ACS NANO

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Advancing Seawater Electrochemical Reaction for Fuel and Chemical Production

Libo Wu, Wei Li Ong, and Ghim Wei Ho*

Cite This: *ACS Nano* 2025, 19, 10779−10795

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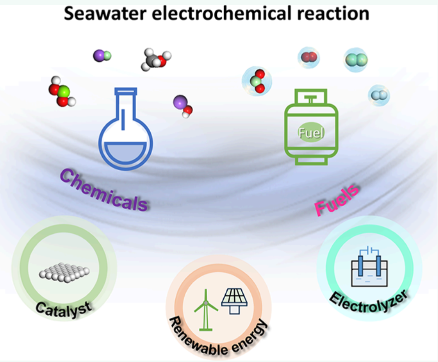
ABSTRACT: As global demand for sustainable chemical processes intensifies, seawater, with its vast availability and rich composition, represents a promising resource for advancing green chemical technologies. Seawater can serve as a feedstock or intermediate for producing fuels and chemicals, including hydrogen, chlorine gas and chloride, sodium, magnesium, and carbon-based compounds through specific electrochemical reactions. While extensive studies have been focused on seawater hydrogen production, systematic exploration of its broader electrochemical reactions remains limited. This review provides a comprehensive overview of current progress in seawater electrochemical reactions, covering its composition, fundamental reaction principles, and existing challenges. Specific examples on the use of seawater to produce fuels and chemicals beyond hydrogen are reviewed, with an emphasis on innovative electrochemical reaction mechanisms, advanced catalyst development, and integrated system designs. Apart from catalyst optimization for existing reactions, we highlight the importance of exploring alternative reactions and scalable systems. Future perspectives focus on expanding research scope, developing efficient catalysts and electrolyzers, testing in real seawater, advancing product separation, and evaluating practical systems to enable sustainable processes for clean fuel and high-value chemical production, supporting global carbon neutrality.

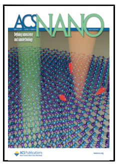


KEYWORDS: *seawater electrochemical reaction, seawater utilization, chlorine evolution reaction, hydrogen evolution reaction, oxygen evolution reaction, catalyst design, membrane electrolyzer, seawater mining, seawater-mediated reaction*

1. INTRODUCTION

Environmental pollution and the greenhouse effect caused by excessive fossil fuel consumption have profoundly impacted human life and threatened global climate stability.[1,2] To achieve the Paris Agreement's goal of limiting global temperature rise to 1.5−2 °C above preindustrial levels before 2100, a transition to renewable energy is essential.[3,4] Among various renewable energy sources and carriers, hydrogen (H_2) stands out for its high energy density, zero carbon emissions, and remarkable versatility.[5] As a clean fuel, hydrogen plays a key role in decarbonizing sectors such as transportation, industry, and power generation, making it indispensable in addressing climate change and serving as a cornerstone of long-term sustainable development.[6,7] Currently, hydrogen is mostly produced by steam methane reforming ($CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$) or coal gasification ($C + 2H_2O \rightarrow 2H_2 + CO_2$), both of which rely on fossil fuels and inevitably result in greenhouse gas emissions.[8−10] In contrast, water electrolysis ($2H_2O \rightarrow 2H_2 + O_2$) offers a carbon-free way to produce "green hydrogen" when powered by renewable energy sources.[8] However, water electrolysis is an energy-consuming process that requires active and stable catalysts as well as efficient electrolyzers. Current water electrolysis systems typically utilize high-purity fresh water as the primary reactant, supplemented with alkaline, acidic, or neutral electrolytes to enhance ionic conductivity and efficiency.[6,11] Considering the strain on fresh water resources caused by large-scale water electrolysis, seawater electrolysis has emerged as a promising alternative resource due to its vast, nearly inexhaustible availability.[12−15] Compared to fresh water, seawater's complex composition introduces challenges to seawater hydrogen production, including corrosion and competing reactions induced by chloride ions, precipitation and side reaction caused by impurities in natural seawater, and detrimental effects of precipitates on catalytic performance.[16−20] Nevertheless, seawater electrolysis to produce hydrogen continues to attract considerable research interest.[21−25]

Received: December 26, 2024
Revised: March 6, 2025
Accepted: March 6, 2025
Published: March 14, 2025



https://doi.org/10.1021/acsnano.4c18818

Table 1. Major Components of Natural Seawater, Accounting for More than 99.5% of the Dissolved Anions and Cations

Ions/cations	Concentration (g/kg seawater)	Percentage	Potential utilizations
Chloride (Cl^-)	19.162	55.03%	Production of chlorine gas and hypochlorite for chemical synthesis and disinfection
Sodium (Na^+)	10.679	30.59%	Production of sodium-based compounds for glassmaking, soap, and paper industries
Sulfate (SO_4^{2-})	2.680	7.68%	Fertilizers, industrial sulfur compounds, and gypsum production
Magnesium (Mg^{2+})	1.278	3.68%	Magnesium extraction, lightweight alloy, and pharmaceuticals production
Calcium (Ca^{2+})	0.41	1.18%	Cement manufacturing, calcium-based chemicals, and bleaches
Potassium (K^+)	0.395	1.11%	Production of potassium-based salts, reducing agent, detergent, and liquid soap
Bicarbonate (HCO^{3-})	0.129	0.41%	pH buffering and carbon dioxide capture
Bromide (Br^-)	0.066	0.19%	Flame retardants, pharmaceuticals, and bromine-based compounds
Strontium (Sr^{2+})	0.013	0.04%	Ceramics, pyrotechnics, and strontium-based materials
Fluoride (F^-)	0.001	0.003%	Dental care products and fluoride-based compounds

As the global demand for sustainable chemical processes grows, exploring seawater as a feedstock or intermediate in chemical processes presents notable opportunities for sustainable development.[12,13,26] The vast availability and rich chemical composition of seawater make it a complementary yet strategically important resource for future daily and industrial applications, especially in areas that require renewable resources. For example, seawater supports key processes such as mineral mining, large-scale energy storage, and carbon capture.[27,28] Electrolytic reaction, which involves the breaking and reorganization of chemical bonds, is an effective approach to convert electrical energy into chemical energy.[29−31] By integrating seawater resources with electrolytic processes, clean fuels and high-value chemicals can be produced through offshore/onshore seawater-based electrorefining platforms. Although much attention is currently focused on seawater hydrogen production, the ocean holds abundant untapped resources that can meet various energy and material needs.[32−34] In addition, electricity generated by offshore renewable energy such as tidal, solar, and wind energy, can be used to drive seawater electrochemical reactions, further reducing costs and promoting sustainable development.

In recent years, there has been a notable increase in publications on the utilization of seawater resources beyond hydrogen production, reflecting growing interest in expanding the applications of seawater-based electrochemistry.[34] While many reviews focus on hydrogen production, few reviews have systematically explored the broader role of seawater in the production of fuels and chemicals. This review aims to fill this gap and promote advancements in seawater resource utilization through electrochemistry. Rather than focusing solely on catalysts, this review highlights the importance of integrated system design in promoting catalytic reaction and in overcoming electrochemistry challenges. A holistic approach, including efficient electrolyzer and system development, will help to open new opportunities in this field. We start with an overview of seawater composition, electrochemical reaction principles, and the current state of seawater electrochemistry, along with associated challenges. We then explore the electrochemical reaction mechanisms and provide specific examples of fuel and chemical production using natural seawater-contained electrolyte, rather than simulated seawater. Finally, we outline perspectives to address current challenges and expand the potential of seawater electrochemistry for diverse applications and underscore the unique role of seawater in fuel and chemical production.

2. SEAWATER-BASED ELECTROCHEMICAL REACTION: COMPOSITIONS, FUNDAMENTALS, AND CHALLENGES

Understanding the main components of seawater is essential for advancing its sustainable utilization. Table 1 lists the common anions/cations in natural seawater, along with their concentrations, percentages, and potential utilizations.[35,36] The following sections focus on several of the most abundant anions/cations. With a concentration of 19.162 g/kg seawater, chloride anion (Cl^-) is the most abundant ion in seawater and can serve as a raw material to produce chlorine (Cl_2) gas and hypochlorite (ClO^-), which are valuable in chemical synthesis and disinfectants. Sodium cation (Na^+), at 10.679 g/kg, is the most abundant cation in seawater. It can be used to produce caustic soda (NaOH) and other sodium-based compounds for glass, soap, and paper manufacturing industries. Magnesium cation (Mg^{2+}, 1.278 g/kg seawater) is another important cation in seawater that can be extracted for the production of magnesium hydroxide [$Mg(OH)_2$] and lightweight magnesium-based alloys, pharmaceuticals, and other chemical products. As for calcium cation (Ca^{2+}, 0.41 g/kg seawater), it can be used to produce cement for the construction industry and as bleaches in the paper industry. Potassium cation (K^+, 0.395 g/kg seawater) can be used to produce reducing agent in organic chemistry and to make detergents and liquid soap. Seawater also contains trace amounts of other elements, including bromide (Br^-), strontium (Sr^{2+}), fluoride (F^-), and lithium (Li^+), which, despite their low concentrations, hold significant economic value. Besides, seawater contains large amounts of dissolved gases such as oxygen (O_2), carbon dioxide (CO_2) and nitrogen (N_2), and the adsorption of CO_2 by seawater becoming increasingly prominent in efforts toward achieving "carbon neutrality". It should be noted that not all elements and chemicals in seawater can be extracted via electrochemical reaction. Beyond serving as raw materials, the diverse ionic content of seawater positions itself as a valuable intermediate in electrocatalytic processes.

Among electrochemical reactions that use seawater-contained electrolyte to produce fuels and chemicals, hydrogen production through seawater electrolysis has attracted the most attention, with the largest number of papers published. Considering the abundance of high-quality reviews on this topic, covering subjects including basic principles,[12,14] catalyst design,[17,37,38] hybrid reactions,[39] electrolyzer design,[13,18,40] and system innovations,[41] we will not delve into it in much detail in this review. Instead, we will use it as an example to introduce the fundamentals and challenges of seawater-based electrolysis. Understanding the electrochemical reaction principle and the role of dissolved ions in seawater is crucial for optimizing the

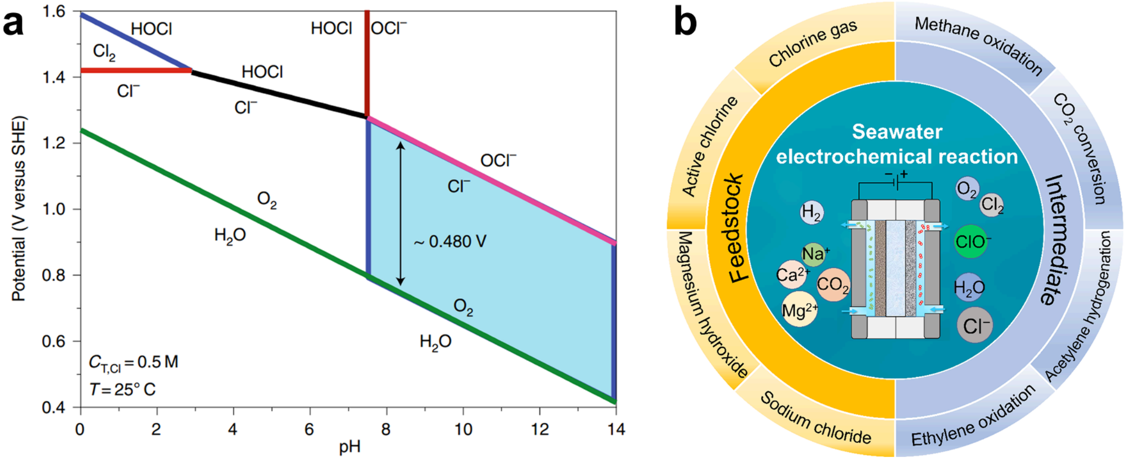


Figure 1. (a) Pourbaix diagram for H_2O/O_2 and $Cl^-/Cl_2/HOCl/ClO^-$ redox couples in a 0.5 M NaCl electrolyte with different pH value. The green line represents the thermodynamic equilibrium between H_2O and O_2. The red line shows the competing acidic oxidation of chloride to Cl_2 gas. The black and purple lines mark the onset of the oxidation of chloride to HClO or ClO^-. SHE means standard hydrogen electrode. Reprinted with permission from ref 14. Copyright 2020 Springer Nature. Data source from ref 42. Copyright 2016 John Wiley and Sons. (b) Representative fuels and chemicals production through seawater electrochemical reactions.

electrolysis process and developing catalysts and systems. In general, electrolysis involves two key electrochemical reactions: anodic oxidation and cathodic reduction. These reactions vary depending on the electrolyte conditions, which can be acidic, alkaline, or neutral, with acidic and alkaline conditions being the most widely used. During water electrolysis for hydrogen production, a hydrogen evolution reaction (HER) occurs at the cathode. Under acidic conditions, protons (H^+) combine with electrons (e^-) to form hydrogen (H_2) gas:

$$2H^+ + 2e^- \rightarrow H_2$$

Under alkaline conditions, water molecules (H_2O) are reduced to produce H_2 and hydroxide ions (OH^-):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Correspondingly, an oxygen evolution reaction (OER) occurs at the anode. Under acidic conditions, H_2O molecules are oxidized to produce oxygen (O_2) gas, H^+, and e^-:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

Under alkaline conditions, OH^- are oxidized to produce O_2 gas, H_2O molecules, and e^-:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

In seawater-based electrolyte, these reactions are further complicated by the presence of various dissolved salts and impurities, which can affect the reaction pathways, energy consumption (overpotential), and efficiency. For example, the presence of Cl^- will introduce an additional competing chlorine evolution reaction (CER) at the anode. Under acidic conditions, two Cl^- can combine to form Cl_2:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Under alkaline conditions, Cl^- will react with OH^- to form ClO^-:

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

Dionigi et al. summarized the Pourbaix diagram (Figure 1a) that shows the potential-pH relationship of OER and CER in artificial seawater with a mass of chlorine species fixed at 0.5 M.[14,42] It was observed that the CER is thermodynamically less favorable than the OER. The theoretical potential difference between these two reactions increases with rising pH until the onset of hypochlorite formation, at which point it stabilizes at its maximum value of approximately 480 mV. In most seawater hydrogen production cases, CER is typically an undesirable side reaction as it leads to corrosive environments and unwanted byproducts. However, for producing chlorine-containing chemicals such as Cl_2 or ClO^-, highly efficient CER is required. Therefore, it is crucial to control the reaction conditions and design specialized OER/CER catalysts for different products. In addition, the highly corrosive environment induced by the abundant halide ions in seawater presents a notable challenge to catalyst stability. Addressing this critical issue requires the rational design of stable catalysts to maintain long-term operational durability, thereby ensuring their feasibility for practical applications in seawater electrochemical reactions. Compared to freshwater electrolysis, seawater electrolysis faces higher overpotential, which is defined as the additional energy required to drive the electrochemical reactions beyond the thermodynamic potential. Overpotential arises in seawater-based electrolysis due to factors such as reaction kinetics, mass transport limitations, and electrode surface properties. This calls for rational design of efficient catalyst with abundant active sites and high corrosion resistance. Besides, the dissolved alkali metal cations (Mg^{2+} and Ca^{2+}) in seawater play another crucial role in the electrochemical reaction process, as they influence the availability of OH^- ions during the electrochemical reaction and the possibility of salt precipitation or scaling on the catalyst. Compounds of these alkali metals, such as $Mg(OH)_2$ and $Ca(OH)_2$, have relatively low solubility in seawater and tend to precipitate under alkaline conditions. In the case of seawater hydrogen production, these precipitates lead to challenges such as electrode scaling and overall efficiency decline. Conversely, if the goal is to extract these alkali metals, it is necessary to design effective catalyst and system to create a localized alkaline environment to facilitate the precipitation and collection of these cations. In general, to unlock the full potential of seawater as a resource for fuel and chemical production, it is essential to go beyond traditional seawater electrolysis reaction. Utilizing intermediates such as H^+, OH^-,

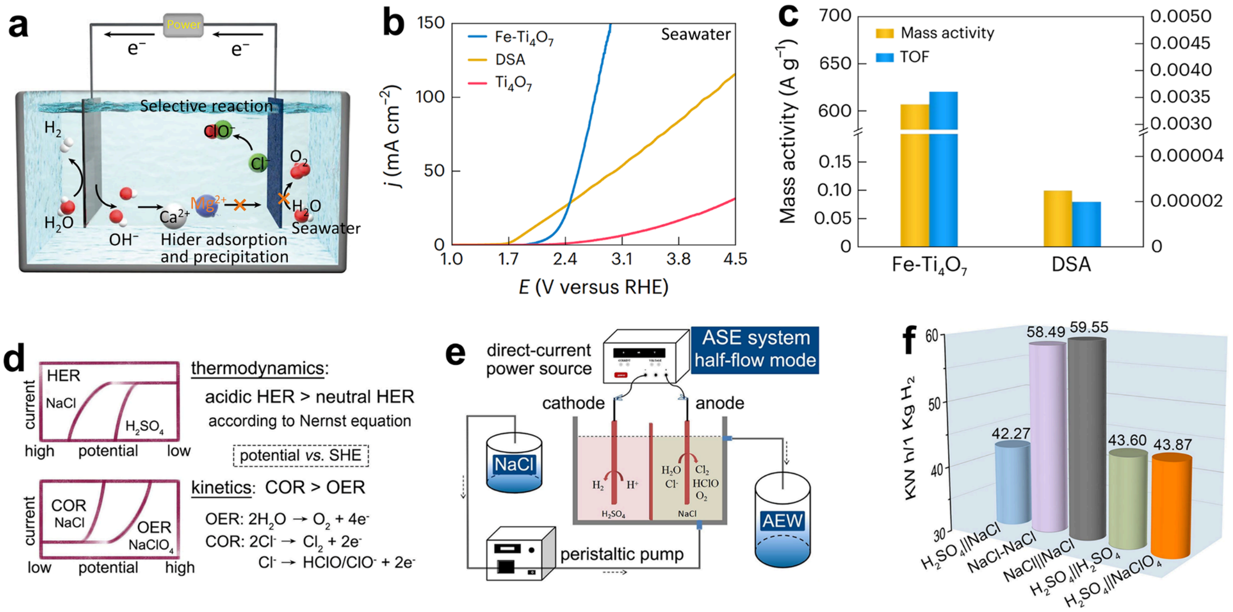


Figure 2. (a) Schematic illustration of seawater electrolysis to produce active chlorine mediated by the Fe−Ti_4O_7 anode. (b) Linear sweep voltammetry (LSV) polarization curves of Ti_4O_7 and Fe−Ti_4O_7 anodes in unbuffered seawater for CER. (c) Mass activity and turnover frequency of the Fe−Ti_4O_7 anode and commercial DSA. Reprinted with permission from ref 48. Copyright 2024 Springer Nature. (d) Two main theoretical basis of acid-saline hybrid electrolysis system design. (e) Schematic model of the hybrid system to generate H_2 and active chlorine in real time. (f) Required quantities of electricity to obtain 1.0 kg H_2 of different electrolysis systems. Reprinted with permission from ref 49. Copyright 2024 John Wiley and Sons.

or Cl^- in seawater to react with dissolved salts can open new pathways for resource recovery and electrochemical synthesis.

3. SEAWATER AS A FEEDSTOCK FOR FUEL AND CHEMICAL PRODUCTION

As mentioned above, the composition of seawater is far more complex than that of freshwater. When research focuses solely on seawater hydrogen production, these components can give rise to many competing side reactions during the electrochemical process. Challenges include, but are not limited to, chloride-induced corrosion at the anode and alkaline metal precipitate formation at the cathode, both of which impede the efficient and stable production of hydrogen from seawater and should be addressed. On the other hand, by shifting the focus from exclusively hydrogen production to exploring a broader range of electrocatalytic reactions using seawater-contained electrolyte, new research opportunities can emerge. For example, chloride anions, sodium cations, and alkali metal cations in natural seawater can be harnessed to generate compounds containing elements such as chlorine, sodium, and magnesium through a series of tailored electrochemical reactions, as illustrated in Figure 1b. Such approaches offer an alternative and meaningful direction, with the potential to contribute to the sustainable development of seawater electrochemistry.

3.1. Chloride Ion Related Reactions. Active chlorine or hypochlorite (ClO^-) is a highly effective disinfectant, which is widely used in wastewater and ballast water treatment.[43] Traditionally, it is produced through the electrolysis of saturated sodium chloride (NaCl, 5−6 mol L^{-1}) solutions in the chlor-alkali process, an industrial electrochemical reaction that plays a crucial role in chemical manufacturing.[43−45] This process provides essential reagents for various industries, including water treatment, organic chemistry, pharmaceuticals, and soaps.[43] During the electrochemical reaction, Cl^- ions are oxidized at the anode to form Cl_2 gas, while saline is reduced at the cathode to produce H_2 gas and OH^- ions, which subsequently react to form sodium hydroxide. The overall reaction of the chlor-alkali process can be illustrated as follows: $2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$.[46] Recent research has explored the selective electrosynthesis of chlorine disinfectants using natural seawater as a chlorine source, expanding the potential of seawater in chlor-alkali process for green chemistry applications.[47] However, using seawater as an electrolyte for ClO^- production presents some challenges, including competition from the OER and the gradual passivation of the anode. Zhao et al. proposed a sustainable method for synthesizing ClO^- from natural seawater using a non-noble-metal based Fe-doped Ti_4O_7 anode (Figure 2a).[48] This catalyst demonstrates high activity, turnover frequency, and mass activity (Figure 2b,c), which are comparable to commercial dimensionally stable anode (DSA) while effectively preventing anode passivation. Corresponding electrochemical performance analysis and CER mechanism studies suggest that Fe doping can enhance the electrophilicity of the oxygen lattice. This enables site-selective chloride activation at lower overpotentials than the OER, thereby promoting chlorine evolution selectivity. X-ray photoelectron spectroscopy analysis shows that Fe doping inhibits the dynamic adsorption of Ca^{2+}/Mg^{2+}cations on the Ti_4O_7 surface due to its high zeta potential. This prevents active sites deactivation and ensures catalyst longevity at a current density of 10 mA cm^{-2} for over 10 days. Furthermore, it was observed that the Fe−Ti_4O_7 anode effectively suppressed the conversion of Cl^- into chlorate (ClO^{3-}) and prevented the formation of hazardous perchlorate (ClO^{4-}). They further designed an integrated membraneless seawater active chlorine production device powered by a commercial Si photovoltaic cell. This device achieved a production rate of 3.15 mg min^{-1} of ClO^- with an 85% Faradaic efficiency, while simultaneously producing H_2 gas as a

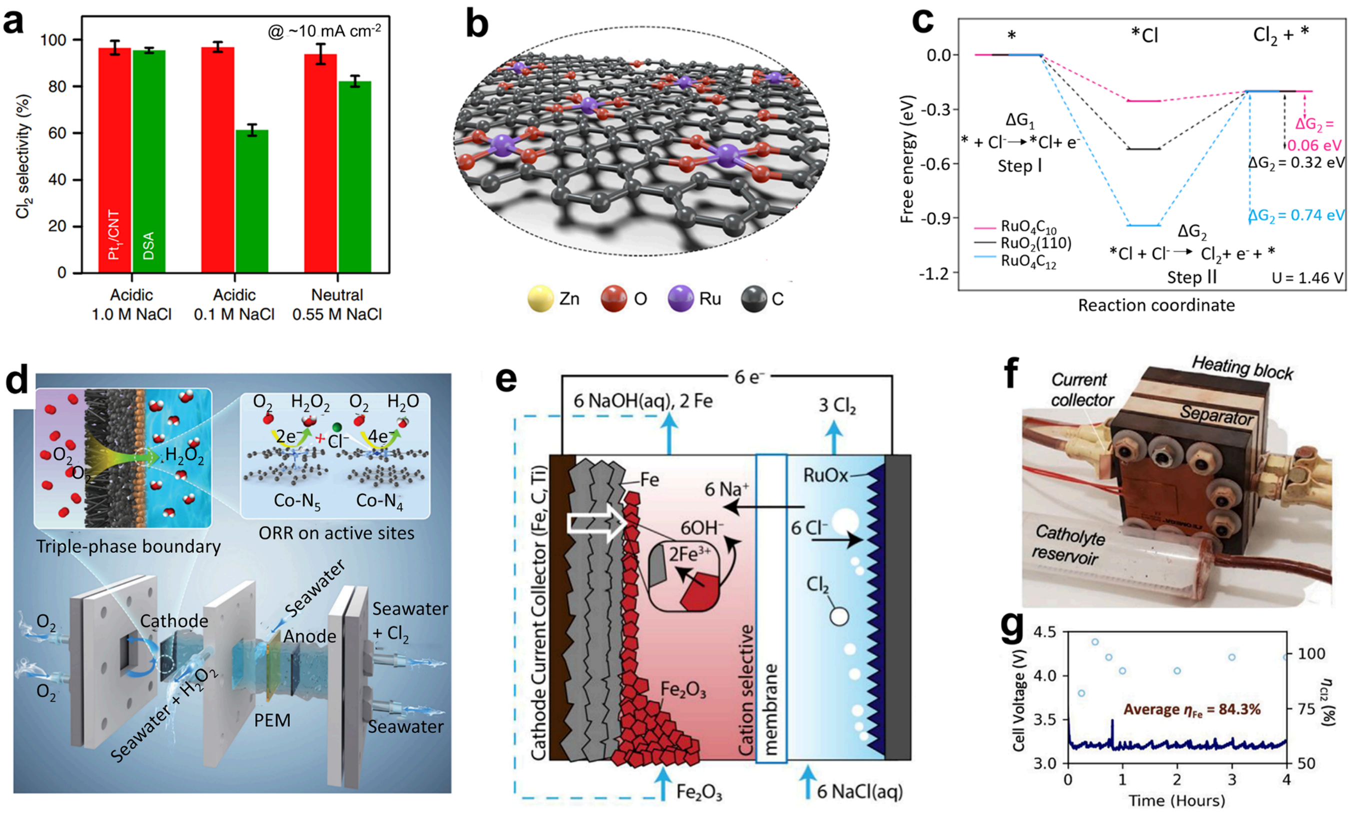


Figure 3. (a) CER selectivity of Pt_1/CNT and DSA catalysts measured by iodometric titration under different electrolyte conditions. Reprinted with permission under a Creative Commons CC BY License from ref 59. Copyright 2020 The Authors. (b) Schematic illustration of the single-atom Ru−O_4 catalyst. Yellow, black, red, and purple spheres represent Zn, C, O, and Ru atoms, respectively. (c) Gibbs free-energy diagram for CER over RuO_4C_{10}, RuO_2(110), and RuO_4C_{12}. Reprinted with permission under a Creative Commons CC BY License from ref 47. Copyright 2023 The Authors. (d) Schematic illustration of the flow cell to produce H_2O_2 and Cl_2 on the triple-phase boundary of the gas diffusion electrode. Reprinted with permission from ref 62. Copyright 2021 Royal Society of Chemistry. (e) Scheme of the chlor-iron process: Fe is reduced from Fe_2O_3 at the cathode, while NaCl is oxidized to Cl_2 at the anode, producing NaOH within the cathode compartment. (f) Flow cell used for the chlor-iron process. (g) Steady-state polarization behavior of the chlor-iron cell. Reprinted with permission from ref 64. Copyright 2024 Elsevier.

byproduct at the cathode, offering a sustainable alternative for portable ClO^- production. Notably, the generated ClO^- demonstrated rapid and complete disinfection of key pathogenic bacteria in ballast water within 5 min, including *Escherichia coli*, *Staphylococcus aureus*, and *Vibrio alginolyticus*, highlighting its potential for water treatment applications on board ships. In a similar approach, nitrogen-doped BiOCl atomic layers were investigated by their group for photocatalytic conversion of carbon-sequestered seawater into carbon monoxide (CO) and ClO^-.[33] The sequestered CO_2 helps maintain the pH of seawater electrolyte at ∼4.2, effectively preventing the precipitation of alkali cations and ensuring outstanding catalytic durability. Later, Zhu et al. proposed that although the overpotential of the chloride oxidation reaction (COR) can be reduced through rational catalyst design, the overall reduction in cell voltage for seawater hydrogen production remains limited.[49] This limitation arises primarily from the relatively high overpotential of the saline HER caused by the extra water dissociation process, the intrinsically high thermodynamic potential, and the low conductivity of seawater. Drawing from two key principles that the thermodynamic potential energy of acidic HER is lower than that of brine HER, and that the kinetic rate of brine COR is faster than that of brine OER (Figure 2d), they introduced an acid-saline hybrid electrolysis system for energy-efficient coelectrosynthesis of ClO^- and H_2 gas. The system utilizes a bifunctional TiRu/Ti electrode with a 0.5 M H_2SO_4 catholyte and a 1 M NaCl anolyte, separated by a bipolar membrane (Figure 2e). Such hybrid design notably reduces energy consumption, requiring only 42.27 kW·h to produce 1 kg H_2, representing a 27.7% reduction in energy consumption compared to direct saline electrolysis (Figure 2f). When measured at a constant current of 10 mA cm^{-2}, this hybrid system exhibits stable operation for 25 h, demonstrating its good stability. The acidified seawater anolyte in this system avoids the formation of Ca/Mg-based precipitates during seawater electrolysis, promoting sustainable H_2 production. Additionally, it enhances the production of hypochlorous acid (HClO), which possesses higher oxidation activity than ClO^-. This electrolyzer enables real-time generation of HClO for rapid pathogen disinfection (e.g., *Escherichia coli* and *Staphylococcus aureus*) and promoting agricultural production (e.g., pea sprouts) when operated in half-flow mode. Considering that the membrane in an electrolyzer could significantly increase costs, Li et al. proposed membrane-less electrolysis of unperturbed and unbuffered natural seawater for H_2 production.[50] Using an optimized $Pt_{0.06}Ru_{0.24}Ti_{0.7}O_x$ anode and MnO_x cathode, they achieved nearly 100% Faradaic efficiency for the COR and HER, effectively producing ClO^- and H_2 gas over 100 h. The $Pt_{0.06}Ru_{0.24}Ti_{0.7}O_x$ catalyst exhibits superior activity for the selective ClO^- production in saline electrolyte at 800 mA cm^{-2} over 500 h, completely inhibiting the OER.

In addition to active chlorine, chlorine (Cl_2) gas is another valuable chemical that may be produced through seawater electrolysis. It serves as a raw material for various industrial applications, including the production of polymers, disinfectants and pharmaceuticals, with global production exceeding 88 million tons annually.[43,51−53] Industrially, Cl_2 gas is typically produced by chlor-alkali process, utilizing DSA made of RuO_2 and TiO_2 coated on a Ti substrate for CER. In this process, RuO_2 acts as the active catalytic component.[53,54] Despite the maturity of the chlor-alkali process, it relies heavily on saturated NaCl electrolytes, which require additional energy input for thermal desalination. Seawater, being abundant and readily available, has the potential to replace concentrated NaCl solutions for Cl_2 gas production. However, two critical challenges impede this approach: the relatively lower stability of traditional DSA in seawater and reduced Cl_2 yield due to the low Cl^- concentration in natural seawater.[55] To address these issues, Chen's group reported a ternary $RuO_2-Sb_2O_5-SnO_2/Ti$ electrode (Sb:Ru:Sn = 10:30:60) featuring a microporous structure for CER in seawater. In this electrode, SnO_2 serves as a dispersing agent, Sb_2O_5 as a dopant, and RuO_2 as a catalyst.[56,57] This ternary electrode exhibits current efficiencies ranging from 86.3% to 90.4% at a current density of 25 mA cm^{-2} at room temperature in seawater, with a service life of ∼266 h at 1 A cm^{-2} at 35 °C in 0.5 M NaCl solution. Later, they reported a dimensionally stable $RuO_2-IrO_2-Sb_2O_5-SnO_2/Ti$ electrode using a similar synthesis method for CER.[55] This quaternary catalyst exhibits a much longer service life of 658 h at a current density of 2 A cm^{-2} under accelerated life test conditions, and is projected to last over 6 years at a current density of 150 mA cm^{-2} at room temperature in seawater. Atomically dispersed or single-atom catalysts possess unique physicochemical properties, such as high atom utilization efficiency, low-coordination environments of metal centers and distinct structures, making them potential catalyst for CER.[58] In 2020, Lim et al. introduced a catalyst comprising atomically dispersed $Pt-N_4$ sites on carbon nanotube (Pt_1/CNT), which exhibited remarkable activity and selectivity for CER. It shows outstanding catalytic activity with nearly ∼100% CER selectivity in acidic media, even at low Cl^- concentrations, surpassing the performance of commercial DSA (Figure 3a).[59] In situ electrochemical X-ray absorption spectroscopy and density functional theory calculations reveal the atomically dispersed PtN_4C_{12} as the active site. Later, Liu et al. synthesized a two-dimensional carbon-supported single-atom catalyst with a $Ru-O_4$ moiety for CER using a seawater-like electrolyte.[47] They in situ anchored single Ru atoms onto the surface of the oxygen group-enriched metal−organic framework nanosheet derivatives through a thermal reduction approach (Figure 3b). Operando spectroscopy characterizations and density functional theory calculations reveal that the single atom $Ru-O_4$ moiety facilitates the formation of Cl*-Ru intermediates through direct chloride adsorption (Figure 3c), thereby enhancing both the activity and selectivity of the catalyst. Consequently, this single-atom catalyst exhibits a low overpotential of 30 mV at a current density of 10 mA cm^{-2} with 99% selectivity in 1 M NaCl acidic solution (pH = 1), outperforming commercial DSA (85 mV overpotential and 95.5% selectivity). They also assembled a flow cell equipped with the $Ru-O_4$ catalyst, which exhibits low overpotential and excellent stability over 1000 h at a current density of 1000 mA cm^{-2}, maintaining Cl_2 selectivity over 98% in simulated seawater media. It should be noted that, although the use of simulated seawater as a feedstock for Cl_2 gas production has been extensively explored, the electrodes may suffer reduced activity and poor stability in natural seawater due to the presence of impurities.[52]

Exploring efficient, stable, and selective catalysts, along with alternative electrolysis system designs, could open new opportunities for the combined production of Cl_2 gas and other valuable chemicals in seawater-based systems. For instance, hydrogen peroxide (H_2O_2) is a widely used chemical and is predominantly produced through the anthraquinone oxidation process (AOP), which requires complex centralized infrastructure and hydrogen as a feedstock.[60,61] Zhao et al. addressed this challenge by developing a flow cell system using single-atom cobalt catalysts for H_2O_2 production through the two-electron oxygen reduction reaction (ORR) pathway at the cathode (cathodic reaction: $O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$).[62] Utilizing commercial RuO_2 as the anodic catalyst, Cl_2 gas is simultaneously generated as a byproduct in simulated seawater (anodic reaction: $2Cl^- - 2e^- \rightarrow Cl_2$) (Figure 3d). This system enables small-scale and on-site synthesis of H_2O_2 and Cl_2, leveraging the simplicity of saline electrolyte preparation and the portability of the flow cell setup. Cl_2 gas production can also be integrated with iron (Fe) production, offering an alternative approach to reduce emissions from the iron and steel industry, which contributes ∼6% of global greenhouse gas emissions due to the large amount of CO_2 (∼1.5 kg of CO_2 per kg of Fe) released during conventional ironmaking processes using blast furnaces.[63] Noble et al. proposed a low-temperature electrochemical electrolyzer that utilizes low-cost Fe_2O_3 and concentrated purified seawater to coproduce high-purity Fe, sodium hydroxide (NaOH), and Cl_2 gas with zero greenhouse gas emissions.[64] The schematic diagram of the electrolyzer reaction is presented in Figure 3e. In this system, a cation-selective membrane separates the anolyte (5.7 mol kg^{-1} NaCl adjusted to pH = 2 using HCl) from the catholyte (25 wt % α-Fe_2O_3 mixed with 7.5 mol kg^{-1} NaOH). This configuration maintains a steady-state pH gradient while permitting Na^+ ions to carry the ionic current between the two compartments. A thin RuO_x film coated on a Ti current collector serves as the anode for the CER while a polished Cu foil serves as the cathode for Fe reduction. They further constructed a flow electrolyzer (Figure 3f) to effectively maintain a constant electrolyte volume and concentration for long-term chlor-iron processes. This electrolyzer can maintain a cell voltage at ∼3.2 V for 4 h at a constant current density of 100 mA cm^{-2}, achieving an average Faradaic efficiency of 84% for Fe production and over 95% for Cl_2 gas production (Figure 3g). The produced Fe can be easily detached from the catalyst surface as freestanding films, while Cl_2 gas can be collected at industrially relevant rates and selectivity. These Fe films consist of compact, dense Fe metal particles with diameters ranging from 10 to 50 μm and a purity exceeding 95 wt %. Additionally, the coproduced low-purity NaOH at the cathode can be used for CO_2 capture from the air or ocean, contributing to a "net-negative-emission" process. It is important to note that Cl_2 is highly reactive and toxic gas. In Cl_2 gas production studies, strict safety measures must be taken and the generated Cl_2 gas should be carefully handled and neutralized to prevent hazardous accumulation.

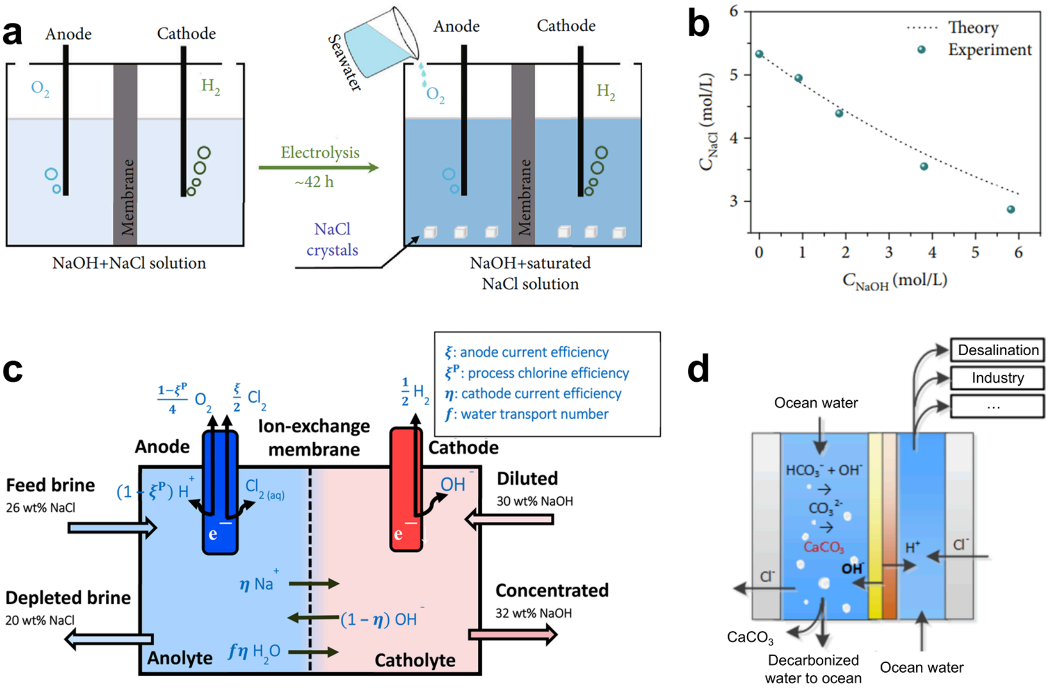


Figure 4. (a) The common-ion effect is introduced into seawater electrolysis to improve the electrochemical performance and produce triple product (H_2, O_2, and NaCl crystals). (b) The concentration changes of NaCl during the seawater electrolysis with different initial concentrations of NaOH. Calculation conditions: the electrode area is about 0.2 m^2; the volume of electrolyte is 3 L; the current density is 500 mA cm^{-2}. Reprinted with permission under a Creative Commons CC BY License from ref 66. Copyright 2020 The Authors. (c) Schematic diagram of a typical cell for the chlor-alkali process, containing an ion-exchange membrane as well as anode and cathode for the reaction. Reprinted with permission from ref 45. Copyright 2018 American Chemical Society. (d) CO_2 mineralization using alkalinization route. Reprinted with permission from ref 67. Copyright 2022 Elsevier.

In organic synthesis area, Yao et al., reported an electro-oxidation strategy of ethynylbenzenes to α,α-dichloroketones by directly utilizing seawater as the Cl source and electrolyte solution.[65] To accelerate the electrosynthesis process, they designed high-curvature $NiCo_2O_4$ nanocones to inhibit competitive OER and CER while facilitating the localized concentration of Cl^- and OH^- ions. They revealed that Cl^- ions are initially electrooxidized to $Cl^\bullet$ radicals, which attack the α- carbon of alkynes to form vinyl radicals for the following transformation. As a result, their approach achieved an α,α-dichloroketone yield 81%, a Faradaic efficiency of 61%, and a production rate of 44.2 mmol $g_{cat.}^{-1}$ h^{-1}.

3.2. Sodium Cation Related Reactions. In addition to Cl^--related ClO and Cl_2 gas production, the abundant Na^+ in seawater offers opportunities for generating NaCl crystals or NaOH, thus increasing the economic viability of seawater electrolysis. For example, Li et al. utilized the "common-ion effect" in the seawater electrolysis process to facilitate the triple production of H_2, O_2, and crystalline NaCl (Figure 4a).[66] The basic principle behind this approach is that the product of the maximum concentrations of positive cations and negative ions in a solution remains constant. An increase in the concentration of one ion reduces the solubility of its counterion. By adding 6 M NaOH (containing Na^+) into treated Ca/Mg-free seawater electrolyte, they effectively reduced the solubility of NaCl (containing Cl^-) (Figure 4b). The reduced Cl^- concentration could effectively mitigate anode corrosion, while the excess OH^-thermodynamically favors OER and simultaneously suppresses COR. Utilizing a bifunctional NiCoFeP catalyst as both anode and cathode, this system demonstrates stable operation at a large current density of 500 mA cm^{-2} for over 100 h. The inclusion of a Nafion membrane significantly enhances the NaCl crystal production rate in the catholyte, increasing it by six times to 220 mg h^{-1}. This enhancement is attributed to the Nafion membrane's ability to facilitate the transfer of Na^+ cations from the anode to the cathode during electrolysis, resulting in higher Na^+ concentration on the cathode side, and thus speeding up crystallization of NaCl due to the common-ion effect. Na^+ cations in natural seawater can also be used to produce NaOH, commonly known as caustic or caustic soda. Du et al. illustrated a model approach for producing NaOH, H_2, and Cl_2 gas (overall reaction: $2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$) from seawater desalination brine using membrane chlor-alkali electrolysis.[45] Initially, seawater reverse osmosis brine undergoes purification through nanofiltration to remove sulfate ions and hardness cations. The resulting permeate is then concentrated by electrodialysis, followed by evaporation or mechanical vapor compression until NaCl saturation is achieved. Finally, this pure and concentrated brine is acidified and fed into the membrane electrolyzer, as depicted in Figure 4c. At the anode, Cl^- anions are oxidized to produce Cl_2 gas, alongside a side reaction of water oxidation. Simultaneously, at the cathode, water is reduced to generate H_2 gas and OH^-, which then react with Na^+ to form NaOH.

3.3. Calcium Cation Related Reactions. To mitigate the damaging impact of CO_2 on the climate, significant advancements have been made in carbon capture and conversion technologies. Among these, oceanic CO_2 capture is particularly advantageous, leveraging the vast atmosphere-ocean interface and eliminating the need for chemical absorbents. On the other hand, calcium carbonate ($CaCO_3$), an important

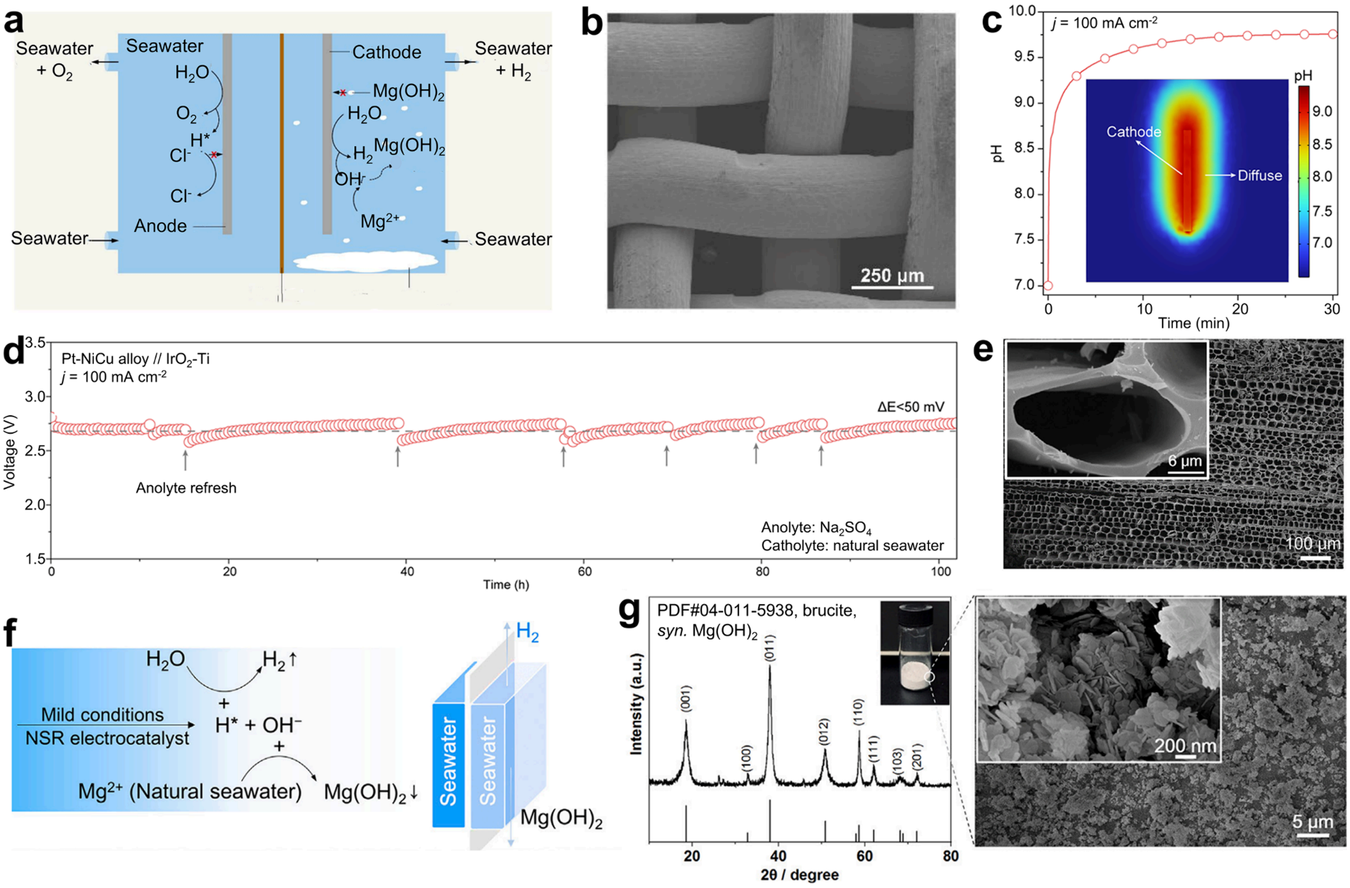


Figure 5. (a) Schematic of simultaneous production of $Mg(OH)_2$ and H_2 via seawater electrolysis. (b) SEM image Pt-NiCu-alloy catalyst. (c) COMSOL model for the pH distribution near the electrode under 100 mA cm^{-2} (regional area: 40 mm × 40 mm). (d) Stability tests of the natural seawater electrolyzer under 100 mA cm^{-2} at room temperature. Reprinted with permission from ref 71. Copyright 2024 American Chemical Society. (e) SEM images with different magnifications showing the top surface of the Pt/carbon electrode with nice porosity. (f) Schematic diagram of an electrolysis system for cosynthesizing $Mg(OH)_2$ and H_2 based on electricity consumption only. (g) XRD pattern and SEM images of the collected precipitates. Reprinted with permission from ref 69. Copyright 2024 Elsevier.

chemical used in industries such as paper, plastics and construction, presents an opportunity for combining marine resources to achieve $CaCO_3$ production and CO_2 capture/conversion. This approach represents killing two birds with one stone. Sharifian et al. explored an *in situ* bipolar membrane electrodialysis (BPMED) method for capturing dissolved inorganic carbon from seawater as solid carbonate minerals through a "alkalinization-route".[67] As shown in Figure 4d, dissolved CO_2 first combines with OH^- to form HCO_3^-, which is further converted into CO_3^{2-} with additional OH^-. Finally, CO_3^{2-} combines with Ca^{2+} cations in natural seawater to precipitate as solid $CaCO_3$. Within an optimal alkaline pH-window, this system captures 60% CO_2 from real seawater and up to 85% CO_2 from synthetic seawater. The $CaCO_3$ production increases linearly with the applied current density, achieving a theoretical maximum extraction efficiency of 97%. Through tuning the current density and flow rate, an energy consumption of 318 ± 29 kJ mol^{-1} $CaCO_3$ is obtained for CO_2 capture from real seawater in a cell containing ten bipolar-cation exchange membrane cell pairs, suggesting the potential for industrial-scale oceanic carbon capture through mineralization.

3.4. Magnesium Cation Related Reactions.

Magnesium hydroxide [$Mg(OH)_2$] is a stable, nontoxic, and noncorrosive chemical with broad industrial applications, including use as an antibacterial agent, fire retardant, neutralizer for acidic waste, antacid in pharmaceuticals, and food additive.[68,69] With Mg^{2+} being the second most abundant cation in seawater (~0.77 g L^{-1}), seawater presents a promising resource for $Mg(OH)_2$ production.[35] However, traditional extraction methods require the addition of expensive alkalis and result in $Mg(OH)_2$ precipitates with varying particle sizes and $Ca(OH)_2$ impurities. Thus, developing cost-effective methods to sustainably recover high-purity Mg/$Mg(OH)_2$ resources from seawater is essential, and seawater electrolysis could be a transformative technology for this purpose.

In 2018, Sano et al. developed a continuous system for recovering Mg through seawater electrolysis.[70] The setup consists of a filter press electrodialysis stack with a 5% sodium sulfate (Na_2SO_4) solution at the anode to prevent Cl_2 gas formation, and deep-ocean water at the cathode as the magnesium source. A cation exchange membrane in the middle retains OH^- ions at the cathode while facilitating the passage of cations. It was found that the $Mg(OH)_2$ formation is related to the amount of electricity input, as increased electricity produced more OH^-, leading to complete precipitation of Mg. Later, Yi et al. proposed a neutral seawater electrolysis model for producing high-purity $Mg(OH)_2$ and H_2 gas.[71] The process shown in Figure 5a involves continuous HER at the cathode, where residual OH^- near the

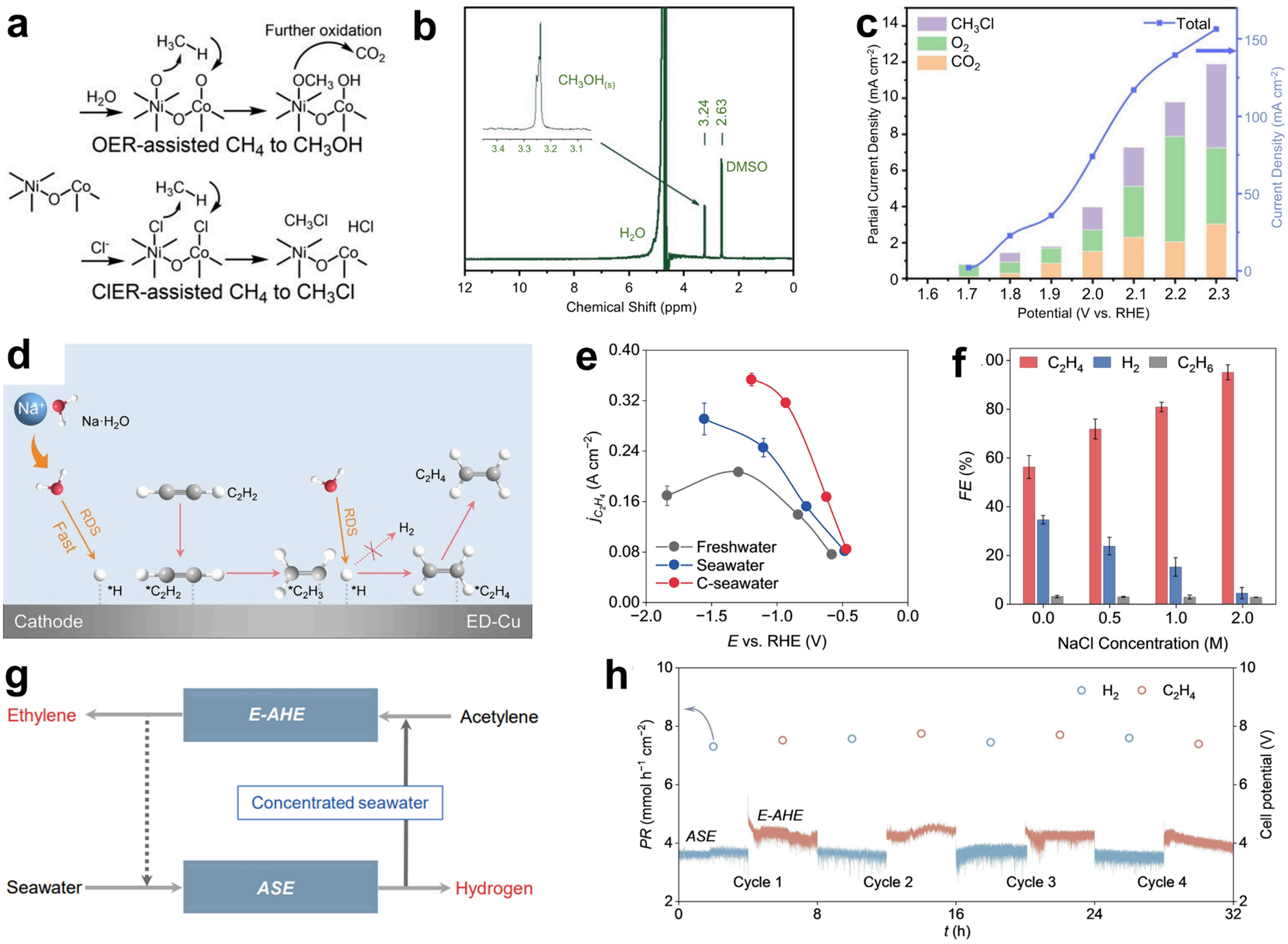


Figure 6. (a) Proposed mechanism of CH_4 oxidation promoted by CER (upper panel) and OER (lower panel). (b) ^1H NMR data of the electrochemical reaction products, using a gas collection solution with 1 M KOH and 1% N_2H_4, where KOH enhances the hydrolysis of CH_3Cl into CH_3OH, and N_2H_4 prevents CH_3OH from being oxidized by Cl_2. (c) Total and partial current densities of products from CH_4 oxidation tested in seawater. Reprinted with permission from ref 73. Copyright 2021 John Wiley and Sons. (d) Schematic mechanism of electrocatalytic acetylene hydrogenation to ethylene. (e) Analysis of partial current density and potential of electrocatalytic acetylene hydrogenation to ethylene in different electrolytes. (f) Electrocatalytic acetylene hydrogenation to ethylene performance at 0.4 A cm^{-2} in different electrolytes. (g) Schematic of alkaline seawater electrolysis and electrocatalytic acetylene hydrogenation to ethylene for hydrogen and ethylene production fed on seawater and acetylene. (h) Practical-long stability test of this system for hydrogen and ethylene production at 0.4 A cm^{-2}. Reprinted with permission under a Creative Commons CC BY License from ref 77. Copyright 2024 The Authors.

electrode reacts with Mg^{2+} in seawater to form solid $Mg(OH)_2$. To prevent electrode deactivation caused by $Mg(OH)_2$ adhesion, they designed a highly disordered NiCu alloy substrate coated with active Pt (Pt-NiCu, Figure 5b). The solidophobic surface property of this electrode promotes $Mg(OH)_2$ formation in the electrolyte rather than on the electrode surface. When measured at a current density of 100 mA cm^{-2} in saline solutions with high concentrations of Mg^{2+} and Ca^{2+}, both the NiCu alloy and Pt-NiCu alloy electrodes exhibit exceptional stability (>1000 h) with negligible voltage increase (<100 mV). The highly disordered Cu distribution within the Ni matrix was found to generate high surface energy, which subsequently introduces a dense layer of adsorbed water. Ab initio molecular dynamics (AIMD) simulations show that Mg^{2+} cations gradually coordinate with water molecules and face large resistance when trying to cross this hydration layer, which reduces $Mg(OH)_2$ nucleation on the electrodes surface. Additionally, this hydration layer effectively prevents direct contact between the electrode and $Mg(OH)_2$, thus avoiding scaling. A COMSOL Multiphysics model was used to map the pH distribution near the catalyst surface (Figure 5c). The results reveal that the surface pH rapidly increased to ∼9.3 and stabilized below 10.0 within three min at 100 mA cm^{-2}. Such a pH value meets the precipitation requirement for Mg^{2+} (∼9.3) but falls short the threshold for Ca^{2+} precipitation (∼12.0). In practical testing, a membrane seawater electrolyzer equipped with a Pt-NiCu alloy cathode and an IrO_2−Ti anode was employed with treated natural seawater and 0.5 M Na_2SO_4 as the catholyte and anolyte, respectively. Figure 5d demonstrates that this electrolyzer can operate at a cell voltage of ∼2.7 V under 100 mA cm^{-2} for over 100 h. After electrolyzing 20 L of filtered seawater, 19.07 g of $Mg(OH)_2$ with over 99.0% purity and particle size of ∼20 μm was produced, along with H_2 gas production. The extraction efficiency of Mg^{2+} reaches 44.6%, which could be improved with higher Mg^{2+} concentrations in the catholyte such as concentrated seawater or salt lake water.

In addition to achieving high purity, the morphology of $Mg(OH)_2$ can also be controlled during seawater electrolysis. Liang et al. proposed a scheme to cosynthesize H_2 gas and $Mg(OH)_2$ nanoflakes by electroreduction of natural seawater using a self-cleaning Pt/carbon electrode.[69] The electrode is fabricated by impregnating treated wood blocks in a K_2PtCl_6 solution, followed by high-temperature annealing under Argon gas. It has uniform and abundant open pores with a pore size of ∼25 μm (Figure 5e), which facilitate the release of gas bubbles and liquid flows, effectively preventing precipitate adhesion. In addition, they introduced an external water flow to in time disrupt the OH^- gradient and carry away the precipitates near the catalyst surface. By reducing natural seawater, localized alkalinity is generated around the electrode, enabling on-site synthesis of $Mg(OH)_2$ nanoflakes (Figure 5f). At a current of −200 mA, the $Mg(OH)_2$ formation rate reaches ∼0.345 g h^{-1} cm^{-2}, with a ∼ 100% Faradaic efficiency for H_2 gas production. Consistent with Sano et al.'s findings, they observed that higher currents result in a more sufficient OH^- supply, thereby increasing the yield rate of $Mg(OH)_2$ nanosheets. Compositional and structural characterizations show that the as-synthesized $Mg(OH)_2$ powder exhibits a uniform nanoflake structure at the micro level (Figure 5g), demonstrating its potential for commercial applications. Although seawater contains Ca^{2+} cations as well, the authors provided extensive evidence showing that their seawater electrolysis process is capable of synthesizing high-purity $Mg(OH)_2$. For example, the concentration of Mg^{2+} in natural seawater is more than three times that of Ca^{2+}; the formation of $CaCO_3$ precipitates requires bicarbonate ions, which are less than 4% of Mg^{2+} in seawater, and $Ca(OH)_2$ is more soluble in water than $Mg(OH)_2$. Experimental results also confirm that the resulting precipitates contain only trace amounts of Ca impurities. Their strategy for synthesizing $Mg(OH)_2$ nanosheets offers several advantages compared to traditional methods: (1) lower operating costs, (2) safer and scalable production due to mild operating conditions, (3) sustainability as it only requires natural seawater and electricity, (4) simpler large-scale separation as H_2 gas and solid $Mg(OH)_2$ naturally separate, and (5) reduced corrosion of electrolytic equipment. In light of these findings, they further proposed a continuous, stable and large-scale natural seawater electrolysis process for H_2 production, H_2 storage and Mg resource recovery. They also suggested that future research could focus on designing electrolytic cells capable of stably producing $Mg(OH)_2$ precipitates over longer periods and effectively discharging the resulting $Mg(OH)_2$ precipitates in membrane electrode assembly (MEA)-based electrolytic cells.

4. SEAWATER AS INTERMEDIATE TO SYNTHESIZE FUELS AND CHEMICALS

In addition to supplying Cl^-, Na^+, Ca^{2+}, and Mg^{2+} anions/cations as raw materials for producing valuable fuels and chemicals, seawater can also serve as an intermediate in various electrochemical processes. Compared to freshwater, natural seawater is enriched with halide ions, which may create a favorable environment for the oxidation of small molecules. The presence of halogen ions can enhance the activation of O−H and C−H bonds or facilitate the formation of halogen-mediated intermediates for small organic molecules.[13] Integrating seawater as an intermediate in fuel and chemical production processes not only optimizes reaction pathways, but also supports sustainable development by utilizing abundant and readily available resources.

4.1. Chlorine-Mediated Methane Oxidation. Methane (CH_4) is a notable byproduct of oil extraction, a significant fuel source in various applications, which is also a potent greenhouse gas with a warming potential far higher than that of CO_2.[72] Developing renewable energy-driven methods for CH_4 utilization is critical to decarbonizing the oil industry. However, the high bond dissociation energy and low polarity of CH_4 present considerable challenges for its activation under mild conditions. To overcome these obstacles, Wang et al. demonstrated a Cl-promoted strategy utilizing a $CoNi_2O_x$ catalyst for electrocatalytic CH_4 oxidation into valuable products such as methanol (CH_3OH).[73] This catalyst is capable of producing *Cl intermediates in saline electrolyte through the CER, facilitating the conversion process. Compared to OER-assisted CH_4 oxidation, which requires higher overpotentials to generate *O species to break the first C−H bond and often leads to overoxidation to unwanted CO_2, CER-assisted CH_4-to-CH_3Cl reaction followed by hydrolysis to CH_3OH offers unique advantages (Figure 6a). First, the lower overpotentials needed to generate *Cl in CER allow more effective activation of the first C−H bond in CH_4 toward the formation of CH_3Cl. Second, the rapid release of gaseous CH_3Cl prevents further conversion of the remaining C−H bonds, minimizing overoxidation of CH_4 to CO_2, ensuring selective product formation. As a result, at an applied potential of 2.3 V vs RHE, the $CoNi_2O_x$ catalyst achieves a CH_3Cl production rate of 364 mmol g^{-1} h^{-1} with a current density of 19.5 mA cm^{-2} in a saturated NaCl electrolyte. The produced CH_3Cl is then converted to CH_3OH through a hydrolysis process utilizing a solution containing 1 M KOH and 1% N_2H_4 (Figure 6b). The catalyst's performance was also tested under seawater salinity conditions to explore its potential application on offshore oil drilling platforms. The $CoNi_2O_x$ catalyst maintained a partial current density of 4.6 mA cm^{-2} at 2.3 V vs RHE for CH_3Cl production (Figure 6c). Furthermore, the selectivity of methane oxidation products was then measured and the $CoNi_2O_x$ catalyst presents a CH_3Cl/CO_2 ratio exceeding 7 in seawater electrolyte, which increased to over 400 in saturated NaCl electrolyte.

4.2. Sodium-Mediated Acetylene Hydrogenation. Ethylene (C_2H_4) is a versatile intermediate for many chemical reactions, such as oxidation, polymerization, and alkylation, positioning it as a crucial component in modern industrial chemistry.[74] Electrocatalytic acetylene (C_2H_2) hydrogenation to C_2H_4 utilizing water as a proton source presents a promising alternative to the traditional energy-intensive thermal-catalytic process. It has been reported that cations in the electrolyte can modify the interfacial water properties, which may promote the catalytic reaction process.[75,76] For instance, Qiao's group investigated this concept by employing concentrated seawater to promote C_2H_2 hydrogenation over a Cu catalyst.[77] They proposed that the in situ formation of $Na{\cdot}H_2O$ complexes facilitates the rate-determining step of H_2O dissociation to protons (*H) (Figure 6d). Under a pure C_2H_2 stream, the absorbed $*C_2H_2$ is hydrogenated by *H to form a $*C_2H_3$ intermediate. Further hydrogenation leads to the formation of absorbed $*C_2H_4$, which subsequently desorbs as C_2H_4. Therefore, the abundance of Na^+ cations in concentrated seawater electrolyte dynamically facilitates *H production, thereby improving both the efficiency and selectivity of C_2H_4 product. They also demonstrated that higher partial current

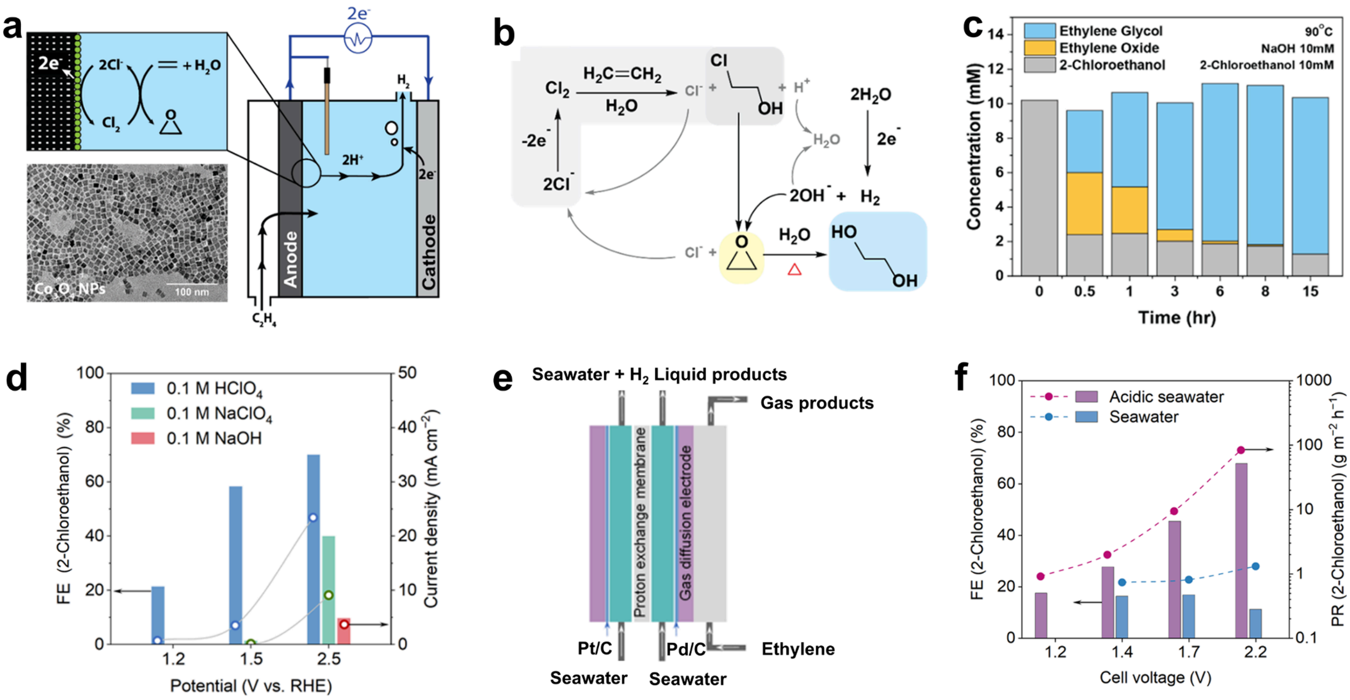


Figure 7. (a) Schematic of ethylene oxidation in an electrochemical cell and a transmission electron microscope image of cobalt oxide nanoparticles. (b) Proposed reaction network for chlorine-mediated ethylene oxidation. (c) Conversion of initial ethylene oxidation product into final products at 90 °C. The initial solution contained 10 mM NaOH, 10 mM 2-chloroethanol, and 590 mM NaCl. Reprinted with permission from ref 81. Copyright 2020 American Chemical Society. (d) Faradaic efficiency of 2-chloroethanol and total current density over Pd/C electrode in three different electrolytes. (e) Schematic illustration of a PEM electrolyzer. (f) Faradaic efficiency and corresponding production rate of 2-chloroethanol at different cell voltages in different electrolytes. Reprinted with permission from ref 82. Copyright 2023 American Chemical Society.

densities and lower potentials can be obtained as NaCl concentration increased. Remarkably, a Faradaic efficiency up to 95.1% is achieved in a 2.0 M NaCl electrolyte at a current density of 0.6 A cm^{-2} (Figure 6e,f). Building on these findings, they built an integrated system where H_2 is produced via alkaline seawater electrolysis, and the obtained concentrated seawater from the first electrolyzer is directly supplied for C_2H_2 hydrogenation to produce C_2H_4 in the second electrolyzer (Figure 6g). The system exhibited stable production rates of ~7.47 and ~7.58 mmol h^{-1} cm^{-2} for C_2H_4 and H_2, respectively, over four continuous cycles during a 32-h operation (Figure 6h).

4.3. Chlorine-Mediated Ethylene Oxidation. Ethylene oxide is a crucial intermediate widely used in the production of various organic chemicals, including ethylene glycol and acetaldehyde.[78] Currently, it is mainly produced through C_2H_4 oxidation using a silver catalyst at elevated temperatures and pressures, a process accompanied by significant emission of CO_2.[79] An electrochemical chlorohydrin process using chlorine as a redox mediator offers a more environmental-friendly alternative, with studies confirming its feasibility.[80] Chung et al. proposed the use of Co_3O_4 nanoparticles as the anode for C_2H_4 oxidation in a simulated seawater (saline) electrolyte (Figure 7a).[81] They found that 2-chloroethanol (C_2H_5ClO) is formed as an initial product when C_2H_4 gas is flowed into the electrolyte, which will then convert into ethylene oxide (C_2H_4O). It is hypothesized that Cl^- ions in the electrolyte are first oxidized to form active chlorine species, which act as a redox mediator to oxidize ethylene and are reduced back into Cl^- ions (Figure 7b). By heating the postelectrolysis solution at 90 °C for 15 h, over 80% of the C_2H_5ClO was transformed into ethylene glycol ($C_2H_6O_2$) (Figure 7c). During this process, C_2H_4O can first be formed as an intermediate, which subsequently hydrolyzes into $C_2H_6O_2$ after several hours. For the cathodic reaction, the studt reported ~100% Faradaic efficiency for H_2 evolution, demonstrating highly efficient H_2 production. They also used filtered seawater as electrolyte, achieving a 71 ± 2% Faradaic efficiency toward C_2H_4 oxidation products, primarily yielding C_2H_5ClO. This efficiency is nearly twice as high as that achieved in 0.6 M NaCl electrolyte (~41%). However, the conversion of C_2H_5ClO into $C_2H_6O_2$ is also more challenging in seawater than in the NaCl electrolyte. Additionally, they systematically studied the selectivity differences caused by the cations in natural seawater during Cl-mediated C_2H_4 oxidation, revealing that the Mg^{2+} cations are responsible for enhancing the selectivity toward C_2H_5ClO. Considering that C_2H_4 electrooxidation is primarily conducted in alkaline or neutral electrolytes, in which COR is somewhat suppressed to produce Cl-intermediates, thus the overall energy efficiency remains limited. Huang et al. proposed that since COR proceeds faster in acidic electrolytes, coupling C_2H_4 oxidation with HER in a PEM electrolyzer could significant lower the overall energy, as cathodic HER is more favorable under acidic conditions.[82] They investigated the oxidation of C_2H_4 to C_2H_5ClO in acidic simulated and natural seawater electrolytes using a commercial Pd catalyst. Their findings showed that both Faradaic efficiency and total current density significantly increased, surpassing those observed in alkaline/neutral electrolytes (Figure 7d). This enhancement is ascribed to more active Cl^- formation and faster generation of active chlorine in acidic environment. On the other hand, the high Cl^- concentration facilitates the

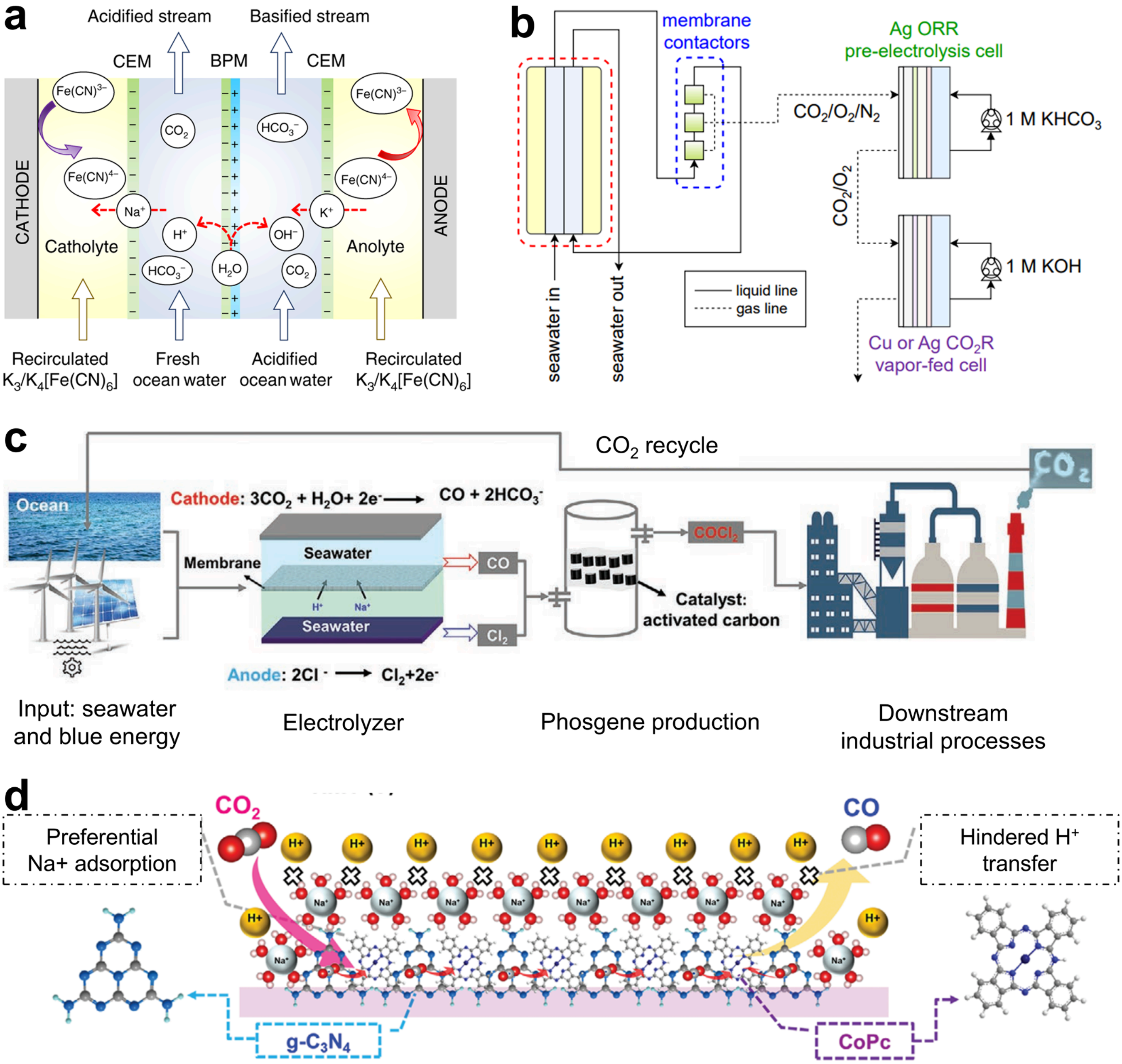


Figure 8. (a) Schematic illustration of the BPM electrodialysis cell. (b) Process flow of electrochemical conversion of CO_2 captured from ocean water. The CO_2 output from the BPMED cell was fed through tandem electrochemical cells. The first O_2 reduction reaction (ORR) pre-electrolysis cell was used to eliminate any O_2 residue from flowing into the CO_2 reduction (CO_2R) cell. Reprinted with permission under a Creative Commons CC BY License from ref 85. Copyright 2020 The Authors. (c) The blueprint of CO and Cl_2 coproduction in seawater for the industrial implementation with looping CO_2 utilization. (d) The schematic of preferential adsorption for Na^+ and hindered H^+ transfer on the electrode surface. Reprinted with permission from ref 89. Copyright 2021 John Wiley and Sons.

formation of adsorbed chlorine ions (*Cl) while suppressing *OH adsorption on the Pd surface. The reduced *OH coverage prevents the formation of double hydroxyl-containing byproducts like $C_2H_6O_2$, favoring C_2H_5ClO production (Figure 7e). They demonstrated a PEM electrolyzer that affords a ∼68% Faradaic efficiency of C_2H_5ClO at 2.2 V in acidic seawater electrolyte. With an implementing potential of 1.6 V, energy consumption of C_2H_5ClO is just $\sim 1.52 \times 10^{-3}$ kW·h g^{-1}. The production rate was ∼64 times greater, and the electrical energy consumption, was ∼6 times lower than that in neutral seawater, respectively (Figure 7f).

The above two works highlight the crucial role of seawater in C_2H_4 oxidation by providing chloride ions that facilitate the generation of active chlorine as a redox mediator. Despite these promising results, several scientific and technological challenges remain to be solved in utilizing seawater as intermediate for C_2H_4 oxidation. Future research should focus on developing efficient methods for separating high-purity liquid organic products from seawater electrolytes. Additionally, low-cost strategies should be developed to adjust the Cl^- ion concentration in seawater, as this may promote reaction efficiency and optimize production selectivity.

4.4. Seawater-Mediated Carbon Dioxide Conversion.

In addition to supplying Cl^- or Na^+ as intermediates for electrochemical reactions, seawater can also function as electrolyte in carbon-neutral processes.[83,84] Over the past 60 years, global CO_2 emissions have increased by ~170%, causing severe damage to the atmosphere and oceans. As the largest carbon sink, the ocean has absorbed ~40% of anthropogenic CO_2 since the industrial era, with a CO_2 concentration of 2.1 mmol kg^{-1} in seawater.[28,85] Integrating electrochemical CO_2 capture and utilization (dilute CO_2 → capture/conversion → products) using seawater as the electrolyte presents a clear advantage over traditional separate methods by eliminating the need for costly capture media recovery and subsequent CO_2 compression process. Digdaya et al. reported an integrated system consisting of a bipolar membrane electrodialysis (BPMED) cell and a vapor-fed CO_2 reduction reaction (CO_2RR) cell for the electrochemical capture and conversion of CO_2 from seawater.[85] As shown in Figure 8a, the bipolar membrane electrodialysis (BPMED) cell is designed to convert natural seawater into acidified and basified streams through electrochemical processes while simultaneously collecting CO_2. The system consists of two seawater compartments separated by a bipolar membrane and two reversible redox-couple compartments (Figure 8b), each separated from the seawater compartments by a cation exchange membrane, along with two electrodes. In the center of the BPMED cell, the bipolar membrane generates H^+ and OH^- fluxes via water dissociation reactions at its interface, acidifying and basifying the seawater streams. Potassium ferro/ferricyanide ($K_3/K_4[Fe(CN)_6)]$) catholyte and anolyte between the electrode and cation exchange membrane function as a reversible redox-couple solution, which is recirculated to reduce polarization losses associated with concentration overpotentials at the electrodes. The acidified seawater at the cathode is directed through a series of three membrane contactors, where dissolved CO_2 is removed using a vacuum pump. As a result, this system demonstrates the ability to capture CO_2 with an electrochemical energy consumption of 155.4 kJ mol^{-1} of CO_2 and a capture efficiency of 71%. The captured CO_2 vapor is then fed directly into a series of electrolyzers using Cu- or Ag-based catalysts for electrochemical reduction.

In addition to its function in CO_2 capture, seawater can further serve as an effective electrolyte for CO_2RR by providing e^- and H^+. For example, Nakata et al. demonstrated the CO_2RR utilizing CO_2 and seawater electrolyte on a boron-doped diamond electrode to produce formaldehyde (HCOH).[86] This approach not only addresses the challenge of low yields of higher-order products but also minimizes H_2 generation. Qu et al. reported that the N-doped Ti_3C_2 MXene nanosheets achieve a maximum CO Faradaic efficiency of 92% and a partial current density of −16.2 mA cm^{-2} for CO_2RR in seawater electrolyte.[87] Phosgene ($COCl_2$) is an important industrial intermediate and is traditionally produced from Cl_2 and CO over activated carbon at ~200 °C, with both Cl_2 and CO gases refined through energy-intensive processes.[88] Considering the high concentration of Cl^- ions and high carbon capacity, Tan et al. proposed a one-step cosynthesis of Cl_2 and CO gases through the electroreduction of CO_2 in seawater electrolyte (Figure 8c).[89] The overall reaction is based on CO_2RR and CER: $3CO_2 + 2NaCl + H_2O \rightarrow CO + Cl_2 + 2NaHCO_3$, with sodium bicarbonate ($NaHCO_3$) as a byproduct. To address the challenges posed by complex ions in seawater, they developed a CoPc molecule-implanted graphitic carbon nitride (CoPc/g-C_3N_4) catalyst for stable and selective CO_2RR. As shown in Figure 8d, the authors claims that this catalyst's unique morphology and enhanced capacitance allow Na^+ to be adsorbed and concentrate in the diffusion layer on the catalyst surface, thus inhibiting H^+ transfer and suppressing HER. They further revealed that the CER, with faster kinetics than the OER, becomes the dominant anodic reaction as the reaction proceeds, thereby facilitating the cathodic CO_2RR. In natural seawater, high ion conductivity achieves the highest current density at a potential of −1.4 V versus Ag/AgCl, the Faradaic efficiency of CO can be up to 89.5% with a partial current density of 16.0 mA cm^{-2}. Although the Cl_2 produced at the anode can react with water to form HCl when measured in a H-type cell, their system still offers an alternative approach for the electrocatalytic production of $COCl_2$ based on seawater electrolysis. Lee et al. demonstrated that calcium carbonate deposits on the catalyst and reduces active sites during seawater CO_2RR.[90] To address this, they proposed a self-powered hybrid CO_2 electrolysis system by coupling a Mg anode with a nanoporous Ag cathode. In a galvanic cell, the Mg alloy is spontaneously oxidized to Mg^{2+} at the anode while Ag^+ is reduced to Ag at the cathode meanwhile promoting the electrocatalytic reduction of CO_2 to CO.

5. PERSPECTIVE

In summary, this review first briefly outlined the properties of seawater and then discussed the principles and challenges associated with electrochemical reactions in seawater-contained electrolytes. We then reviewed the sustainable and efficient production of fuels and high-value chemicals via seawater electrochemical reaction. Compared with freshwater, the widespread use of seawater not only alleviates strain on water resources, but also provides new possibilities and broadens the prospects for green electrochemistry. Therefore, in-depth research on the application of seawater through electrochemical processes holds considerable scientific importance and potential industrial value. Although much progress has been made in this field, several scientific and technical challenges remain, requiring continued innovations. In the following sections, we discuss the key issues that need to be addressed or monitored to advance the utilization of seawater resources.

5.1. The Potential for Seawater Utilization Should Be Further Expanded through Innovative Electrochemical Reaction and System Design.

As previously stated, electrochemical reactions using seawater electrolytes are more complicated and challenging than those in fresh water electrolytes due to the presence of diverse anions and cations. Although considerable research work has been conducted on seawater hydrogen production, there is still a lot of room to explore its potential in other fuels and chemicals production reactions. For example, with appropriate catalyst selection and system design, seawater electrochemical reactions could enable the production of high-purity organic compounds.[91−93] To achieve this goal, systematic research with innovative electrochemical reaction and system designs is essential to overcome existing technical barriers. Thus, research efforts should be devoted to transforming the challenges of seawater electrolysis into opportunities by gaining a deeper understanding of chemical and physical properties of seawater and by developing alternative catalysts. For instance, while the CER is generally regarded as an unwanted side reaction in hydrogen production, it plays a crucial role in generating Cl-related chemicals in alkali-chlorine process. Additionally, the current research focus should expand beyond merely optimizing catalyst performance for existing reactions to exploring new electrochemical reactions and systems, thereby opening up more transformative ways for seawater utilization. This shift will enable the academic field to unlock the diverse potential of seawater and promote its development in green electrochemistry in a broader way.

5.2. Design Effective Catalysts and Electrolyzers and Test Them in Real Seawater Environments to Obtain Accurate Performance Parameters. One of the key factors in advancing seawater electrochemical reactions for producing fuels and chemicals is the development of effective catalysts and electrolyzers. For example, a suitable catalyst can mitigate the corrosive nature of seawater while enhancing reaction selectivity and reducing energy consumption. Similarly, a thoughtful catalyst design can convert $Mg(OH)_2$ from toxic deposits on the electrode into useful products. On the other hand, developing customizable electrolyzers is foundational for achieving scalable seawater electrochemical reactions. Testing catalysts and electrolyzers under real natural seawater conditions is critical for obtaining accurate performance data, as real seawater is more complex than saline or simulated seawater. In fact, testing across freshwater, saline water, and real seawater systems provides a comprehensive understanding of how impurities and complex interactions in seawater affect the electrochemical process, thereby addressing the challenges of seawater electrochemical reaction more effectively. In addition, such testing also improves the adaptability of catalysts and electrolyzers, which need to account for fluctuations in salinity, temperature and contaminant levels that can influence electrode efficiency and lifetime. Given that catalyst stability is a key parameter for practical applications, testing the catalyst's performance at high current densities in real seawater environments enables a more comprehensive assessment of its long-term durability. Such testing not only facilitates the identification of stability challenges but also provides informative feedback for the rational design of stable catalysts.

5.3. Practical Seawater Electrochemical Reaction Applications Need to Focus on Product Purity, Separation, System Economics, and Application Value. The research on seawater electrochemical reactions for fuels and chemicals production, as previously discussed, offers great promise but also encounters challenges in the separation and collection of products due to the inherent complexity of the seawater. Gas-phase products, such as H_2, O_2, and Cl_2 gases, as well as solid-phase products such as $Mg(OH)_2$, NaCl, and NaOH solids, present advantages in separation because they can be easily released or collected. However, some other reactions aimed at producing high-purity solid or liquid chemicals that are soluble in seawater may face separation challenges because of the wide variety of ions and impurities present in seawater. To address this, it is crucial to optimize existing seawater electrolysis technologies and equipment to produce specific high-purity chemicals while expanding the scope of seawater-based electrochemical reactions. As such, future research should focus on managing or eliminating impurities before they interfere with desired reactions and develop rapid and accurate phase separation strategies or devices. Simultaneously, the overall efficiency of seawater electrochemical reactions should also be improved to ensure their economically viability and practical application value. Finally, it is recommended that the energy consumption of the entire reaction system or electrolyzer be calculated and systematically compared. Such analysis will offer valuable insights for optimizing system performance and assessing economic feasibility.

5.4. The rationality and necessity should be considered when designing seawater electrochemical reactions. Not all electrochemical reactions require or are suitable for seawater electrolyte. Among the various reactions explored, H_2 production and CO_2 reduction stand out as promising due to their potential to significantly advance sustainability and carbon neutrality goals. While H_2 production from seawater has been extensively explored, using seawater for CO_2 reduction presents an untapped opportunity to address both carbon capture and chemical production simultaneously. For example, valuable chemicals like syngas or hydrocarbons could be synthesized by coupling seawater electrolysis with CO_2 reduction. Lithium extraction from seawater presents another exciting research direction, given the growing demand for lithium ion battery production.[94] Electrochemical methods could selectively extract lithium ions from seawater, offering a sustainable and environmentally friendly source of this critical element and reducing reliance on conventional mining. Electrochemical methods also hold great potential for extracting other valuable elements beyond lithium. For instance, while adsorption remains the predominant technique for uranium extraction from seawater, seawater electrochemical reactions are being investigated as emerging strategies.[95,96] Seawater electrochemical reaction also has great potential for the conversion of pollutants such as plastic degradation, though this area remains largely underexplored. Investigating reaction mechanisms, particularly the pathways for breaking down plastic components into harmless or even valuable byproducts, is crucial for advancing this field. Additionally, both the metrics and challenges associated with seawater, such as the presence of abundant ions, unwanted side reactions, and catalyst corrosion, must be systematically addressed. All these reactions leverage seawater's unique chemistry, allowing for targeted production of specific fuels or chemicals while contributing to environmental remediation. Therefore, while seawater offers multifaceted resource for sustainable energy and material production, careful considerations should be given to its rational and necessary application when designing seawater electrochemical reactions.

AUTHOR INFORMATION

Corresponding Author

Ghim Wei Ho − *Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117583, Singapore; Centre for Hydrogen Innovations, National University of Singapore, Singapore 117580, Singapore; Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore;* orcid.org/0000-0003-1276-0165; Email: elehgw@nus.edu.sg

Authors

Libo Wu − *Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117583, Singapore; Centre for Hydrogen Innovations, National University of Singapore, Singapore 117580, Singapore*

Wei Li Ong − *Department of Electrical and Computer Engineering, National University of Singapore, Singapore 117583, Singapore*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsnano.4c18818

Author Contributions

L.W. drafted the manuscript, and W.L.O. and G.W.H. commented on and revised the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Agency for Science, Technology and Research (A*STAR) RIE2025 Manufacturing, Trade, and Connectivity (MTC), Individual Research Grant (IRG award M23M6c0105) and Centre of Hydrogen Innovation (CHI-P2024-08).

VOCABULARY

Electrolyzer, a device that employs electricity to split water/seawater or other compounds into their constituent elements or molecular through electrolysis process; **oxidation**, a chemical process involving the loss of electrons by a substance, commonly occurring under oxidation potentials in the electrochemical reaction; **anion exchange membrane**, a semipermeable membrane typically composed of ionomers, designed to selectively transport anions while excluding gases such as oxygen and hydrogen, commonly used in electrochemical systems; **Pourbaix diagram**, a graphical representation illustrating the thermodynamic equilibrium states of a metal−electrolyte system as a function of pH and electrode potential; **alkali metals**, a group of reactive, electropositive, monovalent elements, including lithium, sodium, potassium, rubidium, cesium, and francium, which locate in Group IA (1) of the periodic table, known for forming strongly alkaline hydroxides; **bipolar membrane electrodialysis**, uses the basics of electrodialysis but introduces a bipolar membrane which splits water into H^+ and OH^- within an electrodialysis stack

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