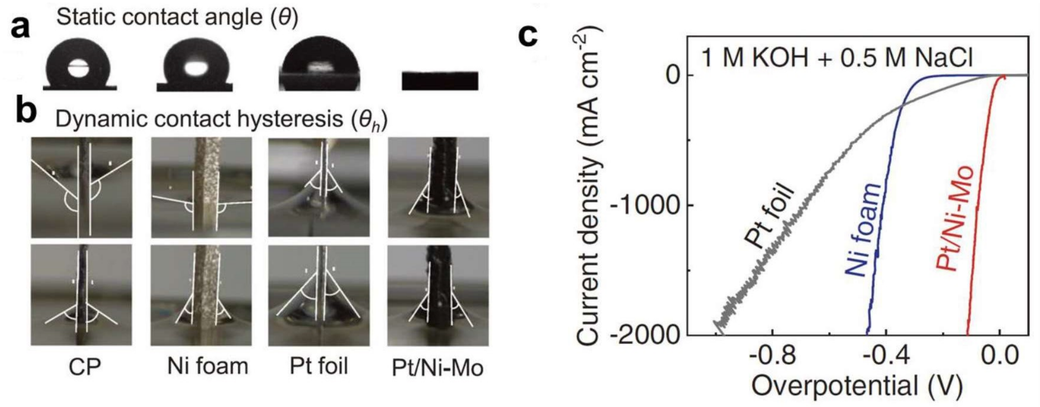

Figure 6 Pt/Ni-Mo electrocatalyst for enhanced mass transfer and catalytic performance. (a) Photographs of the static contact angles, and (b) dynamic contact angle hysteresis images of electrolyte drop on different substrates. (c) Comparation of polarization curves with 85% iR compensation for different catalysts in simulated seawater. Adapted with permission from ref[12]. Copyright 2021, Wiley-VCH. (color on line)

trode surface. As a result, this catalyst exhibited a high-level current density of 2000 mA·cm^{-2} at an ultralow overpotential of 113 mV in the saline-alkaline electrolyte, showing excellent activity and operation durability (Figure 6c). It is believed that such structure engineering of efficient catalysts should be generally considered for the industrial operation.

4 Industrial Electrolyzer for Direct Seawater Electrolysis

We first briefly introduce the established electrolysis technologies, considering the technical evolution and economic perspective. Currently, the common electrolyzer can be divided into three categories based on the cell structure, especially for membrane: alkaline electrolyzer (AE), proton exchange membrane (PEM), and anion exchange membrane (AEM) electrolyzers, as shown in Figure 7a-c[23]. AE is the most mature and cost-effective technology, which has realized the real industrial-scale hydrogen generation. In this device, alkaline water is simultaneously added into two compartments of the AE cell[11, 77]. H_2 and OH^- ions are formed at the cathode under electrolysis condition, while the OH^- ions migrate through the porous diaphragm into the anode compartment, followed by the formation of O_2. However, AE has two inevitable drawbacks, lower energy-conversion efficiency and high sensitivity to CO_2. Moreover, diaphragm materials, such as Zirfon, are approved physically robust, allowing both anions and cations, such as H^+, Na^+, OH^- and Cl^-, to pass through[78]. This may lower the transference rate of the most mobile ions and decrease the overall working efficiency due to poor selectivity. Different from AE technologies, a PEM electrolyzer (PEME) generally consists of a membrane electrode assembly and bipolar plates (Figure 7b), and are characterized by high current density, operation efficiency, and tolerance to fluctuating currents of renewable electricity. During the operation, acidic water is pumped into the anode half-cell to be oxidized into O_2 and the H^+ ions transfer to the cathode to evolve into H_2 through the PEME. Generally, PEME is conducted under corrosive acidic condition, and requires expensive noble-metal catalysts to boost catalytic performance and enhance anti-corrosion. AEM electrolyzers (AEME) have a similar structure to PEME, except for the type of exchange membrane and alkaline operating environment (Figure 7c). With the addition of alkaline water into the cathode compartment, H_2 and OH^- ions are formed during the electrolysis. The OH^- ions pass through the AEM into the anode, evolving into O_2[11]. The AEME electrolysis can use non-noble metals as electrocatalysts including transition metal based species and non-metal materials, showing a significant advantage over PEME in terms of sustainable

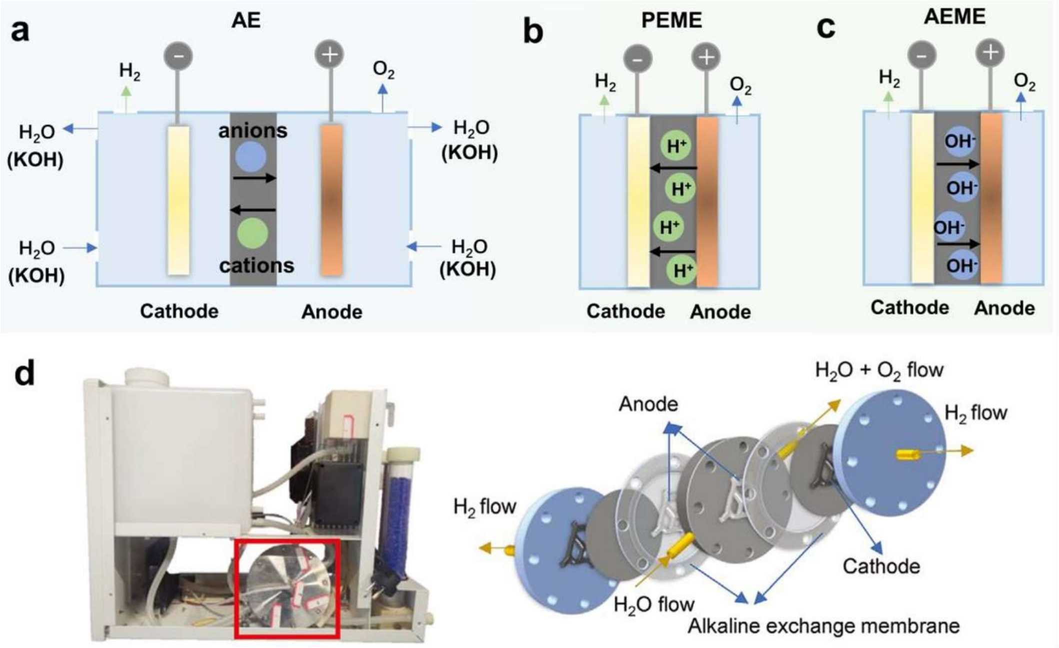

Figure 7 Typical configurations for water electrolyzers. Schematic of (a) alkaline electrolyzer (AE), (b) proton exchange membrane water electrolyzer (PEME), and (c) anion exchange membrane water electrolyzer (AEME). (d) Photograph and schematic of an PEME. Panel d is adapted with permission from ref[12]. Copyright 2021, Wiley-VCH. (color on line)

economic benefits[79]. Figure 7d is the photograph and fine schematic of a commercial PEME electrolysis cell[12]. The membrane stack is assembled by two HER cells on the end sides and two OER cells installed in the middle. The AEM separates the HER cells and OER cells to prevent gas diffusion and allow anions to transfer through.

When the above three kinds of electrolyzers are deployed for direct seawater electrolysis, some new tricky challenges will occur due to the presences of unwanted ions and impurities including bacteria, microbes, and small particles. Alkaline earth metal ions (Cu^{2+}, Ca^{2+}, Mg^{2+}, Pb^{2+}, et al.) in seawater will gradually migrate to the cathode side driven by electronic field, and produce metal precipitates on the electrode. Moreover, the cathode faces hydroxide precipitates under high local pH conditions which are mainly $Mg(OH)_2$ and $Ca(OH)_2$. The unwanted competition between OER and CER still occurs due to the unavoidable Cl^- ions oxidation[80]. To solve these issues, one of most accepted strategies is using the state-of-the-art electrolyzers combined with sufficient seawater prepurification. For industrial applications, seawater should be treated with negative pressure filter to remove large-sized impurities, followed by a further purification step via reverse osmosis (RO) and other purification strategies (Figure 8a). Another feasible way to maintain the exchange membrane performance is through the designed recovery operations. For instance, periodic rest of electrolyzer at open circuit has been applied to partially recover the lost activity because of chloride trapped in the exchange membrane[80]. But this will increase the time cost and cause lower operation efficiency.

During the seawater electrolysis, in the absence of a buffer or cyclic alkaline electrolyte, the local pH will drop drastically at the anode, which may lead to strong acidic corrosion. In contrast, due to the proton consumption, the local pH will increase accordingly, producing large amount of precipitates on the cathode. On the base of AEME, asymmetric electrolyte feed is a smart design proposed by the Strasser group. In this design, a continuously circulated KOH electrolyte is introduced into the anode half-cell, while single-pass seawater is fed into the cathode (Figure 8b). The detected content of Cl^- ions across the AEM is only about 6.4 mmol after standardized long-time operation. Such a low Cl^- concentration minimizes corrosion to the anode material, and endows seawater electrolyzer with high selectivity and operation stability.

Moreover, high-temperature water electrolyzer (HTE) has drawn broad attention as it offers significant higher power and efficiency compared to conventional low temperature electrolyzer (Figure 8c). A typical HTE composes of proton conducting ceramic electrolysis (150 ~ 400 ℃) and solid oxide electrolysis (800 ~ 1000 ℃), in which high temperature water steam is used as feedstock[11]. In this design, steam is fed into the cathode to generate H_2 and O_2^-, and then selectively passes through a solid oxide or ceramic membrane to the anode to produce O_2 via OER[81]. More specially, seawater purified by steam can drastically extend the membrane and electrode life.

5 Conclusions and Outlooks

Water electrolysis is by far one of the most efficient technologies to produce hydrogen and may help accelerate the world's transition to renewable energy. Considering that the planet's oceans supply almost unlimited quantities of seawater, which accounts for 96.5% of the total water resources on the earth, replacing freshwater with seawater will reduce the consumption of freshwater resources and generate new application avenues such as cargo ships and submarines. In this short review, we try to figure out the possibilities of pushing seawater electrolysis towards industrial implementation. Cathode-involved HER, anode-involved OER, and chloride chemistry are introduced and carefully summarized, including their mechanisms and catalyst design strategies, together with the full electrolyzer configuration. To sum up, from the point of industrial application, advanced catalysts for seawater electrolysis should possess at least four superior features: high catalytic performance (activity and stability), enhanced corrosion resistance, acceptable OER selectivity, and optimized mass transport under large current densities. Looking into the future, we propose the research could be focused on the following points.

(1) Specific mechanism investigation for seawater

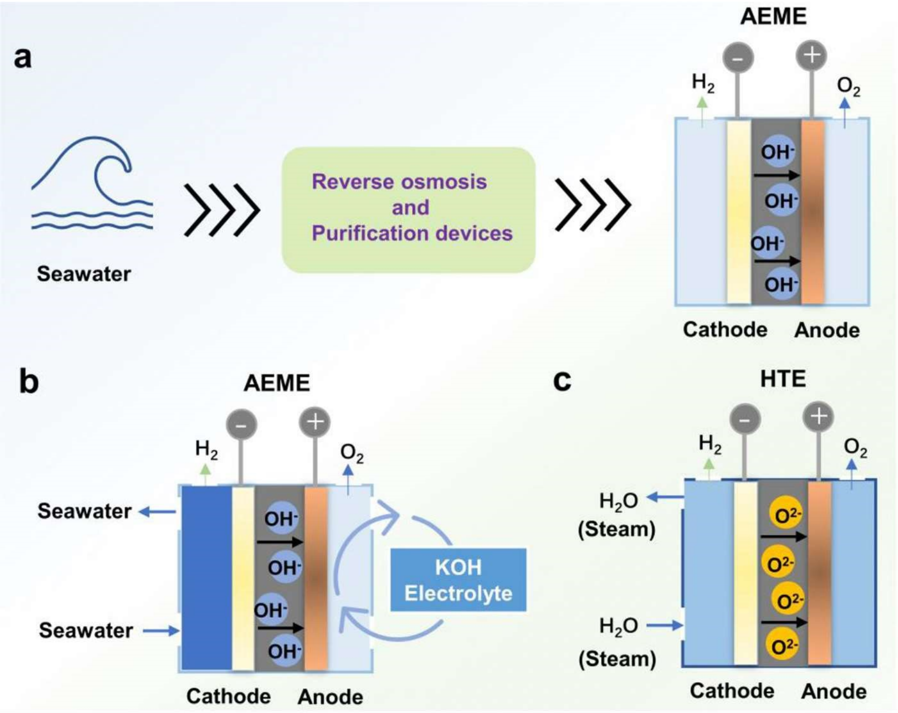

Figure 8 Direct seawater devices. (a) State-of-the-art AEME combined with pre-purification equipment. (b) Asymmetric electrolyte feed AEME. (c) High-temperature water electrolyzer. (color on line)

electrolysis

The research on seawater electrolysis is by far inherited from freshwater splitting research. The most popular research mode in this field is simply replacing pure water electrolyte with simulated seawater electrolyte or buffered seawater to measure the catalytic performance including activity and stability. The OER potential window is strictly limited under 480 mV based on 'alkaline design criterion'. However, as we stated in this review, the Cl-containing elec trolyte systems will dramatically influence the catalytic behavior of catalysts, and the actual OER-only potential window can be finely widened by introducing highly selective OER catalysts. Hence, it is essential to deepen the understanding of the specific mechanism involved in seawater electrolysis, including anti-chlorine corrosion mechanism and OER selectivity mechanism, which would consolidate the theoretical foundation for searching outstanding elec trode materials for seawater electrolysis.

(2) Standardized protocol for catalytic evaluation

From the perspective of designing catalysts for seawater electrolysis, it is necessary to set general standard for evaluating various catalytic structures. Besides catalytic activity and catalytic stability, other parameters including the corrosion resistance over Cl^- containing system as well as the OER selectivity for anode materials will have to be carefully described. All these parameters need to be defined by some simple and reproducible methods. For instance, reliable residual chlorine measurements must be developed to quantitatively describe OER selectivity. Due to the corrosive nature of chlorine species, neither gas chromatography nor fluorometric sensor is suitable for quantifying OER. Colorimetric methods are the most popular way to determine residual chlorine, and the colorimetric reagents include o-Tolidine, N, N-diethyl-p-phenylenediamine and potassium iodide, etc. However, the subtle color changes caused by trace components may not be captured by naked eyes, leading to inaccuracy in conclusion. Therefore, more effective methods are needed to build quantitative parameters for OER selectivity.

(3) Structural evolution under chlorine-containing conditions

The structure transformation of catalysts largely determines the catalytic behavior. It is plausible to infer that Cl^- ions existed in the electrolyte should influence the transformation of a catalytic structure, for instance, valence state transition, phase transforma tion, ion dissolution, and corrosion mechanism. For better understanding, some powerful *in situ* measurements, including Raman, infrared (IR), APXPS, XRD, XAS analyses and so on, are necessary to identify the dynamic behavior of catalytic structures under seawater electrolysis condition. This will help us to figure out the stable building blocks or subunits in Cl^- containing electrolytes, and further identify the real active sites during the catalytic reaction. All these insights should help our design strategies against chlorine corrosion. Additionally, same as freshwater condition, the identification of structural evolution will be impeded by the limited space/time resolution of current in situ measurements; More advanced techniques with higher sensitivity need to be developed.

(4) Theoretical screening for new catalytic structures

With the convenience of first-principles calculations and the development of advanced materials informatics, high-throughput (HT) computing combined with machine learning (ML) algorithms provides new routes to save experimental time and cost in a more delicate way. These theoretical methods have been proven successful in searching potential structures that are suitable for materials for various energy conversions and storage processes[82,83], including seawater electrolysis. However, since the applications of HT and ML in catalysis science are still in an early stage, several aspects for achieving efficient theoretical screening need to be carefully considered, including the reliability of the theoretical model, the applicability of calculation parameters, the generality and interpretability of descriptor and prediction accuracy of ML model, etc. Another pivotal concern is, if it is possible, to skip the construction of descriptor and correlate the structure to catalytic performance di rectly. For this purpose, more advanced ML models such as active learning and deep learning should be developed or integrated as multi-stage workflows. And of course, the predicted promising structure or desired subunits should be further verified through controllable synthesis from the experimental level.

(5) Practical scale seawater electrolysis

For industrial seawater electrolysis, the first thing to consider is whether we should choose direct seawater electrolysis or the seawater purification plus electrolysis system. It is recently pointed out that the later two-step approach is more economical than the current direct seawater electrolysis, considering the mature technology of water purification. However, this comparison may not be fair since the seawater electrolysis technology is still in its infancy. Meanwhile, compared to the large infrastructure of reverse osmosis plants, it might be viable to combine advanced solar, wind, or tide energy harvesting system with the seawater electrolysis for both coastal area and offshore operations. Accordingly, direct seawater electrolysis is more suitable for decentralized small-scale H_2 production. There are three aspects need to be carefully considered for seawater electrolysis application, including electrolyzer configuration, electrolyte and portable seawater pretreatment. For electrolyzer configuration, the AEME is more compatible with the direct seawater electrolysis, which exhibits acceptable performance in the presence of Cl^-. The possibility that AEM electrolysis can use non-precious metal based catalysts also shows a strong advantage of AEM over PEM in terms of significantly lower cost. In case of electrolyte, alkaline seawater electrolysis should be more suitable for large-scale production of H_2 at high current densities of 500 $mA\cdot cm^{-2}$ being more than acidic or neutral ones considering both pH design criterion and electrolyte condition. Additionally, due to the complexity of seawater composition, some portable low pressure suction filtration system and RO membrane also need to be developed, which may remove most of the impurities from seawater, such as bacteria, microbes, and small particles, and thus minimize the damage to electrolyzers. Even though these technologies are in academic research stage, they have the development potential towards a closed loop of green energy conversion when the produced hydrogen and oxygen are converted back into electricity and pure water via fuel cells.

Acknowledgements

This work is financially supported from the Singapore Ministry of Education by Academic Research Fund Tier 1 (RG125/21) and the National Natural Science Foundation of China (No.: 22005116).

Conflict of Interest

The authors declare no conflict of interest.

References:

[1] Gray H B. Powering the planet with solar fuel[J]. Nat. Chem., 2009, 1(1): 7-7.

[2] Turner J A. Sustainable hydrogen production[J]. Science, 2004, 305(5686): 972-974.

[3] Zhou Y, Hao W, Zhao X X, Zhou J D, Yu H M, Lin B, Liu Z, Pennycook S J, Li S Z, Fan H J. Electronegativity-induced charge balancing to boost stability and activity of amorphous electrocatalysts[J]. Adv. Mater., 2022, 34(20): 2202598.

[4] Zhang T, Liu Y P, Yu J, Ye Q T, Yang L, Li Y, Fan H J. Biaxial strained MoS_2 nanoshells with controllable layers boost alkaline hydrogen evolution[J]. Adv. Mater., 2022, 34 (27): 2202195.

[5] Jin H Y, Liu X, Vasileff A, Jiao Y, Zhao Y Q, Zheng Y, Qiao S Z. Single-crystal nitrogen-rich two-dimensional Mo_5N_6 nanosheets for efficient and stable seawater splitting[J]. ACS Nano, 2018, 12(12): 12761-12769.

[6] Wang C Z, Zhu M Z, Cao Z Y, Zhu P, Cao Y Q, Xu X Y, Xu C X, Yin Z Y. Heterogeneous bimetallic sulfides based seawater electrolysis towards stable industrial-level large current density[J]. Appl. Catal. B, 2021, 291: 120071.

[7] Dresp S, Dionigi F, Klingenhof M, Strasser P. Direct electrolytic splitting of seawater: Opportunities and challenges [J]. ACS Energy Lett., 2019, 4(4): 933-942.

[8] Liu S J, Ren S J, Gao R T, Liu X H, Wang L. Atomically embedded Ag on transition metal hydroxides triggers the lattice oxygen towards sustained seawater electrolysis[J]. Nano Energy, 2022, 98: 107212.

[9] Ke S C, Chen R, Chen G H, Ma X L. Mini review on electrocatalyst design for seawater splitting: Recent progress

and perspectives[J]. Energy & Fuels, 2021, 35(16): 12948-12956.

[10] Kuang Y, Kenney M J, Meng Y T, Hung W H, Liu Y J, Huang J E, Prasanna R, Li P S, Li Y P, Wang L, Lin M C, McGehee M D, Sun X M, Dai H J. Solar-driven, highly sustained splitting of seawater into hydrogen and oxygen fuels[J]. Proc. Natl. Acad. Sci., 2019, 116(14): 6624-6629.

[11] Tong W M, Forster M, Dionigi F, Dresp S, Erami R S, Strasser P, Cowan A J, Farràs P. Electrolysis of low-grade and saline surface water[J]. Nat. Energy, 2020, 5(5): 367-377.

[12] Yang F N, Luo Y T, Yu Q M, Zhang Z Y, Zhang S, Liu Z B, Ren W C, Cheng H M, Li J, Liu B L. A durable and efficient electrocatalyst for saline water splitting with current density exceeding 2000 mA·cm^{-2}[J]. Adv. Funct. Mater., 2021, 31(21): 2010367.

[13] Sarno M, Ponticorvo E, Scarpa D. Active and stable graphene supporting trimetallic alloy-based electrocatalyst for hydrogen evolution by seawater splitting[J]. Electrochem. Commun., 2020, 111: 106647.

[14] Dong G F, Xie F Y, Kou F X, Chen T T, Wang F Y, Zhou Y W, Wu K C, Du S W, Fang M, Ho J C. Nife-layered double hydroxide arrays for oxygen evolution reaction in fresh water and seawater[J]. Mater. Today Energy, 2021, 22: 100883.

[15] Marini S, Salvi P, Nelli P, Pesenti R, Villa M, Kiros Y. Stable and inexpensive electrodes for the hydrogen evolution reaction[J]. Int. J. Hydrogen Energy, 2013, 38(26): 11484-11495.

[16] Sun Y Q, Zhang T, Li C C, Xu K, Li Y. Compositional engineering of sulfides, phosphides, carbides, nitrides, oxides, and hydroxides for water splitting[J]. J. Mater. Chem. A, 2020, 8(27): 13415-13436.

[17] Sriram P, Su D S, Periasamy A P, Manikandan A, Wang S W, Chang H T, Chueh Y L, Yen T J. Hybridizing strong quadrupole gap plasmons using optimized nanoantennas with bilayer MoS_2 for excellent photo-electrochemical hydrogen evolution[J]. Adv. Energy Mater., 2018, 8(29): 1801184.

[18] Dionigi F, Reier T, Pawolek Z, Gliech M, Strasser P. Design criteria, operating conditions, and nickel-iron hydroxide catalyst materials for selective seawater electrolysis[J]. ChemSusChem, 2016, 9(9): 962-972.

[19] Bigiani L, Barreca D, Gasparotto A, Andreu T, Verbeeck J, Sada C, Modin E, Lebedev O I, Morante J R, Maccato C. Selective anodes for seawater splitting via functionalization of anganese oxides by a plasma-assisted process [J]. Appl. Catal. B, 2021, 284: 119684.

[20] Yu L, Zhu Q, Song S W, McElhenny B, Wang D Z, Wu C Z, Qin Z J, Bao J M, Yu Y, Chen S, Ren Z F. Non-noble metal-nitride based electrocatalysts for high-performance alkaline seawater electrolysis[J]. Nat. Commun., 2019, 10: 5106.

[21] Liu P, Chen B, Liang C W, Yao W T, Cui Y Z, Hu S Y, Zou P C, Zhang H, Fan H J, Yang C. Tip-enhanced electric field: A new mechanism promoting mass transfer in oxygen evolution reactions[J]. Adv. Mater., 2021, 33(9): 2007377.

[22] Kienitz B L, Baskaran H, Zawodzinski T A. Modeling the steady-state effects of cationic contamination on polymer electrolyte membranes[J]. Electrochim. Acta, 2009, 54(6): 1671-1679.

[23] Bolar S, Shit S, Murmu N C, Kuila T. Progress in theoretical and experimental investigation on seawater electrolysis: Opportunities and challenges[J]. Sustain. Energy Fuels, 2021, 5(23): 5915-5945.

[24] Suen N T, Hung S F, Quan Q, Zhang N, Xu Y J, Chen H M. Electrocatalysis for the oxygen evolution reaction: Recent development and future perspectives[J]. Chem. Soc. Rev., 2017, 46(2): 337-365.

[25] Li J H, Liu Y P, Chen H, Zhang Z K, Zou X X. Design of a multilayered oxygen-evolution electrode with high catalytic activity and corrosion resistance for saline water splitting[J]. Adv. Funct. Mater., 2021, 31(27): 2101820.

[26] Seh Z W, Kibsgaard J, Dickens C F, Chorkendorff I B, Nörskov J K, Jaramillo T F. Combining theory and experiment in electrocatalysis: Insights into materials design[J]. Science, 2017, 355(6321): eaad4998.

[27] Bennett J E. Electrodes for generation of hydrogen and oxygen from seawater[J]. Int. J. Hydrogen Energy, 1980, 5(4): 401-408.

[28] Trasatti S. Electrocatalysis in the anodic evolution of oxygen and chlorine[J]. Electrochim. Acta, 1984, 29(11): 1503-1512.

[29] Zhu J, Hu L S, Zhao P X, Lee L Y S, Wong K Y. Recent advances in electrocatalytic hydrogen evolution using nanoparticles[J]. Chem. Rev., 2020, 120(2): 851-918.

[30] Zou X X, Zhang Y. Noble metal-free hydrogen evolution catalysts for water splitting[J]. Chem. Soc. Rev., 2015, 44 (15): 5148-5180.

[31] Gayen P, Saha S, Ramani V. Selective seawater splitting using pyrochlore electrocatalyst[J]. ACS Appl. Energy Mater., 2020, 3(4): 3978-3983.

[32] Kirk D W, Ledas A E. Precipitate formation during sea water electrolysis[J]. Int. J. Hydrogen Energy, 1982, 7

(12): 925-932.

[33] Lu X Y, Pan J, Lovell E, Tan T H, Ng Y H, Amal R. A sea-change: Manganese doped nickel/nickel oxide electrocatalysts for hydrogen generation from seawater [J]. Energy Environ. Sci., 2018, 11(7): 1898-1910.

[34] Zhang B, Wang J, Wu B, Guo X W, Wang Y J, Chen D, Zhang Y C, Du K, Oguzie E E, Ma X L. Unmasking chloride attack on the passive film of metals[J]. Nat. Commun., 2018, 9: 2559.

[35] Scott S B, S?rensen J E, Rao R R, Moon C, Kibsgaard J, Shao-Horn Y, Chorkendorff I. The low overpotential regime of acidic water oxidation part II: Trends in metal and oxygen stability numbers[J]. Energy Environ. Sci., 2022, 15(5): 1988-2001.

[36] Wang C, Shang H Y, Jin L J, Xu H, Du Y K. Advances in hydrogen production from electrocatalytic seawater splitting[J]. Nanoscale, 2021, 13(17): 7897-7912.

[37] Lan C, Xie H P, Wu Y F, Chen B, Liu T. Nanoengineered, Mo-doped, Ni_3S_2 electrocatalyst with increased Ni-S coordination for oxygen evolution in alkaline seawater[J]. Energy & Fuels, 2022, 36(5): 2910-2917.

[38] Hegner F S, Garcés-Pineda F A, González-Cobos J, Rodríguez-García B, Torréns M, Palomares E, López N, Galán-Mascarós J R. Understanding the catalytic selectivity of cobalt hexacyanoferrate toward oxygen evolution in seawater electrolysis[J]. ACS Catal., 2021, 11(21): 13140-13148.

[39] d'Amore-Domenech R, Leo T J. Sustainable hydrogen production from offshore marine renewable farms: Techno-energetic insight on seawater electrolysis technologies [J]. ACS Sustain. Chem. Eng., 2019, 7(9): 8006-8022.

[40] You H H, Wu D S, Si D H, Cao M N, Sun F F, Zhang H, Wang H M, Liu T F, Cao R. Monolayer NiIr-layered double hydroxide as a long-lived efficient oxygen evolution catalyst for seawater splitting[J]. J. Am. Chem. Soc., 2022, 144(21): 9254-9263.

[41] You B, Sun Y J. Innovative strategies for electrocatalytic water splitting[J]. Acc. Chem. Res., 2018, 51(7): 1571-1580.

[42] Skúlason E, Tripkovic V, Björketun M E, Gudmundsdóttir S, Karlberg G, Rossmeisl J, Bligaard T, Jónsson H, Nörskov J K. Modeling the electrochemical hydrogen oxidation and evolution reactions on the basis of density functional theory calculations[J]. J. Phys. Chem. C, 2010, 114(42): 18182-18197.

[43] Zheng J J. Binary platinum alloy electrodes for hydrogen and oxygen evolutions by seawater splitting[J]. Appl. Surf. Sci., 2017, 413: 72-82.

[44] Li H Y, Tang Q W, He B L, Yang P Z. Robust electrocatalysts from an alloyed Pt-Ru-M (M = Cr, Fe, Co, Ni, Mo)-decorated Ti mesh for hydrogen evolution by seawater splitting[J]. J. Mater. Chem. A, 2016, 4(17): 6513-6520.

[45] Mahmood A, Lin H F, Xie N H, Wang X. Surface confinement etching and polarization matter: A new approach to prepare ultrathin ptagco nanosheets for hydrogen-evolution reactions[J]. Chem. Mater., 2017, 29(15): 6329-6335.

[46] Chen Y, Zheng X X, Huang X Y, Wang A J, Zhang Q L, Huang H, Feng J J. Trimetallic ptrhco petal-assembled alloyed nanoflowers as efficient and stable bifunctional electrocatalyst for ethylene glycol oxidation and hydrogen evolution reactions[J]. J. Colloid Interface Sci., 2020, 559: 206-214.

[47] Chen H Y, Niu H J, Han Z, Feng J J, Huang H, Wang A J. Simple fabrication of trimetallic platinum-nickel-cobalt hollow alloyed 3D multipods for highly boosted hydrogen evolution reaction[J]. J. Colloid Interface Sci., 2020, 570: 205-211.

[48] Wu L B, Zhang F H, Song S W, Ning M H, Zhu Q, Zhou J Q, Gao G H, Chen Z Y, Zhou Q C, Xing X X, Tong T, Yao Y, Bao J M, Yu L, Chen S, Ren Z F. Efficient alkaline water/seawater hydrogen evolution by a nanorod nanoparticle-structured Ni-MoN catalyst with fast water-dissociation kinetics[J]. Adv. Mater., 2022, 34(21): 2201774.

[49] Jin H Y, Wang X S, Tang C, Vasileff A, Li L Q, Slattery A, Qiao S Z. Stable and highly efficient hydrogen evolution from seawater enabled by an unsaturated nickel surface nitride[J]. Adv. Mater., 2021, 33(13): 2007508.

[50] Fei H L, Dong J C, Arellano-Jiménez M J, Ye G L, Kim N D, Samuel E L G, Peng Z W, Zhu Z, Qin F, Bao J M, Yacaman M J, Ajayan P M, Chen D L, Tour J M. Atomic cobalt on nitrogen-doped graphene for hydrogen generation[J]. Nat. Commun., 2015, 6: 8668.

[51] Lei C J, Wang Y, Hou Y, Liu P, Yang J, Zhang T, Zhuang X D, Chen M W, Yang B, Lei L C, Yuan C, Qiu M, Feng X L. Efficient alkaline hydrogen evolution on atomically dispersed Ni-N_x species anchored porous carbon with embedded Ni nanoparticles by accelerating water dissociation kinetics[J]. Energy Environ. Sci., 2019, 12(1): 149-156.

[52] Chen W X, Pei J J, He C T, Wan J W, Ren H L, Zhu Y Q, Wang Y, Dong J C, Tian S B, Cheong W C, Lu S Q, Zheng L R, Zheng X S, Yan W S, Zhuang Z B, Chen C, Peng Q, Wang D S, Li Y D. Rational design of single molybdenum atoms anchored on N-doped carbon for

effective hydrogen evolution reaction[J]. Angew. Chem. Int. Ed., 2017, 56(50): 16086-16090.

[53] Chen W X, Pei J J, He C T, Wan J W, Ren H L, Wang Y, Dong J C, Wu K L, Cheong W C, Mao J J, Zheng X S, Yan W S, Zhuang Z B, Chen C, Peng Q, Wang D S, Li Y D. Single tungsten atoms supported on MoF-derived N-doped carbon for robust electrochemical hydrogen evolution[J]. Adv. Mater., 2018, 30(30): 1800396.

[54] Zang W J, Sun T, Yang T, Xi S B, Waqar M, Kou Z K, Lyu Z Y, Feng Y P, Wang J, Pennycook S J. Efficient hydrogen evolution of oxidized Ni-N_3 defective sites for alkaline freshwater and seawater electrolysis[J]. Adv. Mater., 2021, 33(8): 2003846.

[55] Hung W H, Xue B Y, Lin T M, Lu S Y, Tsao I Y. A highly active selenized nickel-iron electrode with layered double hydroxide for electrocatalytic water splitting in saline electrolyte[J]. Mater. Today Energy, 2021, 19: 100575.

[56] Vos J G, Wezendonk T A, Jeremiasse A W, Koper M T M. MnO_x/IrO_x as selective oxygen evolution electrocatalyst in acidic chloride solution[J]. J. Am. Chem. Soc., 2018, 140(32): 10270-10281.

[57] Deng J, Deng D H, Bao X H. Robust catalysis on 2D materials encapsulating metals: Concept, application, and perspective[J]. Adv. Mater., 2017, 29(43): 1606967.

[58] Yu L, Deng D H, Bao X H. Chain mail for catalysts[J]. Angew. Chem. Int. Ed., 2020, 59(36): 15294-15297.

[59] Deng J, Ren P J, Deng D H, Bao X H. Enhanced electron penetration through an ultrathin graphene layer for highly efficient catalysis of the hydrogen evolution reaction[J]. Angew. Chem. Int. Ed., 2015, 54(7): 2100-2104.

[60] Zhang T, Sun Y Q, Hang L F, Bai Y, Li X Y, Wen L L, Zhang X M, Lyu X J, Cai W P, Li Y. Large-scale synthesis of Co/CoO_x encapsulated in nitrogen-, oxygen-, and sulfur-tridoped three-dimensional porous carbon as efficient electrocatalysts for hydrogen evolution reaction[J]. ACS Appl. Energy Mater., 2018, 1(11): 6250-6259.

[61] Jadhav A R, Kumar A, Lee J J, Yang T, Na S, Lee J S, Luo Y G, Liu X H, Hwang Y, Liu Y, Lee H. Stable complete seawater electrolysis by using interfacial chloride ion blocking layer on catalyst surface[J]. J. Mater. Chem. A, 2020, 8(46): 24501-24514.

[62] Zhang T, Bai Y, Sun Y Q, Hang L F, Li X Y, Liu D L, Lyu X J, Li C C, Cai W P, Li Y. Laser-irradiation induced synthesis of spongy auagpt alloy nanospheres with high-index facets, rich grain boundaries and subtle lattice distortion for enhanced electrocatalytic activity[J]. J. Mater. Chem. A, 2018, 6(28): 13735-13742.

[63] Zhang T, Sun Y Q, Li X J, Li X Y, Liu D L, Liu G Q, Li C C, Fan H J, Li Y. Ptpdag hollow nanodendrites: Template-free synthesis and high electrocatalytic activity for methanol oxidation reaction[J]. Small Methods, 2020, 4(1): 1900709.

[64] Tu W Z, Luo W J, Chen C L, Chen K, Zhu E B, Zhao Z P, Wang Z L, Hu T, Zai H C, Ke X X, Sui M L, Chen P W, Zhang Q S, Chen Q, Li Y J, Huang Y. Tungsten as “adhesive” in $Pt_2CuW_{0.25}$ ternary alloy for highly durable oxygen reduction electrocatalysis[J]. Adv. Funct. Mater., 2020, 30(6): 1908230.

[65] Wang H M, Chen Z N, Wu D S, Cao M N, Sun F F, Zhang H, You H H, Zhuang W, Cao R. Significantly enhanced overall water splitting performance by partial oxidation of Ir through Au modification in core-shell alloy structure[J]. J. Am. Chem. Soc., 2021, 143(12): 4639-4645.

[66] Wu L B, Yu L, Zhang F H, McElhenny B, Luo D, Karim A, Chen S, Ren Z F. Heterogeneous bimetallic phosphide Ni_2P-Fe_2P as an efficient bifunctional catalyst for water/seawater splitting[J]. Adv. Funct. Mater., 2021, 31(1): 2006484.

[67] Zhuang L Z, Li J K, Wang K Y, Li Z H, Zhu M H, Xu Z. Structural buffer engineering on metal oxide for long-term stable seawater splitting[J]. Adv. Funct. Mater., 2022, 32 (25): 2201127.

[68] Yang Q F, Cui Y C, Li Q Y, Cai J H, Wang D, Feng L. Nanosheet-derived ultrafine $CoRuO_x$@NC nanoparticles with a core@shell structure as bifunctional electrocatalysts for electrochemical water splitting with high current density or low power input[J]. ACS Sustain. Chem. Eng., 2020, 8(32): 12089-12099.

[69] Jian J, Yuan L, Qi H, Sun X J, Zhang L, Li H, Yuan H M, Feng S H. Sn-Ni_3S_2 ultrathin nanosheets as efficient bifunctional water-splitting catalysts with a large current density and low overpotential[J]. ACS Appl. Mater. Interfaces, 2018, 10(47): 40568-40576.

[70] Yao Y, Zhu Y H, Pan C A Q, Wang C Y, Hu S Y, Xiao W, Chi X, Fang Y R, Yang J, Deng H T, Xiao S Q, Li J B, Luo Z, Guo Y B. Interfacial sp C-O-Mo hybridization originated high-current density hydrogen evolution[J]. J. Am. Chem. Soc., 2021, 143(23): 8720-8730.

[71] Luo Y T, Zhang Z Y, Chhowalla M, Liu B L. Recent advances in design of electrocatalysts for high-current-density water splitting[J]. Adv. Mater., 2022, 34(16): 2108133.

[72] Jothi V R, Karuppasamy K, Maiyalagan T, Rajan H, Jung C Y, Yi S C. Corrosion and alloy engineering in rational design of high current density electrodes for efficient water splitting[J]. Adv. Energy Mater., 2020, 10(24): 1904020.

[73] Feng J R, Lv F, Zhang W Y, Li P H, Wang K, Yang C,

Wang B, Yang Y, Zhou J H, Lin F, Wang G C, Guo S J. Iridium-based multimetallic porous hollow nanocrystals for efficient overall-water-splitting catalysis[J]. Adv. Mater., 2017, 29(47): 1703798.

[74] Wu T, Song E H, Zhang S N, Luo M J, Zhao C D, Zhao W, Liu J J, Huang F Q. Engineering metallic heterostructure based on Ni_3N and 2M-MoS_2 for alkaline water electrolysis with industry-compatible current density and stability[J]. Adv. Mater., 2022, 34(9): 2108505.

[75] Wen Q L, Yang K, Huang D J, Cheng G, Ai X M, Liu Y W, Fang J K, Li H Q, Yu L, Zhai T Y. Schottky heterojunction nanosheet array achieving high-current-density oxygen evolution for industrial water splitting electrolyzers[J]. Adv. Energy Mater., 2021, 11(46): 2102353.

[76] Seenivasan S, Kim D H. Engineering the surface anatomy of an industrially durable $NiCo_2S_4$/$NiMo_2S_4$/NiO bifunctional electrode for alkaline seawater electrolysis[J]. J. Mater. Chem. A, 2022, 10(17): 9547-9564.

[77] Carmo M, Fritz D L, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis[J]. Int. J. Hydrogen Energy, 2013, 38(12): 4901-4934.

[78] Schalenbach M, Lueke W, Stolten D. Hydrogen diffusivity and electrolyte permeability of the zirfon perl separator for alkaline water electrolysis[J]. J. Electrochem. Soc., 2016, 163(14): F1480-F1488.

[79] Zhang Z, Jiang C, Li P, Yao K G, Zhao Z L, Fan J T, Li H, Wang H J. Benchmarking phases of ruthenium dichalcogenides for electrocatalysis of hydrogen evolution: Theoretical and experimental insights[J]. Small, 2021, 17(13): 2007333.

[80] Dresp S, Dionigi F, Loos S, de Araujo J F, Spöri C, Gliech M, Dau H, Strasser P. Direct electrolytic splitting of seawater: Activity, selectivity, degradation, and recovery studied from the molecular catalyst structure to the electrolyzer cell level[J]. Adv. Energy Mater., 2018, 8(22): 1800338.

[81] Laguna-Bercero M A. Recent advances in high temperature electrolysis using solid oxide fuel cells: A review[J]. J. Power Sources, 2012, 203: 4-16.

[82] Abbasi E A J, Sahu H, Javadpour S M, Goharimanesh M. Interpretable machine learning for developing high-performance organic solar cells[J]. Mater. Today Energy, 2022, 25: 100969.

[83] Allam O, Kuramshin R, Stoichev Z, Cho B W, Lee S W, Jang S S. Molecular structure-redox potential relationship for organic electrode materials: Density functional theory-machine learning approach[J]. Mater. Today Energy, 2020, 17: 100482.

工业级碱性海水电解:近期进展和展望

张 涛[1#],刘一蒲[2#],叶齐通[2],范红金[1*]
(1. 南洋理工大学数理学院,新加坡 637371; 2. 海南大学材料科学与工程学院,
南海海洋资源利用重点实验室,海南 海口 570228,中国)

摘要: 由太阳能、风能和海洋等可再生能源驱动的工业级水分解产氢为能源和环境的可持续性发展开辟了一条极具潜力的道路。然而，在工业上最先进电解技术使用高纯水作为氢源，这将带来严重的淡水资源危机。海水分解为饮用水短缺提供了一条切实可行的解决途径，但仍面临规模工业化生产的巨大挑战。在这里，我们总结了海水分解的最新进展，包括反应机制、电极设计标准和直接海水分解的工业电解槽。深入讨论了应对海水电解中的关键挑战，如活性位点、反应选择性、耐腐蚀性和传质能力等的解决方案。此外，该文章重点总结了海水电解设备的最新发展，并提出了设计长寿命直接海水电解装置的有效策略。最后，我们对直接海水电解的未来机遇和挑战提出了自己的观点。

关键词: 海水电解;抗腐蚀设计;电极设计标准;工业电解槽