MINI REVIEW

Cutting-edge methods for amplifying the oxygen evolution reaction during seawater electrolysis: a brief synopsis

Xiang Lyu (iD)* and Alexey Serov

Electrochemical water splitting has been considered a clean and continual way for hydrogen (H_2) production. Direct seawater electrolysis is a potentially attractive technology due to the ample access to seawater and scarce freshwater resources in some regions. However, the presence of impurities (*e.g.*, Cl^-, Mg^{2+}) and the resulting corrosion and side reactions, such as the chloride oxidation reaction (ClOR), makes seawater electrocatalysis more challenging than that of fresh or alkaline water due to competition with the oxygen evolution reaction (OER) at the anode. Consequently, much effort has been devoted to developing approaches to enhance OER performance and suppress the ClOR. In this minireview, we summarize three general strategies for enhancing OER activity and selectivity in seawater electrolysis based on three different concepts: (1) the sole development of robust and high-performance OER catalysts in pure seawater electrolytes, (2) the introduction of additives to seawater electrolytes (*e.g.*, alkalis and/or salts without chloride) to enhance the potential equilibrium gap between the ClOR and OER in combination with regular highly active OER catalysts, and (3) a combination of approaches (1) and (2). Finally, the current challenges and potential opportunities for green H_2 production from seawater electrolysis are briefly presented.

Keywords: Electrochemical seawater splitting; Alkaline seawater electrolysis; Oxygen evolution reaction; Hydrogen production; Electrocatalysts.
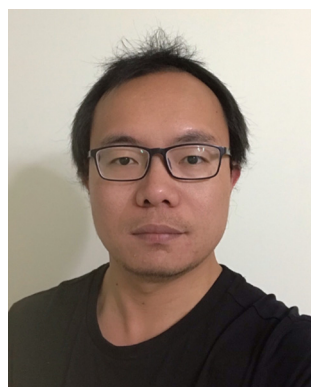
1 Introduction

The growth of the global energy crisis, along with environmental pollution caused by fossil fuels, has strongly

Electrification and Energy Infrastructures Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. E-mail: lyux@ornl.gov

Dr. Lyu joined the ORNL in 2021 as a postdoc research associate. Currently, he dedicates his research to PEMFCs, electrolysis in acidic/alkaline/seawater media, and CO_2 reduction. He received his Ph.D. Degree in Chemical Engineering in 2020 from Ohio University, where he mainly worked on water electrolysis, fuel cells, and catalyst design and synthesis.

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driven the pursuit of renewable energy sources.[1–4] Green hydrogen (H_2), produced from water electrolysis using renewable energy sources (*e.g.*, wind, solar, and tide), accomplished with high-efficiency fuel cells,[5–7] has been recognized as a promising alternative to fossil fuels because of its high energy density and free pollution.[8–15] Water distribution issues may arise if vast amounts of purified water are used for water splitting to mitigate the global energy crisis.[16,17] Thus, seawater is preferred to freshwater due to its high abundance on the earth compared to freshwater sources.[18–20]

In electrochemical water splitting, the oxygen evolution reaction (OER) at the anode – a four-electron transfer reaction – is more kinetically sluggish than the hydrogen evolution reaction (HER) at the cathode – a two-electron transfer reaction.[21,22] Consequently, the OER determines the overall efficiency of water splitting.[23,24] Additionally, the reactions at the anode in seawater media are more complex because of the presence of metal chlorides. Catalysts can be severely corroded by chlorine gas (Cl_2, in acidic media) or hypochlorite (ClO^-, in alkaline media) formed from the chloride oxidation reaction (ClOR), resulting in low electrochemical activity and poor durability.[19,25–29] Therefore, the ClOR must be suppressed in electrochemical seawater splitting. The reactions at the anode in seawater splitting can be represented based on different electrolytes as follows:
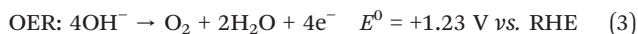
Fig. 1 Seawater electrolyzer performance using bifunctional Fe,P–NiSe₂ NF catalysts. (a) Comparison of the HER (left) and OER (right) overpotentials required to achieve different current densities for a₁(Fe,P–NiSe₂ NFs), a₂ (Fe–NiSe₂ NFs), and a₃ (P–NiSe₂ NFs); (b and c) comparison of Tafel slopes and overpotentials required to achieve current densities of 10 mA cm⁻² for the HER (b) and 100 mA cm⁻² for the OER (c) of Fe,P–NiSe₂ NFs with those of benchmark catalysts; (d) the electrical conductivity of all samples; (e) schematics of AEM electrolyzers using different electrolyte feeding modes; (f) the current density of AEM electrolyzers at E_{cell} values of 1.7 and 1.8 V in different seawater feeding modes; (g) FE of O₂ using the asymmetric device I (solid) and symmetric device III (dotted) feeding modes using natural seawater as a feedstock solution at different E_{cell} values; (h) long-term operation test of asymmetric device I and symmetric device III seawater electrolyzers showing high selectivity and stability at 1.8 V. Reprinted with permission from ref. 43. Copyright 2021 John Wiley and Sons.

Eqn (1)–(3) in acidic media:

$$\text{OER: } 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23 \text{ V } vs. \text{ RHE} \quad (1)$$

$$\text{ClOR: } 2Cl^- \rightarrow Cl_2 + 2e^- \quad E^0 = +1.36 \text{ V } vs. \text{ RHE} \quad (2)$$

Eqn (3) and (4) in alkaline media:

$$\text{OER: } 4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad E^0 = +1.23 \text{ V } vs. \text{ RHE} \quad (3)$$

$$\text{ClOR: } Cl^- + 2OH^- \rightarrow ClO^- + H_2O + 2e^- \quad E^0 = +1.72 \text{ V } vs. \text{ RHE} \quad (4)$$

According to the thermodynamic potentials of eqn (1)–(4), the selectivity for the OER and ClOR is dependent on the pH and chloride concentration. The OER equilibrium potential is only 130 mV higher than that of the ClOR in acidic media, while the ClOR possesses a kinetic advantage compared to the OER due to its two-electron transfer reaction, resulting in a considerable challenge for achieving high selectivity to the OER, especially at high current density and potential.[30] In contrast, alkaline seawater electrolysis is thermodynamically more favorable for the OER than the ClOR, with a potential difference of 490 mV, which is desirable for suppressing the ClOR. The corrosion of catalysts and substrates may still be a concern even with highly active OER catalysts in alkaline media, as the aggressive chloride ions can corrode *via* metal chloride–hydroxide formation mechanisms.[31] Consequently, various strategies have been devoted to enhancing the OER and simultaneously suppressing the ClOR during seawater splitting in the past decade.

Fig. 2 Seawater electrolysis performance of various catalysts. (a) Overall seawater splitting performance of CoO_x, NiMo‖Fe-doped NiOOH and Pt/C‖RuO_2; (b) long-term durability test of CoO_x at 1.90 V in natural and alkaline seawater; (c) overall seawater splitting performance of Cr_2O_3–CoO_x in natural seawater, with the inset showing the high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image of Cr_2O_3–CoO_x; (d) long-term durability test of Cr_2O_3–CoO_x at 1.90 V in natural seawater. Reprinted with permission from ref. 44. Copyright 2023 Springer Nature.

According to a literature review,[32–38] approaches for enhancing OER selectivity in seawater splitting can be roughly categorized into three types: (1) solely developing catalysts with high OER activity and selectivity in pure seawater electrolytes (natural or simulated seawater), (2) the introduction of additives to seawater electrolytes (e.g., alkalis and/or salts without chloride) combined with regular highly active OER catalysts, where the OER becomes thermodynamically favorable, and (3) the combination of catalyst development and electrolyte preference, as described in types (1) and (2). In this minireview, we emphasize the three general types that have guided critical developments in seawater electrolysis for H_2 production and their implications for future research. Two examples are given for each type of approach. Ultimately, we summarize the challenges and give perspectives on the seawater electrolysis strategies, which could be the potential direction to speed up seawater splitting for green H_2 production.

2 Approaches for enhancing OER selectivity in seawater splitting

2.1 Solely developing robust catalysts with high OER activity and selectivity

The sole development of robust catalysts with high OER activity and selectivity is an ideal strategy for direct pure seawater electrolysis, although the requirement for this kind of catalyst to survive in pure seawater is super critical, especially at high current density and voltage. Most catalysts could not persist at high current density and voltage for a long time due to the corrosion caused by chloride and the resulting ClOR, so reports on this kind of catalyst are limited based on a literature review.[39–42] Usually, two general principles can be applied to design this kind of catalyst: (1) developing robust OER catalysts with low overpotential and high current density (e.g., <490 mV at 500 mA cm^{-2}) and (2)
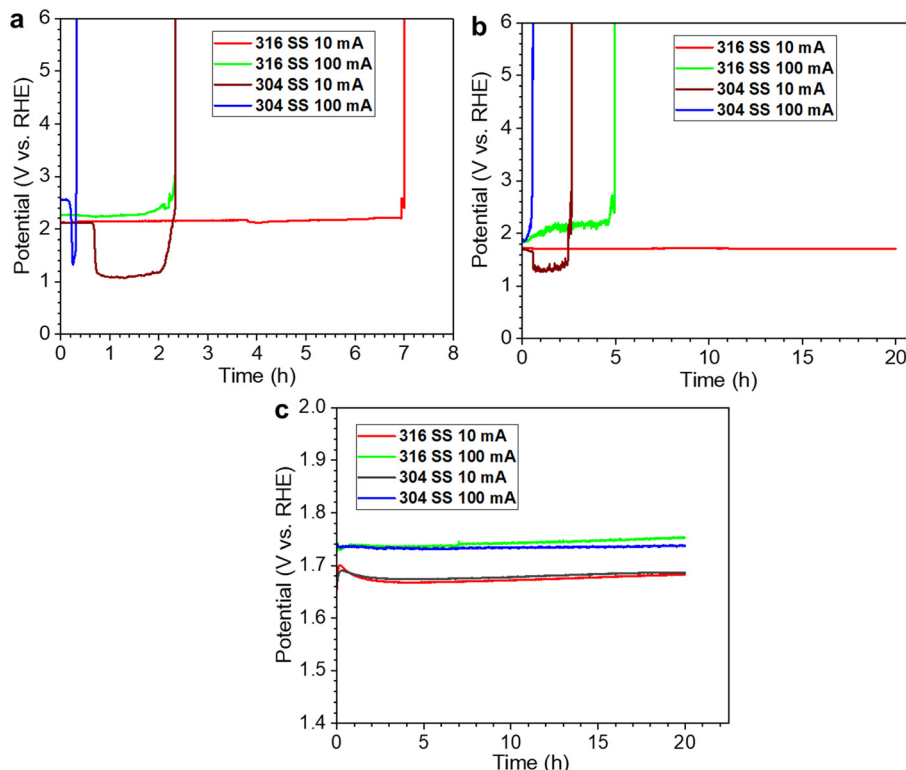
Fig. 3 Stability tests with the 304 and 316 SS electrodes in different electrolytes: (a) pure natural seawater; (b) natural seawater containing 0.1 M NaOH; (c) natural seawater electrolyte containing 1 M NaOH. All currents shown here are also the current density, as 1 cm^2 electrodes were used. Reprinted with permission from ref. 58. Copyright 2023 Elsevier.

modifying the microenvironment near the anode surface *via* rational catalyst design to switch the potential equilibrium from the ClOR to the OER.

Chang *et al.* rationally designed iron and phosphor dual-doped nickel selenide nanoporous films (Fe,P–NiSe$_2$ NFs) as bifunctional catalysts for the OER and HER for direct seawater electrolysis and observed excellent performance toward the OER, as shown in Fig. 1.[43] The overpotential for the OER at 500 mA cm^{-2} is less than 400 mV with the obtained Fe,P–NiSe$_2$ NF catalysts, and a high current density of 800 mA cm^{-2} with high OER selectivity (>90%) and long-term stability (200 h) was achieved at a cell voltage of 1.8 V. The authors claimed that the doping of Fe cations enhanced the activity and selectivity for the OER, and the doping of P anions improved the electronic conductivity and corrosion resistance by forming a passivation layer consisting of P–O species.

Recently, Guo *et al.* reported that introducing a hard Lewis acid layer (for example, Cr$_2$O$_3$) over various transition metal oxide catalysts can manipulate their local reaction microenvironment (introducing OH$^-$ anions) at the anode surface in direct seawater electrolysis.[44] A substantial activity enhancement was observed with this *in situ* artificially created local alkaline environment on the surface of Lewis acid-modified electrodes (Cr$_2$O$_3$–CoO$_x$). Simultaneously, the ClOR was suppressed due to the low chloride concentration near the catalyst surface, as shown in Fig. 2. It can be seen

that the performance of Cr$_2$O$_3$–CoO$_x$ in natural seawater significantly surpassed that of CoO$_x$ in natural seawater and approached that of CoO$_x$ in alkaline seawater electrolytes. Additionally, Cr$_2$O$_3$–CoO$_x$ exhibited much higher stability in natural seawater with high selectivity (>90%) compared with CoO$_x$ catalysts in both natural and alkaline seawater electrolytes. The authors found that the pH near the Cr$_2$O$_3$–CoO$_x$ anode surface (~14) was much higher than that in the bulk electrolyte (~8), and they attributed the high performance toward the OER to the local pH increase by the introduction of the hard Lewis acid Cr$_2$O$_3$, where the OER becomes thermodynamically favorable over the ClOR. This work provides a novel potential approach to design catalysts for direct seawater electrolysis rationally.

2.2 The introduction of additives to seawater electrolytes

As we described earlier, the selectivity for the OER and ClOR depends on the pH (H$^+$) and chloride concentration, and the introduction of an alkali favors the selectivity to the OER over the ClOR. Consequently, alkaline seawater electrolysis has been investigated extensively in the past decade.[45–56] We evaluated 316 stainless-steel (SS) mesh and Ni foam electrodes for the OER in alkaline (0.1, 0.5, and 1 M NaOH/KOH) seawater (simulated seawater, 0.5 M NaCl) electrolysis and observed that the overpotentials at 10 mA cm^{-2} for both electrodes decreased with the increase of alkali
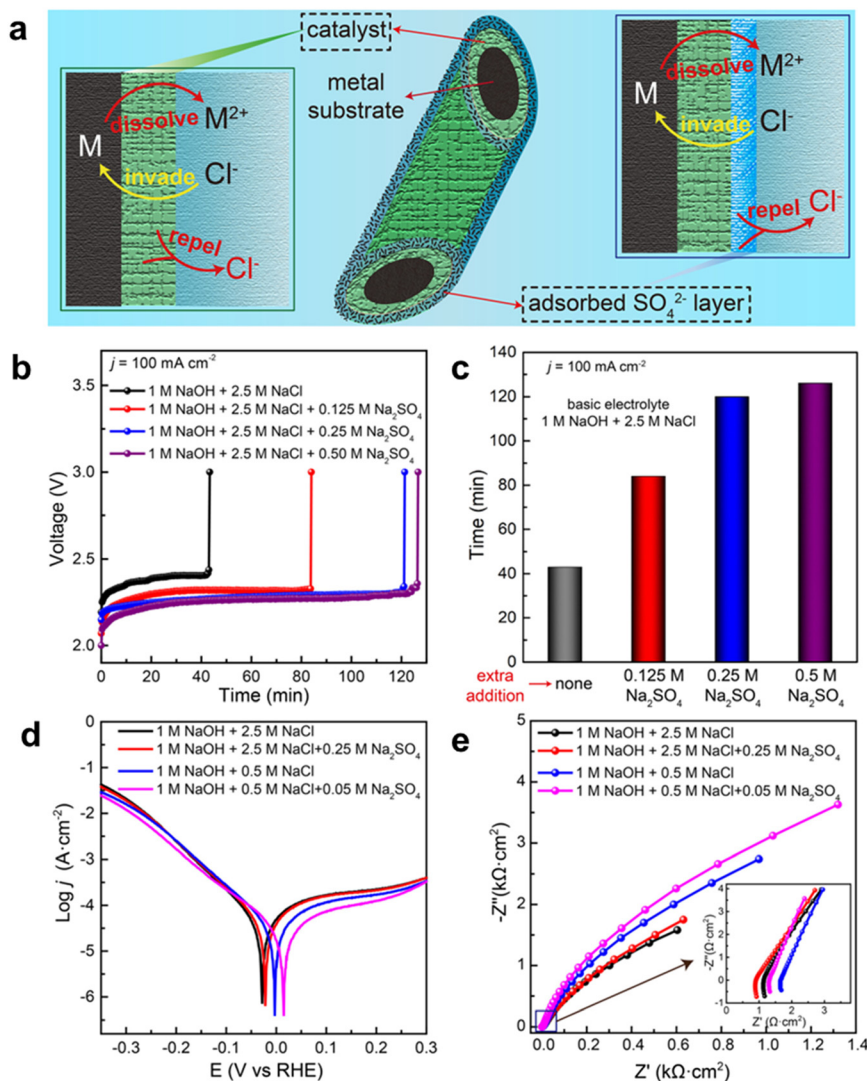
Fig. 4 Schematic illustration of chloride repulsion and performance evaluation in various electrolytes. (a) Catalyst optimization (left) and electrolyte optimization (right) to protect the metal substrate from Cl⁻ corrosion; (b) stability tests recorded at a constant current of 100 mA cm⁻² for pure NF in electrolytes with different proportions of Na_2SO_4; (c) the durability of NF in different electrolytes; (d) and (e) Tafel plots and Nyquist impedance plots of NF in different electrolytes (1 M NaOH + 2.5 M NaCl with and without 0.25 M Na_2SO_4; 1 M NaOH + 0.5 M NaCl with and without 0.05 M Na_2SO_4). Reprinted with permission from ref. 60. Copyright 2021 John Wiley and Sons.

concentration.[57] The lowest overpotential of 352 at 10 mA cm⁻² was achieved with the SS mesh electrode, which was ~150 mV less than that of the Ni foam electrode and comparable to those of commercial RuO_2 and IrO_2 catalysts. Recently, we reported that the performance of the 316 SS mesh electrode was promising and comparable to that of the 304 SS electrode in high alkalinity (1 M NaOH) natural seawater electrolyte, while it was much superior to the 304 SS electrode in pure natural and low alkalinity (0.1 M NaOH) seawater electrolytes regarding the electrocatalytic activity and corrosion resistance, as shown in Fig. 3.[58] The finding indicated that the slight difference in material composition (e.g., Ni, Cr, and Mo) between 316 and 304 SS could cause a considerable difference in corrosion resistance for seawater electrolysis, even though their electrocatalytic activities toward the OER were similar in pure alkaline or highly alkaline seawater electrolytes, which suggests that both the OER performance and corrosion resistance are critical parameters in catalyst design for alkaline seawater electrolysis.

Besides adding an alkali to the seawater electrolyte, salts without chloride (e.g., sulfate and phosphate) can also be added to suppress the ClOR and minimize the corrosion effect,[36,59] as the presence of sulfate and phosphate anions near the anodic catalyst surface could decrease the local chloride concentration while these anions would not be oxidized. Ma et al. investigated the addition of sulfate for the OER with a Ni foam anode for alkaline seawater electrolysis and found that the addition of sulfate could significantly enhance the corrosion resistance, resulting in prolonged operating durability, as shown in Fig. 4.[60] According to in situ experiments and theoretical simulations, they demonstrated
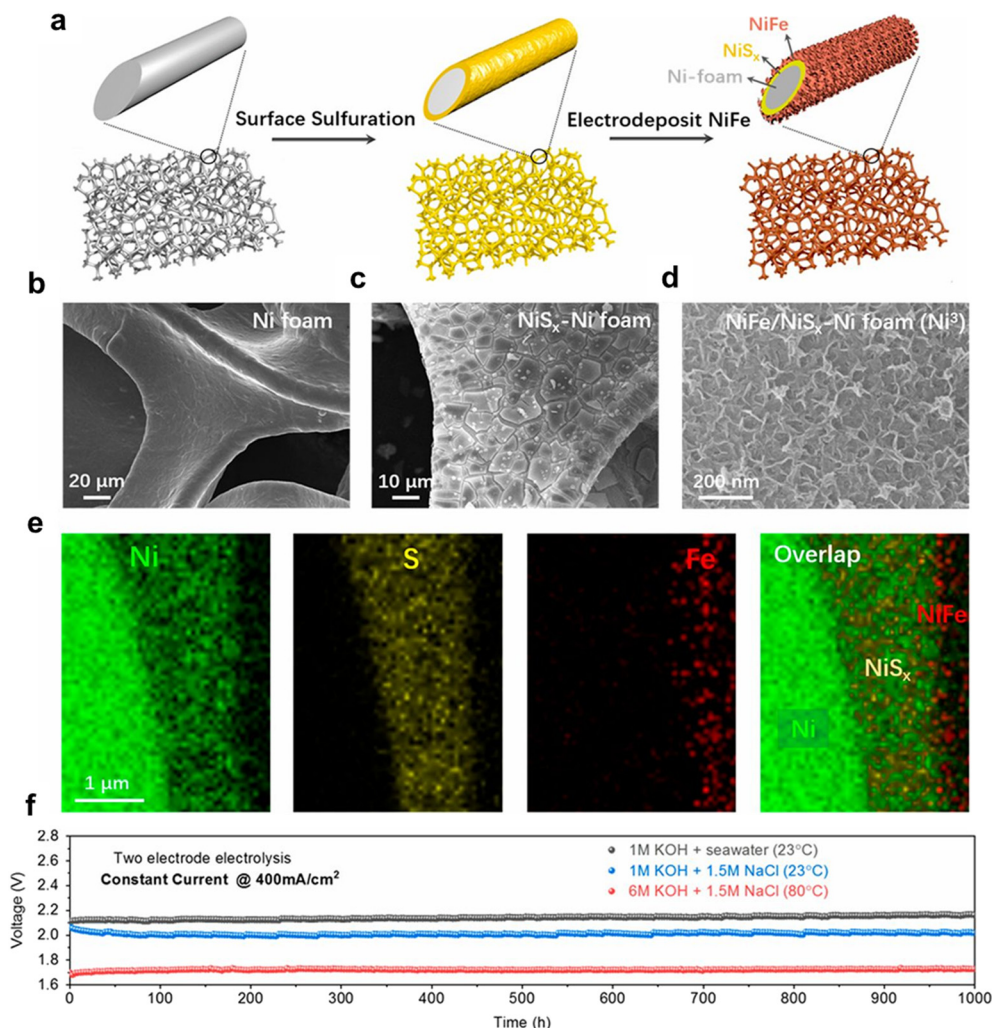
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Fig. 5 Fabrication and structure of the dual-layer NiFe/NiS$_x$-Ni foam (Ni3) anode for seawater splitting. (a) Schematic drawing of the fabrication process, including a surface sulfuration step and *in situ* electrodeposition of NiFe; (b–d) SEM images of untreated nickel foam, NiS$_x$ formed on nickel foam, and electrodeposited NiFe on the NiS$_x$ surface; (e) elemental mapping of a cross-section of NiFe/NiS$_x$ on a Ni wire in the Ni foam, revealing the Ni wire, NiS$_x$, and NiFe layers; (f) durability tests (1000 h) performed at a constant current of 400 mA cm^{-2} for the seawater-splitting electrolyzer in 1 M KOH + real seawater at room temperature and 6 M KOH electrolyte at 80 °C. Reproduced from ref. 31 with permission from the PANS.

that sulfate anions were preferentially adsorbed on the anode surface and then formed a negative charge layer, which repulsed the chloride anions *via* electrostatic repulsion. The adsorbed sulfate exhibited *ca.* 5 times stability and maintained a similar OER activity compared to the traditional alkaline seawater electrolyte. This work provides potential salt additives to seawater electrolytes, which can be a general approach for highly active OER catalysts in seawater electrolysis.

2.3 The combination of catalyst development and electrolyte preference

The corrosion of electrodes may still be a concern even with highly active OER catalysts in alkaline seawater media due to the metal chloride–hydroxide corrosion mechanism; the combination of robust and highly active OER catalysts and

appropriate electrolyte preference is a promising way to achieve super OER performance and minimize electrode corrosion.[61–71] Kuang *et al.* developed a multilayer anode containing a nickel–iron hydroxide electrocatalyst layer uniformly coated on a nickel sulfide layer on porous Ni foam (NiFe/NiS$_x$–Ni), as shown in Fig. 5, and observed superior catalytic activity and corrosion resistance in alkaline seawater electrolysis operating at industrially required current densities (0.4 to 1 A cm^{-2}) for over 1000 h.[31] They observed that passivating layers were formed in the anode surface due to the *in situ*-generated carbonate-rich and polyatomic sulfate products, resulting in repelling chloride and exhibiting superior corrosion resistance in alkaline seawater electrolysis.

Yu *et al.* reported a facile one-step approach for synthesizing S-doped Ni/Fe (oxy)hydroxide catalysts on a Ni foam substrate with high porosity and good hydrophilicity and observed that the prepared electrode exhibited

Fig. 6 Performance evaluation of seawater electrolysis with various catalysts and electrolytes. (a) Polarization curves and (b) corresponding Tafel plots of the Ni foam, IrO_2, and S–(Ni,Fe)OOH electrodes. The inset in (a) shows the polarization curve of S–(Ni,Fe)OOH over a small current density range; (c) polarization curves, (d) C_{dl} values, and (e) EIS Nyquist plots of the S–(Ni,Fe)OOH electrodes prepared using different reaction times; (f) polarization curves and (g) comparison of the overpotentials required to achieve current densities of 100, 500, and 1000 mA cm^{-2} for the S–(Ni,Fe)OOH electrode tested in different electrolytes; (h) long-term stability tests at a constant current density of 100 mA cm^{-2} for the S–(Ni,Fe)OOH electrode in different electrolytes. Reproduced from ref. 72 with permission from the Royal Society of Chemistry.

extraordinary OER performance in alkaline seawater electrolysis, as shown in Fig. 6.[72] The authors found that the doped S could enhance both the activity and stability of Ni/Fe (oxy)hydroxide catalysts toward the OER. The high activity may contribute to the optimization of the absorption energy of OER intermediates *via* changing the valence state of Ni/Fe by doping S, and the reason leading to superior corrosion resistance is still under investigation.

3 Summary and outlook

Electrochemical seawater splitting has been considered a clean and continual way to produce green H_2 fuel from earth-abundant renewable seawater resources, which is vital for the future energy structure. However, the presence of impurities and their interference, especially high chloride content, make seawater electrocatalysis much more challenging than fresh

or alkaline water electrocatalysis by competing with low hydroxide anion content for anodic reactions. The key is the development of effective strategies to enhance the selectivity and activity for the OER and suppress undesired electrochemical reactions mainly associated with the ClOR, which can lead to low OER selectivity and corrosion issues. In this minireview, we summarize three general approaches used in seawater electrolysis based on three concepts: (1) the sole development of robust and high-performance OER catalysts in pure seawater electrolytes, (2) the introduction of additives to seawater electrolytes (*e.g.*, alkalis and/or salts without chloride) to favor the OER and suppress the ClOR, and (3) the combination of approaches (1) and (2).

The sole development of robust and high-performance OER catalysts is an ideal approach for direct pure seawater electrolysis, although the requirement for this kind of catalyst to survive is super critical, especially at high current

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density and voltage. The use of additives to seawater electrolytes (*e.g.*, alkalis and/or salts without chloride) integrating with regular highly active OER catalysts is a potential way to realize green H_2 production at the industrial level, although corrosion may still be a concern due to the metal chloride–hydroxide corrosion mechanism. The combination of catalyst development and electrolyte preference is the most practical approach for the large-scale production of green H_2, but the cost is also the highest. Besides the selectivity and activity toward the OER in seawater electrolysis, the long-term durability of OER catalysts, which may play an even more important role in large-scale electrolysis industrialization, has been much less emphasized. Electrocatalysts for achieving long-term stability in natural seawater electrolytes face more challenges compared with those in seawater mimics (*e.g.*, 0.5 M NaCl), as biofouling and trace metal deposition on both electrodes also hurt the performance for long-term operation in natural seawater electrolysis, and a regular clean of the system may be required. Therefore, the effect of natural seawater electrolytes on the long-term stability should be considered and addressed when developing OER catalysts for seawater electrolysis. We believe that the green H_2 generated from seawater electrolysis will accelerate the transformation of the world's energy scheme and provide a clean energy future with the development of catalyst design, electrolyte preference, and electrolyzer optimization.

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Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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