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Alkaline Water Electrolysis for Efficient Hydrogen Production

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Abstract: Hydrogen production from water electrolysis is a sustainable and environmentally benign strategy in comparison with fossil fuel-based hydrogen. However, this promising technique suffers from the high energy consumption and unsatisfactory cost due to the sluggish kinetics of both half reaction and inferior stability of electrocatalysts. To address this challenge, herein, we present a timely and comprehensive review on advances in alkaline water electrolysis that is already commercialized for large scale hydrogen production. The design principles and strategies with aiming to promote the performance of hydrogen generation are discussed from the view of electrocatalyst, electrode, reaction and system. The challenges and related prospects are presented at last, hopefully to provide essential ideas and to promote the wide application of hydrogen production.

Key words: water electrolysis; hydrogen production; integrated electrode; coupled reaction

1 Introduction

With the issues of global energy crisis and environmental problems, great efforts have been focused on the development of sustainable energy system towards low-carbon or carbon-free energy. Hydrogen is considered to be a promising substance to achieve energy conversion and carbon neutrality with the merits of abundant resources, no greenhouse gas emission, and high efficiency[1, 2]. The overall hydrogen energy industry involves production, storage, transportation, as well as refueling and applications (Figure 1a). According to the "Global Hydrogen Review 2021" of International Energy Agency, the global hydrogen demand reached 90 Mt in 2020, practically all for the refining chemical and ammonia industries, showing a broad prospect. However, the current hydrogen production industrial system relies too much on fossil fuels, with steam reforming and coal gasification being the most dominant approaches, which results in nearly 900 Mt of CO_2 emissions. Therefore, it is imperative to develop a sustainable and efficient approach to produce hydrogen with mitigating the environmental concerns.

Recently, water electrolysis powered by renewable electricity is attracting growing interest to produce high-purity hydrogen owing to stable output, environmental-friendly and feasibility of largescale production[3]. Although the research related to water electrolysis is increasing every year (Figure 1b), it accounts for only 4% of the worldwide hydrogen supply. A key barrier for the development of hydrogen production from water electrolysis is the cost gap with that from fossil fuels (Figure 1c). Typically, electricity accounts for more than 80% of the current cost of hydrogen production from water electrolysis. With the carbon price rising and the cost of electricity falling,

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the hydrogen production from water electrolysis is approaching the competitiveness threshold, especially with the merit of nearly net zero CO_2 emissions.

Presently, water electrolysis is rapidly moving towards upscaling and commercialization, but there remain some key challenges in both basic and applied researches. In addition to the aforementioned high cost, the long-term stability of electrocatalysts needs to be improved for technological commercialization (Figure 1d)[4-31]. It is worth noting that most electrocatalysts reported so far operate below 200 $mA\cdot cm^{-2}$ with high overpotentials, further restricting practical use and large-scale implementation[32]. Moreover, the integrated system of water electrolysis and renewable clean energy remains a challenge due to the hardly maintained energy conversion efficiency and grid fluctuation.

The water electrolysis technologies can be categorized into alkaline water electrolysis (AWE, Figure 2a), polymer electrolyte membrane water electrolysis (PEMWE, Figure 2b), and solid oxide water electrolysis (SOWE, Figure 2c) according to the structure, electrolyte, ionic agents and operation parameter[1]. Although SOWE has a higher efficiency of ~98% than AWE (~70%) and PEMWE (~72%), the high operating temperature (~950 ℃) and low hydrogen production rate limit its widespread application and commercialization currently (Figure 2d-g). After years of development, the low-temperature water electrolysis (AWE and PEMWE) has become a mature and commercial technology. With pure water as an electrolyte, PEMWE needs expensive electrocatalysts (Pt-based materials for HER and Ir-based materials for oxygen evolution reaction (OER)) and proton exchange membrane materials, which results into the problems of high overall cost (~1200 $\$\cdot kW^{-1}$) and limited resources (Figure 2k). In contrast, AWE is characterized by relatively low capital costs due to the avoidance of precious materials and superior long-term durability. Moreover, AWE can couple with electrochemical refinery to realize the production of high value-added chemicals, further reducing the cost of generated hydrogen. However, the problem of low current density faced by AWE hinders its commercialization, which can be resolved via optimizing the electrocatalysts and upgrading the electrolysis system.

In recent years, some high-quality reviews have

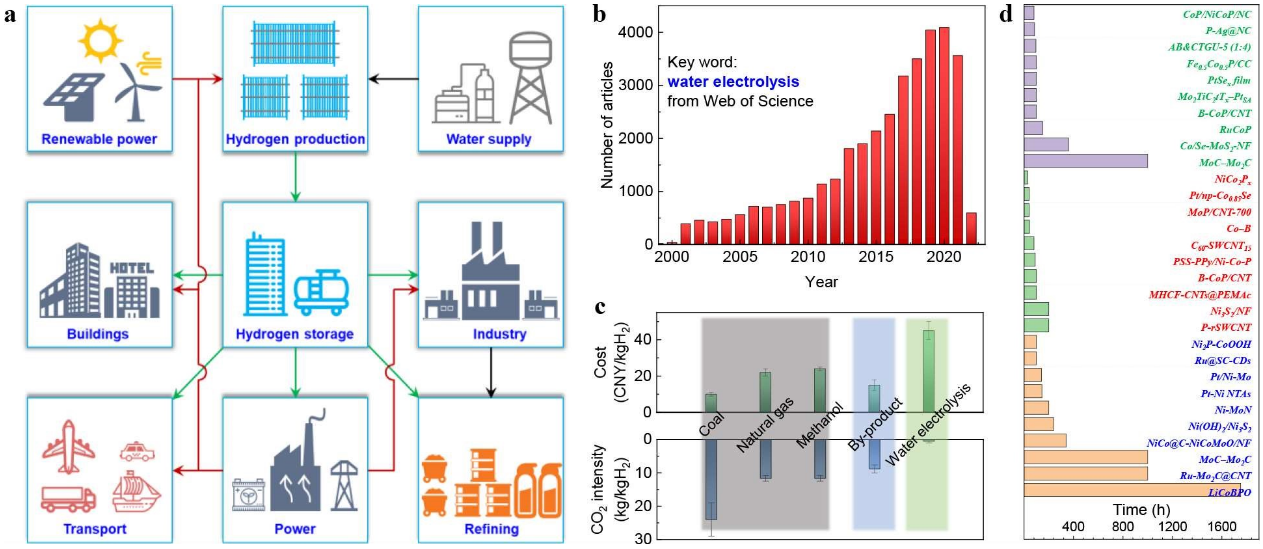

Figure 1 (a) A schematic illustration of the hydrogen value chain from supply to end-use. (b) Statistics on the numbers of publications related to water electrolysis in the last few decades. (c) The cost and CO_2 emission values for various hydrogen production techniques. (d) Comparison of stability for the reported hydrogen evolution reaction (HER) electrocatalysts in acid (purple), neutral (green) and alkaline (orange) media. (color on line)

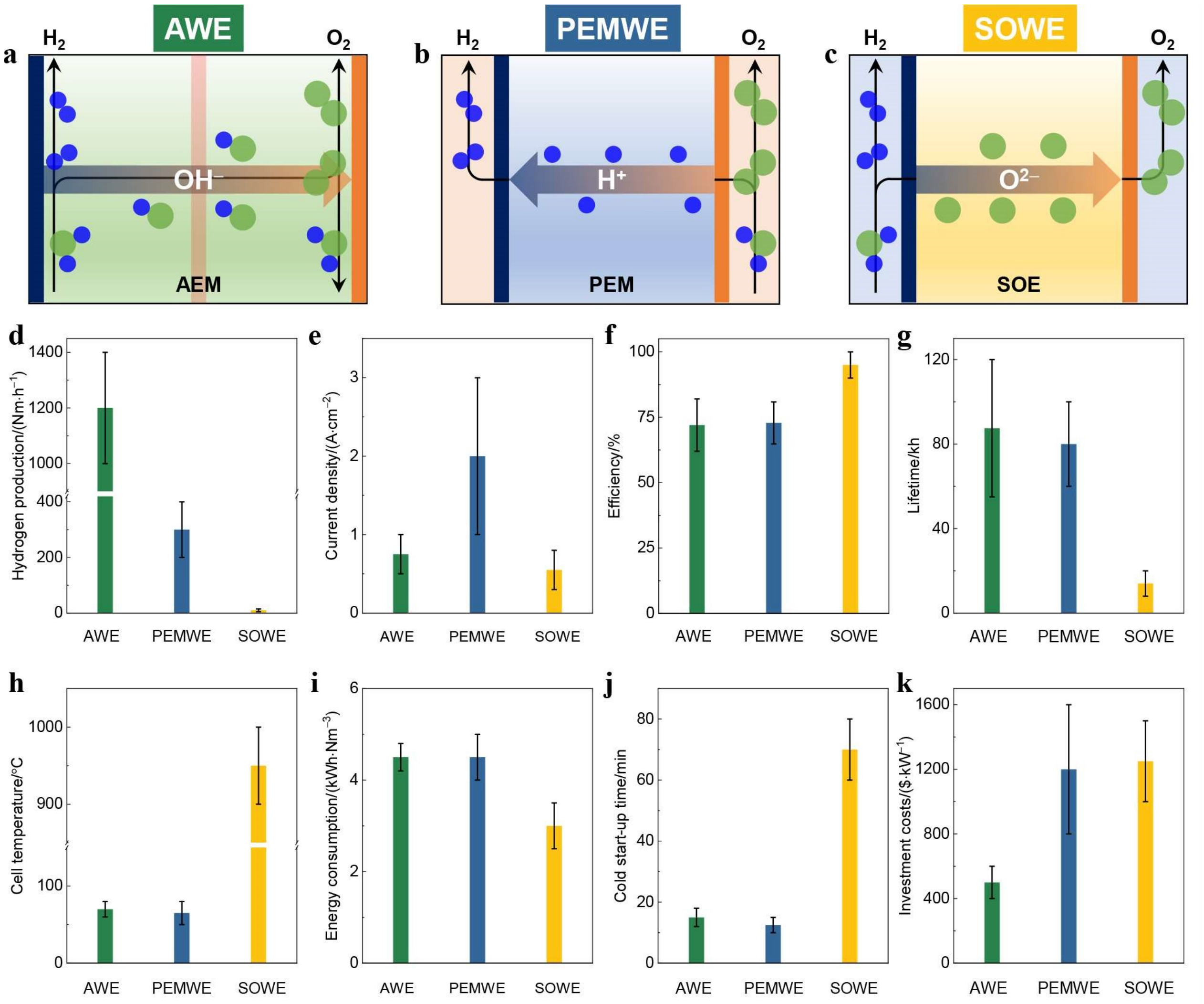

Figure 2 Schematic diagrams of (a) AWE, (b) PEMWE and (c) SOWE. Comprehensive comparisons of AWE, PEMWE and SOWE in terms of (d) hydrogen production rate, (e) current density, (f) efficiency, (g) lifetime, (h) cell temperature, (i) energy consumption, (j) cold start-up time and (k) investment costs. (color on line)

summarized the development of AWE from the perspectives of electrocatalyst exploration, intrinsic activity optimization, structure modulation and catalytic mechanism revelation[33-36], yet few of them are based on the practical application. In addition, there is less reviews on cost-down strategy for AWE via coupling with organic oxidation and integrating with renewable energy. Considering the mature and wide development of AWE, herein, we present a timely and comprehensive review on recent advances in AWE. The background, type and development history of AWE are firstly introduced, aiming to provide a panorama view of AWE. Further, various strategies for enhancing the efficiency of AWE from electrode-to-reaction, and cell-to-system are discussed. Finally, we outlook the future research directions, opportunities and challenges regarding the AWE, with the purpose of providing essential ideas and promoting the wide application of hydrogen energy.

2 Strategies for Enhancing the Performance of AWE

2.1 Designing Efficient Electrocatalysts

Water electrolysis has attracted an abundant deal of attention since AWE, PEM and SOCE were developed by Troostwijk in 1789, Grubb in 1960s and

Donitz in 1980s, respectively (Figure 3a)[33]. And the development of appropriate electrocatalysts with suitable physical and chemical properties is highly required for water electrolysis. During the past few decades, numerous electrocatalysts, including noble metal, non-noble metal and metal-free electrocatalysts with single-atom, nanocluster, nanoparticle and nanoarray structure, have been widely explored for water electrolysis[37]. Stimming and co-workers concluded that Pt is the better electrocatalyst than other metals for HER in 2005 via analyzing the relationship between hydrogen chemisorption energies and the exchange current of HER, thus providing a theoretical foundation for the subsequent development of electrocatalyst for HER[38]. Considering scarce and expensive Pt group metals are not suitable for large scale applications, it is therefore crucial to find alternatives to the Pt group electrocatalysts. Through density functional theory (DFT) calculations, Nörskov and co-workers found that MoS_2 nanoparticles supported on graphite with a moderate overpotential of 0.1 ~ 0.2 V is a promising electrocatalyst for HER[39]. Then Chorkendorff and co-workers determined that the edge of MoS_2 nanoparticles is the real active sites for HER via tuning the size of nanoparticles, further providing an experimental foundation for optimizing the intrinsic activity of electrocatalyst[40]. Considering metal-based electrocatalysts may suffer from corrosion under harsh environment, Qiao and co-workers reported a metal-free electrocatalyst for HER via coupling nitrogen-doped graphene with graphitic-carbon nitride in 2014, which exhibited an overpotential of ~240 mV at current density of 10 $mA \cdot cm^{-2}$[41]. In addition to the development of different types electrocatalysts and the regulation of intrinsic activity, researchers realized that the structure of electrocatalyst also has a huge impact on its performance. Hence, Sun and co-workers reported a fabrication of nanoporous cobalt phosphide with self-supported nanowire arrays on carbon cloth, which exhibited a low onset potential of 38 mV and long-term stability of more than 20 hours in acidic media for HER[42]. With the merits of maximum atom utilization efficiency and adjustable coordination structure, single-atom catalysts (SACs) have shown great promise in water electrolysis in recent years[43]. For instance, nitrogen-doped graphene nanosheets supported Pt-SAC was fabricated by Sun and co-workers in 2016 by atomic layer deposition, which exhibited much high activity and stability for HER than commercial Pt/C[44].

Along with the deepening of water electrolysis, numerous electrocatalysts have shown promising activity and stability for HER. For example, γ-MnO_2 electrocatalyst developed by Nakamura and co-workers could operate continuously for more than 8000 hours[45] and Pt/Ni-Mo electrocatalyst developed by Liu and co-workers realized an ultrahigh current density of 2000 $mA \cdot cm^{-2}$ at an overpotential of 113 mV[46], demonstrating the feasibility for practical water electrolysis. Meanwhile, Hu and co-workers prepared a bimetallic-structured phosphide electrocatalyst, which exhibited superior HER performance in acidic, alkaline and neutral conditions, expanding the dimensional of both scientific and industrial fields[15]. On the other hand, various technologies have been well employed to reveal the catalytic mechanism of water electrolysis and monitor the evolution of electrocatalysts in electrochemical operando conditions besides designing electrocatalysts. For instance, Agnoli and co-workers determined the real active sites for HER via the electrochemical scanning tunnelling microscopy, providing a powerful tool to derive accurate structure-activity relationships in water electrocatalysis[47].

Among various electrocatalysts, layered double hydroxides (LDHs) are considered to be one of the most promising materials for AWE owing to their superior OER performance[48-50]. Moreover, LDHs can be transformed into other efficient materials (e.g., oxides, sulfides and phosphides) benefitting from the versatility in chemical composition and architectural structure, which further promoted the development of AWE and other energy conversion technologies[51, 52]. For instance, our group prepared (Ni, Fe)S_2@MoS_2 heterostructures with NiFe-LDH as a precursor via a hydrothermal method, which shows remarkable activity and durability for AWE (Figure 3b)[53]. The overpotentials at the current density of 10 mA·cm^{-2} for HER and OER were 130 and 270 mV, respectively, outperforming most reported electrocatalysts. Moreover, we synthesized various metal-doped CoP electrocatalysts by using metal-doped Co-LDHs as precursors via an *in-situ* phosphidation transformation, in which FeCoP exhibited significantly enhanced activity toward AWE (Figure 3c)[54]. The electrolyzer assembled by FeCoP required only 1.6 V to derive the current density of 10 mA·cm^{-2}. After more than ten years of continuous exploration, we developed a variety of synthetic methods for nanostructured LDHs, including electrodeposition and hydrothermal method, and regulated their morphology and structure rationally and controllably (Figure 3d)[55-57]. Meanwhile, metal alloys, oxides, carbides, sulfides, nitrides, selenides and phosphides were synthesized with LDHs as precursors through topological transformation strategy, which opens up an effective route to rational design and fabrication of electrocatalysts with high activity and stability for energy storage and conversion applications[51].

In addition to LDHs and their derivatives, other electrocatalysts have also been developed for water electrolysis (Table 1)[24, 28, 53, 54, 58-64]. For instance, Lei and co-workers synthesized a series of transition metal chalcogenides through a two-step hydrothermal treatment for water splitting[64]. Among them, FeCoNi(S) showed low overpotentials of 252 and 293 mV to deliver current densities of 100 and 500 mA·cm^{-2}, respectively. Moreover, FeCoNi(S) could operate constantly under a cell voltage of 1.84 V over 2000 h,

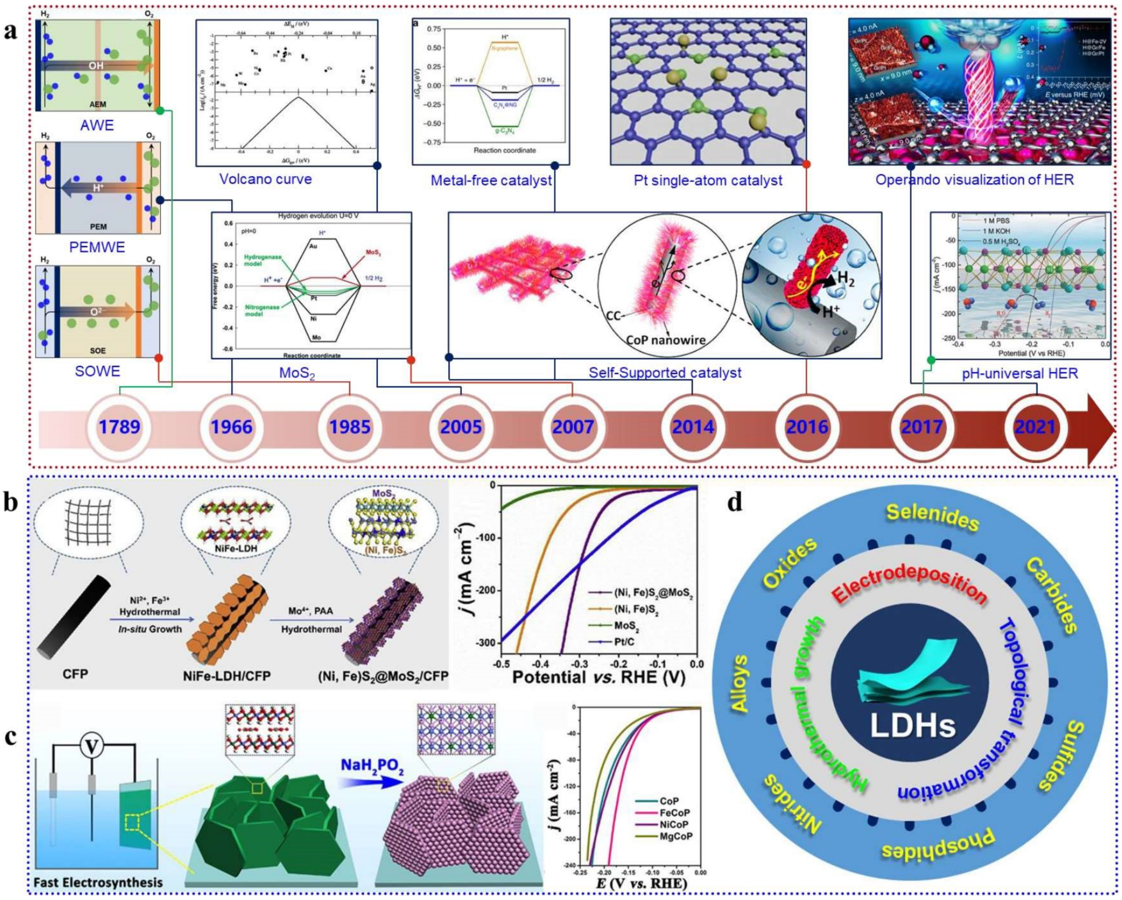

Figure 3 (a) Timeline of recent developments for water electrolysis. (b) Illustration and HER performance of (Ni, Fe)S$_2$@MoS$_2$[53]. Reproduced with permission of Ref. 53, copyright Elsevier. (c) Illustration and HER performance of FeCoP[54]. Reproduced with permission of Ref. 54, copyright Elsevier. (d) Schematic presentation of LDHs-derived materials. (color on line)

Table 1 Summary of AWE performance from recently reported work

Electrocatalyst	Overpotential/V	Stability/h	Ref.
C: CoNiP@LDH A: CoNiP@LDH	1.44@10 mA·cm^{-2}	20@10 mA·cm^{-2}	[59]
C: (Ni,Fe)S_2@MoS_2 A: (Ni,Fe)S_2@MoS_2	1.56@10 mA·cm^{-2}	24@10 mA·cm^{-2}	[53]
C: Ni-MoN A: stainless-steel mat	1.613@100 mA·cm^{-2}	100@100 mA·cm^{-2}	[28]
C: $Ni(OH)_2/Ni_3S_2$ A: $Ni(OH)_2/Ni_3S_2$	1.49@10 mA·cm^{-2}	120@20 mA·cm^{-2}	[24]
C: NF-Na-Fe-Pt A: NF-Na-Fe-Pt	1.56@10 mA·cm^{-2}	12@10 mA·cm^{-2}	[62]
C: FeCoP A: FeCoP	1.60@10 mA·cm^{-2}	20@10 mA·cm^{-2}	[54]
C: FeCoNi(S) A: FeCoNi(S)	1.53@10 mA·cm^{-2}	2000@500 mA·cm^{-2}	[64]
C: Ni-Co-Fe-P A: Ni-Co-Fe-P	1.46@10 mA·cm^{-2}	100@100 mA·cm^{-2}	[60]
C: $Ni^{III}Co^{II}$Fe-O@NF A: $Ni^{III}Co^{II}$Fe-O@NF	1.455@10 mA·cm^{-2}	100@1.53 V	[61]
C: CoFeP TPAs A: CoFeP TPAs	1.47@10 mA·cm^{-2}	100@20 mA·cm^{-2}	[63]

demonstrating an excellent durability. Although non-noble metal electrocatalysts have witnessed considerable progress, noble metal-based electrocatalysts (such as Pt and Ru) still play an irreplaceable role in water electrolysis. Numerous studies have shown that Pt is the benchmarking HER electrocatalyst, while its overall water splitting performance is still restrained by inferior OER activity. Based on this, Cheng and co-workers reported a fabrication of Pt-$Ni(OH)_2$-CeO_2 hybrid on graphite, which needs only overpotentials of 76 and 186 mV to afford 100 mA·cm^{-2} for HER and OER, respectively[65]. Additionally, the assembled symmetric water electrolyzer based on Pt-$Ni(OH)_2$-CeO_2 delivered a current density of 10 mA·cm^{-2} at an applied voltage of 1.5 V, and sustained over 85 h at 1000 mA·cm^{-2}.

2.2 Optimizing Electrode and Cell

During AWE process, the required potential for cell is always higher than theoretical potential, which is resulted from several effects (Figure 4a). In addition to the overpotential of electrocatalysts in catalyzing process at an anode and a cathode, the ohmic resistance caused by electron transfer of electrode, ions diffusion of electrolyte and membrane, and generated gas bubbles, further increasing the applied potential. Through rational designing the structure of current collector not only can improve the mass-loading of electrocatalyst, but also promote the desorption and diffusion of generated gas, which is conducive to the progress of AWE (Figure 4b).

Compared to designing current collector, designing and regulating the morphology and structure of electrocatalyst are more efficient and universal strategy to enhance the performance of AWE[66]. The ideal electrocatalyst should possess a large surface area, high electronic conductivity, favorable hydrophilicity and gas permeability, and excellent stability for long-term operation. However, the traditional electrode is prepared by mixing the electrocatalyst and binder (e.g., Nafion, polyvinylidene fluoride), and then dropping them on current collector. The dependence of binder severely increases the cost of AWE. Additionally, the using of binder can bring about severe aggregation of electrocatalyst and limited diffusion of electrolyte, and thus result in inferior performance. In addition, the harsh electrolyte environment or continuous operation will lead to the decomposition of binder and detaching of electrocatalyst, resulting in poor stability, which seriously limits its practical application.

Constructing electrocatalyst directly on current collector with rational structure is a promising strategy to enhance the performance of AWE. Until now, our group has fabricated numerous integrated electrodes with various nanostructures (e.g., nanorod, nanosheet, nanowall and hierarchical structure) through electrodeposition, topological transformation and hydrothermal methods (Figure 4c)[59, 67-70]. The integrated structure not only can accelerate the electron transfer between electrocatalyst and current collector, but also realize sufficient ions diffusion through the space between the structure units[71]. The generated gas bubbles during AWE process can also be desorbed instantaneously owing to the ordered structure (Figure 4d), thus letting the active site be exposed and participate next catalytic process[72]. Moreover, the integrated structure can also strengthen the connection between electrocatalyst and collector, and improve the electrode cycling stability.

Traditional cell of AWE with two plates suffers from poor voltage efficiency (Figure 4e), particularly at high current densities (> 300 mA·cm^{-2}) due to high internal resistance[73]. In addition, the permeation and diffusion of generated gas are another problem that needs to be solved. With the continuous development of hydrogen energy, the requirements for AWE devices are increasing. Stirred-tank reactors were developed to facilitate the mass transport process[74]. Later, the zero-gap cell with compressed porous electrode was applied, significantly promoting the efficiencies of AWE (Figure 4f). In this setup, the ohmic resistance

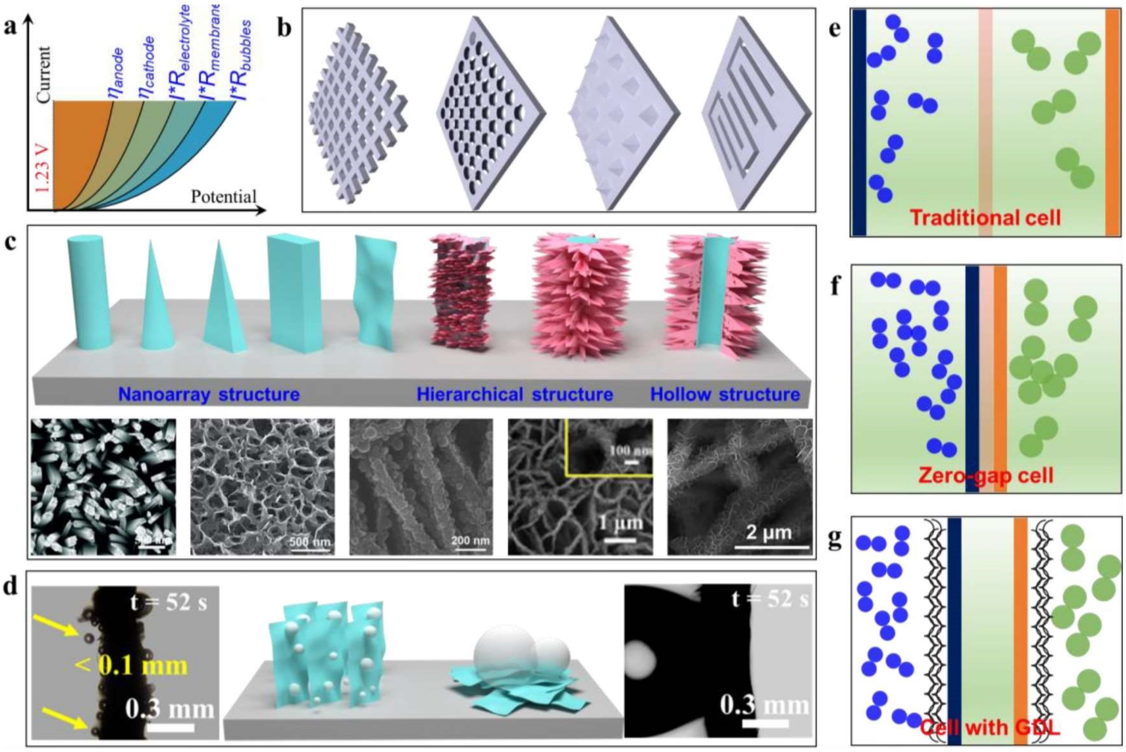

Figure 4 (a) Graph showing the contributions to cell voltage from the components of the cell resistance. (b) Schematic illustration of various current collectors. (c) Various strategies to boost performance via structure design. (d) Schematic illustration of bubbles releasing at the surface of traditional coating electrode and integrated electrode. The configuration of (e) traditional AWE cell, (f) zero-gap AWE cell and (g) AWE cell with GDL. (color on line)

generated from the electrolyte between two electrodes is decreased since the distance between two electrodes is almost the same thickness of membrane. To further accelerate the removal of the gas products during AWE, the gas diffusion layer is integrated with the bipolar plate (Figure 4g).

2.3 Coupling with Organic Oxidation

During AWE process, the anodic OER needs to undergo a complex four-electron reaction process and consumes more than 90% input energy, which seriously restricts the hydrogen production efficiency of the cathode. In addition, the low value-added product of OER (O_2) needs additional gas separation steps further increasing the cost of hydrogen production. Therefore, how to reduce the overpotential of anodic reaction and achieve efficiently *in-situ* use of generated oxygen is very important for the development of hydrogen production from AWE. Recently, we proposed a concept of electrochemical hydrogen evolution coupled with alternative oxidation (EHCO), in which the anodic OER can be replaced with other easy oxidation reactions, such as organic (e.g., alcohols, aldehydes and amines) oxidation reaction [75]. The EHCO route not only reduces the anodic oxidation overpotential and improves the efficiency of hydrogen production at the cathode, but also obtains the high value-added chemicals and further reduces the cost of hydrogen production, which is expected to provide a new idea for the development of hydrogen production technology (Figure 5a). Coincidentally, the electrosynthesis of chemicals in parallel with hydrogen production was also proposed by Shi and other groups, which jointly promoting the vigorous development of this field[76-78]. However, it is still a challenge to select the appropriate anodic reaction and develop the corresponding electrocatalyst to boost the hydrogen production.

Our group has recently reported a self-supported ultrathin CoAl-LDH nanosheet array by using *in-situ* electrochemical exfoliation method (denoted as E-CoAl-LDH-NSA), which displays superior performance for electrochemical hydrogen evolution coupled with 5-hydroxymethylfurfural (HMF) oxidation (Figure 5b)[57]. The *in-situ* exfoliation strategy introduces abundant oxygen vacancies on the CoAl-LDH, which regulates the electronic structure of LDHs, and facilitates the adsorption and oxidation process of HMF. As a result, the E-CoAl-LDH-NSA exhibited outstanding performance for the oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) with a low potential of 1.30 V vs. RHE at 10 $mA\cdot cm^{-2}$ as well as much high Faradaic efficiency (FE) for FDCA (99.4%) even at 1.52 V vs. RHE, which are the highest level compared with the reported electrocatalysts. Based on the E-CoAl-LDH-NSA, we constructed HMF oxidation coupled hydrogen generation system in a two-electrode cell, which exhibited a low voltage of 1.74 V to reach 50 $mA\cdot cm^{-2}$, high H_2 yield of 44.16 $L\cdot h^{-1}\cdot m^{-2}$ (4 times higher than overall water splitting) as well as excellent stability. A hierarchical CoNi-LDHs with abundant Ni vacancies (VNi-CoNi-LDH) was reported by our group, which exhibited superior activity for both anodic HMFOR and cathodic HER[79]. The EHCO based on VNi-CoNi-LDH successfully realized the continuous synthesis of highly-pure FDCA and enhanced hydrogen production (49.25 $L\cdot m^{-2}\cdot h^{-1}$). In order to further enhance the bifunctional activity of LDH-based electrocatalyst for both HMFOR and HER, we prepared a bifunctional CoNiP nanosheet integrated electrode (CoNiP-NIE) via a phosphidation process based on LDHs, which shows the enhanced HER performance compared with CoNi-LDH, while maintains its HMFOR performance (Figure 5c)[80]. The overpotential to drive -10 $mA\cdot cm^{-2}$ for HER over CoNiP-NIE was only 107.56 mV, much low than that over CoNi-LDH (278.44 mV). Moreover, CoNiP-NIE delivered high FE for HMFOR to FDCA (more than 82%) in a wide potential from 1.40 V to 1.70 V vs. RHE, outperforming most reported electrocatalysts. Furthermore, the EHCO system was constructed based on the bifunctional CoNiP-NIE, which exhibited a low potential of 1.46 V at 20 $mA\cdot cm^{-2}$, accelerated evolution rate of H_2 (41.2 $L\cdot h^{-1}\cdot m^{-2}$) and high FDCA yield rate (85.5 $g\cdot h^{-1}\cdot m^{-2}$). The EHCO system even can be driven by a commercial Si solar cell, which achieved 0.8% of solar-to-FDCA and 5.5% of solar-to-H_2 conversion efficiency.

In addition to electrochemical hydrogen evolution coupled with HMF oxidation, our group further developed a EHCO route with glycerol oxidation reaction (GOR) as anodic reaction, and carbon nanosheet array supported CoPt nanoparticles (CNs@CoPt) as bifunctional electrocatalyst (Figure 5d)[72]. The CNs@CoPt exhibited an extremely low overpotential of 19.1 mV to reach a current density of 10 mA·cm^{-2} for HER, and small onset potential of 1.32 V for GOR, respectively, which outperforms the references and most reported electrocatalysts. Based on above results, we then constructed a hydrogen evolution coupled with glycerol oxidation system with CNs@CoPt as a bifunctional electrode. Surprisingly, this coupling system showed the dramatically enhanced hydrogen production rate (48 L·h^{-1}·m^{-2}) in a cathode, larger than traditional water splitting system (27 L·h^{-1}·m^{-2}), and gains high value-added formate (113 g·h^{-1}·m^{-2}) in an anode. Although EHCO offers a promising approach to co-produce high value-added chemicals and hydrogen, it still faces the problem of low current density at an anode, limiting the overall hydrogen productivity.

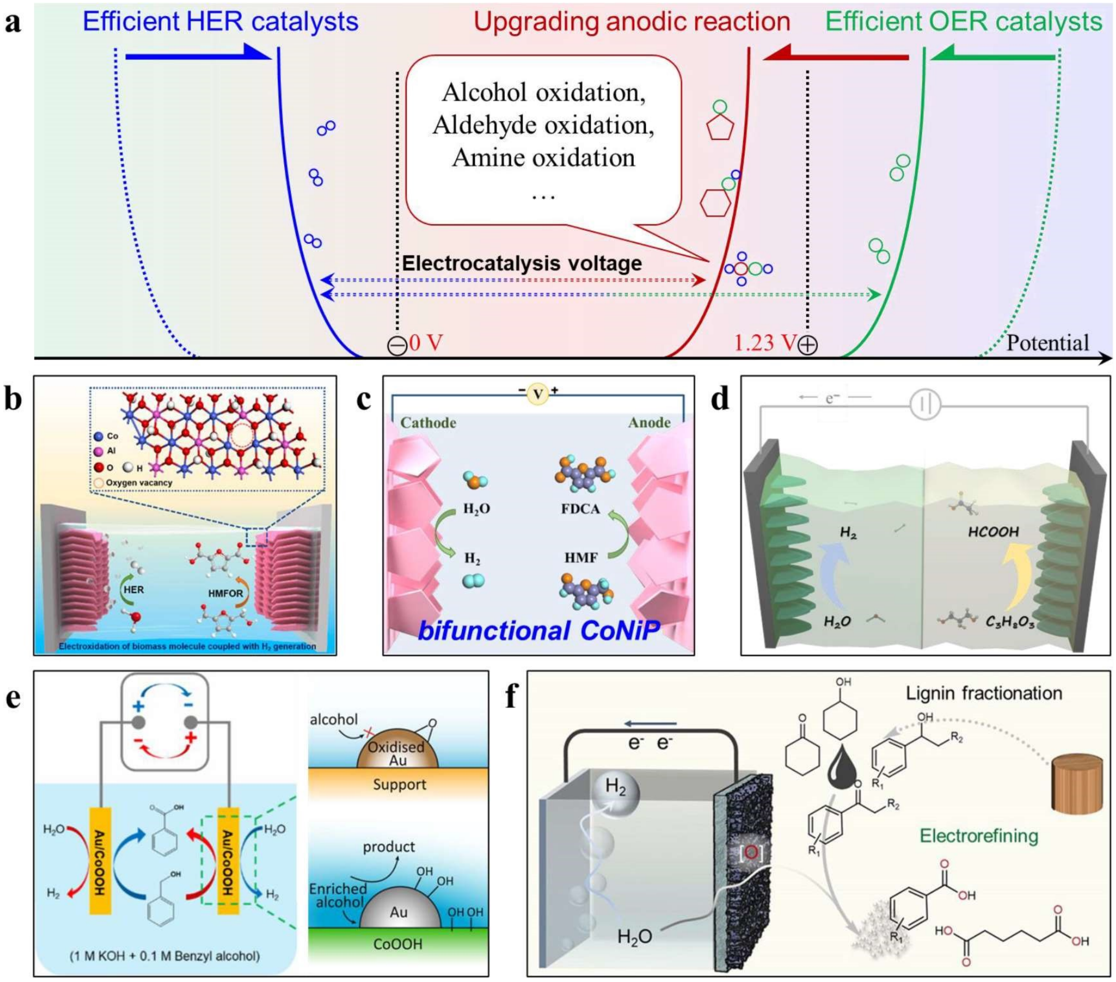

Figure 5 (a) Schematic illustration of reducing the voltage and improving the economic benefits for AWE. Electrochemical hydrogen evolution coupled with 5-hydroxymethylfurfural oxidation over (b) E-CoAl-LDH-NSA[57] and (c) CoNiP-NIE[80]. Reproduced with permissions of Refs. 57 and 80, copyright Elsevier. Electrochemical hydrogen evolution coupled with benzyl alcohol oxidation over (d) CNs@CoPt[72] and (e) Au/CoOOH[81]. Reproduced with permission of Ref. 72, copyright Elsevier. Reproduced with permission of Ref. 81, copyright Springer Nature Ltd. (f) Electrochemical hydrogen evolution coupled with lignin derivatives oxidation over MnCoOOH[82]. Reproduced with permission of Ref. 82, copyright Wiley. (color on line)

Given that, Duan and co-workers synthesized a cooperative electrocatalyst of Au nanoparticles supported on cobalt oxyhydroxide nanosheets (Au/CoOOH), which realizes superior performance for benzyl alcohol oxidation at high current density (Figure 5e)[81]. Deep studies reveal that the benzyl alcohol is enriched at Au/CoOOH interface, thus is easily oxidized by the electrophilic OH* generated on CoOOH with low reaction barrier, leading to higher activity than pure Au. The Au/CoOOH exhibited the current densities of 340 and 540 mA·cm^{-2} at potential of 1.3V and 1.5 V vs. RHE, respectively, representing the highest current density value reported so far. Moreover, the benzyl alcohol conversion rate and hydrogen production rate reached 3.19 mmol·cm^{-2}·h^{-1} and 117.9 mL·cm^{-2}·h^{-1}, respectively, at the potential of 1.3 V vs. RHE, which is 26- and 28-fold higher than that of Au. Furthermore, Duan and co-workers developed a MnCoOOH electrocatalyst for efficient upgrading of lignin-derived secondary alcohols or ketones into carboxylates coupling with hydrogen production (Figure 5f)[82]. The yield and operational stability for alcohols and ketones to corresponding carboxylates over MnCoOOH could reach to 64% ~ 99% and 200 h. As proof of concept, diverse lignin aromatics and KA oil featuring C(OH)-C and C(O)-C units were also reformed to benzoate and adipate with high yields (91.5% and 64.2%).

2.4 Integrating with Renewable Energy

Using renewable clean energy (e.g., solar, wind, water and geothermal resources) to drive water electrolysis system is an important approach to green hydrogen production and achieve a significant reduction in the cost of hydrogen production[83]. With the developments of water electrolysis and energy capture, storage and conversion technology, various green energy powered water splitting devices have been reported, and have achieved promising results (Figure 6a). Sunlight can be absorbed by photo-electrocatalyst to power water splitting, or be converted to electricity, which can be effectively employed to power water electrolysis[84]. Wind and tide can also be converted to electricity by wind turbines or triboelectric nanogenerator (TENG), thus realizing hydrogen production from water electrolysis. Meanwhile, sunlight, low-grade waste heat or natural temperature changes can be converted to electricity by thermoelectricity (TE), offering an alternative external energy to power water electrolysis.

Among various green energy powered water electrolysis systems, solar powered water electrolysis systems have been widely designed and applied owing to their convenience, simplicity and high stability. However, the hydrogen production from this technology is still limited by price and efficiency factors. Currently, the efficiencies of industrial AWE systems and mainstream solar panels are ~70% and ~18%, respectively, resulting a STH efficiency of ~13% and a hydrogen cost of ~10$·kg^{-1}. Based on this, Zhao and co-workers presented a direct solar powered AWE system through coupling NiMo hydrogen evolution electrocatalyst and NiFe-based oxygen evolution electrocatalyst with high-performance perovskite-Si tandem cells (Figure 6b)[85]. The overpotential to drive 10 mA·cm^{-2} over NiMo electrocatalyst was only 6 mV. After coupling with NiFe-based oxygen evolution electrocatalyst, the potential to drive 10 mA·cm^{-2} was 1.48 V and the stability for overall water splitting reached 100 h. A perovskite solar cell with high open circuit voltage (1.271 V) was employed to power AWE cell, exhibiting a high solar-to-hydrogen (STH) efficiency (20.01%) and fulfilling the 2020 DOE target. The STH efficiency could be increased to 25% after optimizing the perovskite cell. The levelized cost of hydrogen of 4.1 $·kg^{-1} could be achieved based on STH efficiency of 20%, demonstrating a promising approach to realize cheap renewable hydrogen. Until now, with the efficiencies of AWE and solar panels increasing, the STH efficiency has been improving (Figure 6c)[85-94], which is believed that the solar powered AWE system will become mainstream for low-cost solar hydrogen production.

The inexhaustible sunlight not only can be converted directly into electricity, but also can be converted into electricity by the solid-state TE generator through heat-to-electricity energy conversion process, which effectively resolve the conflicts between solar cells and electrocatalysts. Based on this, Zhou and co-workers proposed a TE device composed of multi-functional Ni nanosheets array to power AWE system (Figure 6d)[95]. The Ni nanosheets array grown on the hot side of TE device can play the role of photothermal conversion layer to provide temperature difference for TE, and active electrocatalysts for HER. As a result, the Ni nanosheets array exhibited a low overpotential of 173 mV at a current density of 10 $mA\cdot cm^{-2}$ and superior stability of 20 h. The TE powered AWE system was then constructed, which delivered a high hydrogen production rate of 1.818 $mmol\cdot h^{-1}$. Furthermore, Bowen and co-workers utilized lead zirconate titanate as an external charge source to generate electricity through undergoing hot-cold thermal cycles, which exhibited a maximum voltage of 2.34 V and micro-level current of ~ 7 μA (Figure 6e)[96]. Then, an AWE system powered by pyroelectrics was constructed, which can produce continuous hydrogen with a rate of 0.655 $\mu mol\cdot h^{-1}$.

Harvesting more stable green energy from environment to power water electrolysis is important for the widespread application of hydrogen production. Compared to solar energy, wind energy is independent of time, and even can generate electricity 24 hours a day. Herein, Fan and co-workers employed a coaxial rotatory freestanding triboelectric nanogenerator (CRF-TENG) to harvest wind energy for hydrogen production from AWE (Figure 6f)[97]. The output current could be regulated by changing rotational speeds. A short-circuit current of 50 μA and output power of 10 mW were realized with the rotational speed reaching 900 $r\cdot min^{-1}$. A self-powered AWE system based on the CRF-TENG was constructed, which exhibited a hydrogen production rate of 6.9685 $\mu L\cdot min^{-1}$ when the wind speed was 10 $m\cdot s^{-1}$, opening up an efficient route for the development of hydrogen energy. Furthermore, Wang and co-workers constructed a self-powered AWE system using a water-flow-driven TENG, expanding the external energy source for AWE (Figure 6g)[98]. The cell could exhibit a high hydrogen production rate of 6.25×10^{-3} $mL\cdot min^{-1}$, with the spinning speed of TENG reaching 600 $r\cdot min^{-1}$. Moreover, the TENG could be driven by the flow of normal tap water, demonstrating the fully self-powered capability. The above works have initiated a research direction in the field of TENG-driven AWE in general.

3 Conclusions and Outlooks

Hydrogen has received extensive attention from all over the world, and exploring water electrolysis for industrial hydrogen production is one of the most promising works today. In this review, we present a comprehensive review on advances in AWE from the perspectives of electrocatalyst, reaction and system. Despite many important developments of hydrogen production from AWE, there are still a long way to go in the view of industrial applications because of high production cost and low energy efficiency. In order to promote the development of AWE, attention should be paid to the following aspects:

(1) Electrocatalyst/electrode

The performance of AWE for hydrogen production can be enhanced via regulating the electronic and morphological structures of electrocatalyst. Through designing the appropriate surface interfacial structure and hydrophilic properties of integrated electrode, the reaction efficiency and durability can be further improved. However, the universal structure-activity relationship to guide the electrocatalyst design is impractical and contradictory. In addition, most reported electrocatalysts are unable to meet the requirements of stability (>10000 h) and current density (> 400 $mA\cdot cm^{-2}$) in industrial applications. Therefore, further researches, including experimental works and computational simulation, are necessary to elucidate the structure-activity relationship and design principle of electrocatalyst. From the perspective of electrocatalyst preparation, despite various synthetic methods, including water/solvent thermal method, electrodeposition method and chemical vapor deposition method, have been widely applied for the fabrication of integrated electrode, the issues about preparation cost, time, operability and repeatability need to be considered. Meanwhile, it is urgent to develop

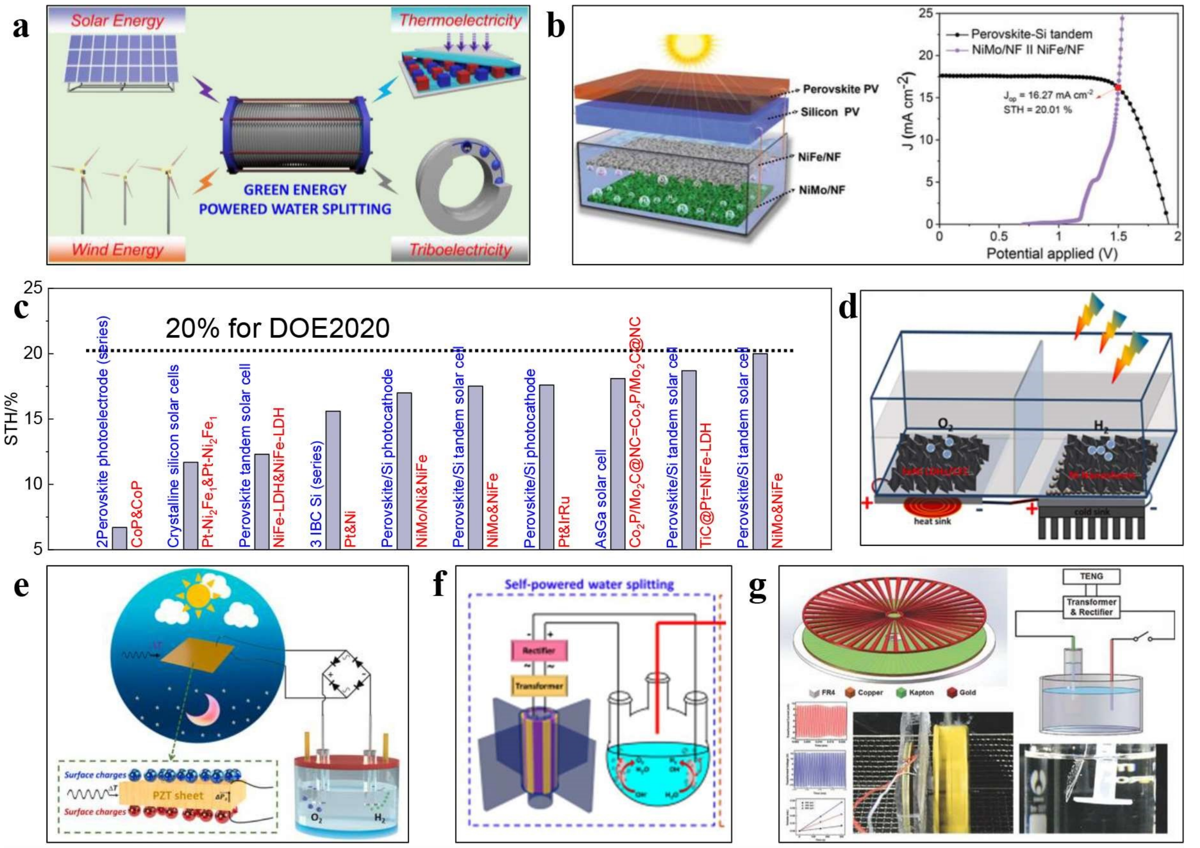

Figure 6 (a) Schematic illustration of water splitting powered by various green energy systems. (b) Schematic illustration, *J-V* curve and LSV curve of solar powered AWE system[85]. Reproduced with permission of Ref. 85, copyright Wiley. (c) Comparison in the STH efficiency of solar powered AWE system. (d) Illustration of TE powered AWE system[95]. Reproduced with permission of Ref. 95, copyright Elsevier. (e) Schematic of pyroelectric as an external source for AWE system[96]. Reproduced with permission of Ref. 96, copyright Elsevier. (f) Schematic diagram of CRF-TENG wind energy harvester driven self-powered AWE system[97]. Reproduced with permission of Ref. 97, copyright Elsevier. (g) Schematic illustration of self-powered AWE system using a water-flow-driven TENG[98]. Reproduced with permission of Ref. 98, copyright Wiley. (color on line)

automated preparation process to realize the construction of integrated electrode with large surface area and high mass-loading, which is of great significance to the commercialization of AWE. In addition, new developed synthetic methods for integrated electrode need to avoid harsh preparation conditions such as high temperature and high pressure if they are to be commercially available.

(2) Reaction/cell

At present, the researches related to the hydrogen generation coupled with organic oxidation have received more and more attention. However, the current inferior selectivity and stability of anodic reaction result into low energy efficiency, which is difficult to match cathodic and anodic reactions. In order to improve the activity and selectivity of anodic oxidation reaction and match the reaction efficiency of both cathodic and anodic reactions, more techniques combined with DFT calculations are needed to monitor the generated active oxygen species qualitatively and quantitatively on the surface of electrode. Moreover, regulating the hydrophilic nature as well as the oil-water affinity of electrocatalyst deserves special attention. In addition to the developments of highly efficient electrocatalyst and newly coupled reaction, the adaptation of electrode/electrolyte/membrane should be seriously considered. The influences of the organic on the performance and stability of membrane should be deeply studied. In order to improve the reaction efficiency of the electrolysis system and the yield of the target product, researchers should innovate the way of feeding reactants (undersaturated feeding to avoid side reactions) and the electrolysis method (intermittent electrolysis). At the same time, to improve production efficiency, the *in-situ* separation and purification of products also require special attention.

(3) System/device

Currently, one of the factors that limits the large-scale application of AWE is the high cost of hydrogen production. Integrating AWE with renewable and clean energy is the key to reduce the cost of hydrogen production. However, the low conversion efficiency of renewable energy to electricity greatly hinders its application in AWE. In addition, some renewable energies with intermittent and seasonal nature, including solar and wind energy, are easily influenced by the external environment, which have a detrimental impact on power grid. Hence, exploring new renewable energy to achieve local utilization of energy is expected to promote the widespread development of AWE. One other thing to note is that techno-economic analysis (TEA) should be employed to estimate the feasibility for the system of renewable energy powered AWE. In addition to electricity, the cost of input chemicals, product separation, installation and maintenance should be considered in TEA.

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碱性电解水高效制氢

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摘要: 与传统化石能源制氢技术相比，利用可再生能源驱动电解水制氢技术具有绿色可持续和制氢效率高等优势，被认为是目前最具前景的制氢方式。然而，由于电解水两极反应动力学缓慢、催化剂稳定性较差，限制了其大规模发展。此外，阳极析氧反应存在较高的过电势，从而导致当前制氢能耗与成本较高，严重制约了其商业化应用。为了解决上述问题与挑战，本文对当前发展较为成熟的碱性电解水技术进行了综合讨论与分析。首先，对电解水发展历程中的重要节点进行了总结，便于读者了解该领域。进一步，从电催化剂、电极、反应和系统的角度深入总结了提升电解水制氢性能的有效策略。作者分别介绍了近年来层状双金属氢氧化物基电解水催化剂、电解水制氢耦合氧化反应以及可再生能源驱动的电解水系统的重要研究进展；同时对结构化催化剂在电解水应用中的构效关系进行了深入分析。最后，对该领域存在的挑战和未来发展方向进行了展望，希望能为氢能的发展和推广提供一定的思路。

关键词: 电解水；制氢；结构化电极；耦合反应