Hydrogen Production Technology Promotes the Analysis and Prospect of the Hydrogen Fuel Cell Vehicles Development under the Background of Carbon Peak and Carbon Neutrality in China

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ABSTRACT: Hydrogen fuel cell vehicles have always been regarded as the main direction for developing new energy vehicles in the future due to their advantages of zero emission, high cruising range, and strong environmental adaptability. Currently, although the related technologies have gradually matured, there are still many factors hindering its development. One of the main reasons is that the price of hydrogen fuel increases the cost of using vehicles, which puts it at a competitive disadvantage compared with traditional fuel vehicles and pure electric vehicles. Herein, we summarize the recent development status of hydrogen fuel cell vehicles at home and abroad, and analyze the cost and sustainability brought by the latest scientific research progress to the hydrogen production industry, which is derived from basic research on electrocatalysts used in industrial electrocatalytic water splitting with an alkaline electrolyte. Finally, the development of hydrogen fuel cell vehicles was analyzed and prospected, which is one of the main application fields of hydrogen in the future.
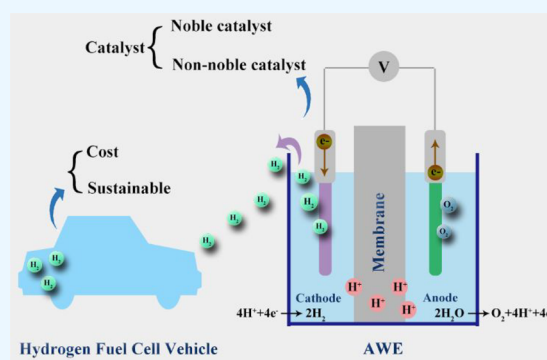
1. INTRODUCTION

With the end of the 2022 Winter Olympics and Paralympics, hydrogen fuel cell vehicles are once again in the public eye due to their high environmental protection and high adaptability. Such development of hydrogen fuel cell vehicles fits the theme of China's "double carbon" policy, which has been considered as one of the ultimate directions for the development of new energy vehicles.[1−4] Compared to traditional fuel vehicles, hydrogen fuel cell vehicles have great shortcomings in manufacturing and use costs, which is attributed to the high preparation cost of hydrogen fuel. Therefore, development of the hydrogen production industry plays a crucial role in the development of hydrogen fuel cell vehicles. Such green and low-carbon development advocated by the automobile industry is of great significance for promoting the implementation of the dual-carbon strategy. Fossil fuel hydrogen production and industrial byproduct hydrogen production technologies coincide with environmental pollution arising from carbon pollution emissions, which is gradually replaced by green hydrogen technologies. Electrolytic water hydrogen production technology is expected to become the mainstream development direction in the future. However, up to now, there is still no review paper on the combination of hydrogen production techniques and hydrogen fuel cell vehicles.

In the review, we summarize the development status of hydrogen fuel cells and the policies proposed by governments.

In addition, in order to improve hydrogen production yield, we discuss the research status of metal and non-noble-metal-based catalysts, and by comparison, we conclude that non-noble-metal-based catalysts are promising candidates for precious metals. Finally, the necessity for developing an alkaline water electrolysis hydrogen production technology is discussed from the perspective of cost and sustainability, and the challenges are also discussed.

2. DEVELOPMENT OF HYDROGEN FUEL CELL VEHICLES AND RELATED POLICIES

At present, the development of hydrogen fuel cell vehicles in China is mainly focused on passenger cars. Although the hydrogen fuel cell technology of China has not yet reached the world's first-class level, its research and development started at an early stage and accumulated a lot of achievements and experience, which has a good industrial development foundation. Also, we need to admit that there are still many

bottlenecks in the development of China's hydrogen fuel car industry, and many core technologies have yet to be broken through. Moreover, the relevant supporting facilities are still insufficient. With the elimination of cheap coal hydrogen production technology, the cost of hydrogen preparation is on the rise, and the cost of hydrogen fuel cell vehicles in China alone is about 20% higher than that of fuel cars.
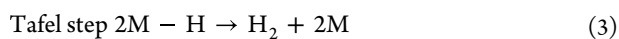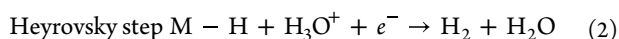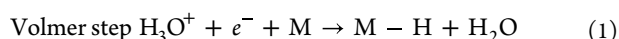
After the "double carbon" strategic goal was put forward, the new energy business has been developing rapidly.[5,6] At present, China has become the world's largest market for new energy vehicle consumption. According to the "New Energy Vehicle Industry Chain Database" released by GGII, Q1 global new energy passenger vehicle sales were about 1.023 million units in 2021 up, increased by 127% percentage points year-on-year. Among them, the new energy passenger car sales of China accounted for nearly half of the global market share, with a year-on-year growth rate of 334%. Moreover, hydrogen fuel cell vehicles are not only an important component in the development of new energy vehicles in China but also a core part of building our own core technology, contributing to transition from a big auto country to a strong auto country.[7,8] At the city level, more than 30 cities have formulated and released development plans for the hydrogen production industry, hydrogen fuel cell industry, hydrogen refueling stations, and other infrastructure construction, while special funds have been allocated to support the implementation of the relevant plans on the ground. At the national level, in order to strengthen the development of hydrogen fuel cell vehicles, China is further strengthening its support for the development of the hydrogen fuel cell vehicle industry and related supporting facilities and has issued a number of support policies in recent years (Table 1).

3. FUNDAMENTAL KNOWLEDGE FOR ELECTROCATALYTIC WATER SPLITTING

3.1. Mechanism of Electrocatalytic Water Splitting.
Currently, many methods have been used to obtain hydrogen such as fossil fuel hydrogen production, water gas reaction, ammonia borane hydrolysis, methane reforming, electrocatalytic water splitting, and petroleum gas cracking. Electrocatalytic hydrogen production is a process that directly converts electrical energy into chemical energy, which has merits of simple equipment, high hydrogen yield, high hydrogen purity, and environmental friendliness.[9] Furthermore, natural water resources are widely distributed, and electrocatalytic technology has become the main means of obtaining hydrogen in industry. Electrocatalytic water splitting is a hydrogen evolution reaction (HER) that occurs at the cathode. The main device is shown in Figure 1,[10] which consists of cathode and anode electrode plates, electrolyte solution, and an external power supply. The pH of electrolyte affects the reaction mechanism. The specific formula is as follows:[11,12]

Acid:

$$\text{Volmer step } H_3O^+ + e^- + M \rightarrow M - H + H_2O \tag{1}$$

$$\text{Heyrovsky step } M - H + H_3O^+ + e^- \rightarrow H_2 + H_2O \tag{2}$$

$$\text{Tafel step } 2M - H \rightarrow H_2 + 2M \tag{3}$$

Alkaline/Neutral:

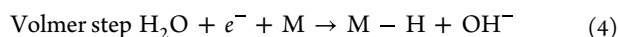$$\text{Volmer step } H_2O + e^- + M \rightarrow M - H + OH^- \tag{4}$$

Table 1. Some Policies Related to Hydrogen Energy Vehicles Issued by China in Recent Years

release time	policy name	related contents
2013	Notice on the Continuation of the Promotion and Application of New Energy Vehicles	Fuel cell passenger car subsidy is 200,000 RMB/vehicle, fuel cell commercial vehicle subsidy is 500,000 RMB/vehicle
2014	Strategic Action Plan for Energy Development (2014–2020)	Hydrogen energy and fuel cell technology innovation is listed as one of the 15 key tasks, and the hydrogen energy industry is elevated to the height of national energy development strategy for the first time
2015	Made in China 2025	Hydrogen fuel cell vehicles as the main development direction of new energy vehicles
2016	Notice on the Financial Support Policy for the Promotion and Application of New Energy Vehicles from 2016 to 2020	Subsidy standards for models other than fuel-cell vehicles are appropriately declining from 2017 to 2020
2018	Notice on Adjusting and Improving the Financial Subsidy Policy for the Promotion and Application of New Energy Vehicles	Subsidies of 200,000 to 500,000 RMB per vehicle are provided for different vehicle types depending on the ratio of the rated power of the fuel cell system to the rated power of the drive motor
2019	Action Plan for the Battle against Diesel Truck Pollution	Encourage local organizations to carry out demonstration operations of fuel cell trucks and build a number of hydrogens refueling demonstration stations
2020	Notice on Improving the Financial Subsidy Policy for the Promotion and Application of New Energy Vehicles	Strive to establish the hydrogen energy and fuel cell vehicle industry chain in about 4 years, make breakthroughs in key core technologies, and form a good situation of reasonable layout and coordinated development
2021	Notice on the Launch of Demonstration and Application of Fuel Cell Vehicles	Hydrogen fuel cell vehicle demonstration applications in city clusters submitted by Beijing, Shanghai, and Guangdong approved for official launch
2022	Medium and long-term plan for the development of hydrogen energy industry (2021–2035)	By 2025, the basic mastery of core technology and manufacturing process; by 2030, the formation of a more complete hydrogen energy industry technology innovation system; by 2035, the formation of hydrogen energy diversified application ecology
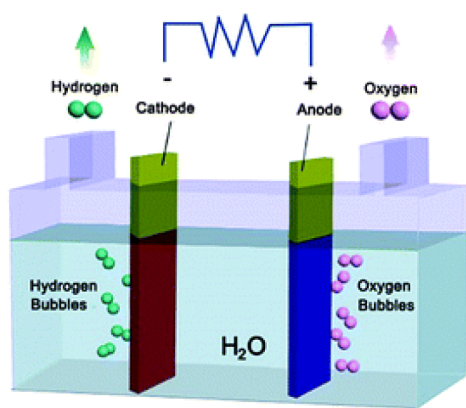
Figure 1. Device for producing hydrogen by electrocatalytic water splitting. Reprinted with permission from ref 10. Copyright 2015 The Royal Society of Chemistry.

Heyrovsky step $M - H + H_2O + e^- \rightarrow H_2 + OH^-$ (5)

Tafel step $2M - H \rightarrow H_2 + 2M$ (6)
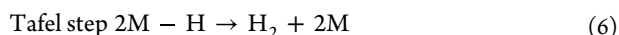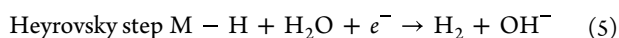
There are three technical routes thatcan be selected for electrocatalytic hydrogen production in industry, including alkaline water electrolysis (AWE), proton exchange membrane fuel cell (PEMFC), and solid oxide fuel cell (SOFC).[13−16] Compared to the latter two ways, AWE is a more mature technology at present, with low cost and high economic benefits (Table 2). However, it has high power consumption ($4.5-5.5$ kw·h·N^{-2}·m^{-3}). Therefore, it is necessary to choose high selectivity, high activity catalysts for accelerating reaction process, reducing energy consumption during reaction, and further cutting costs. Moreover, the alkaline electrolyte involves a H_2O splitting kinetics step, contributing to catalytic activity lower than that of the acid electrolyte. Thus, the electrocatalysts with a wide pH range remains to be considered.[17,18] However, the acid environment needs complicated equipment to protect electrocatalysts from corrosion. Thus, considering the cost, the research status of catalysts in alkaline electrolytes are discussed in the following.

3.2. Research Status of Catalysts for Alkaline Electrolysis of Water for Hydrogen Production.

At present, there are four standards to evaluate the catalytic performance of catalysts: (i) there are abundant activity sites in the surface of catalyst per area; (ii) there are high catalytic activity per active site; (iii) there is high conductivity for providing high-effective electron transport; (iv) there is high stability.[19−25] Precious metals Pt group metals such as Pd, Ir, and Ru, and their alloys are still the preferred catalysts for alkaline water electrolysis for hydrogen production due to their high catalytic activity. However, limited storage and the high cost of noble metals hinder the large-scale industrial production, while the non-precious-metal-based catalysts and their complexes can resolve this contradiction. They have become a candidate for replacing precious metals.[26] This section introduces the current research progress of alkaline water electrolysis catalysts from two aspects of noble-metal-based and non-noble metal-based catalysts.

3.2.1. Platinum Group Metals-Based Electrocatalysts. It is well-known that the binding energy between the intermediate H_{ad} and the catalyst determines the rate-determining step of the reaction process based on the Sabatier principle.[27−29] Too strong binding of H_{ad} limits to the release of H_2, reducing reaction speed. Conversely, the weaker binding energy makes H_{ad} difficult to adsorb. Therefore, the moderate adsorption and desorption energy is beneficial to the electrocatalytic reaction process. Sheng et al.[30] investigated the HER activity of a series of single-metal surfaces (Pt, Au, Ag, Cu, etc.) and established the relationship between the exchange current density and metal-H binding energy in alkaline electrolytes, with the energy calculated by density functional theory (DFT). The relationship of the volcano plot was drawn (Figure 2a). Similar to the acid HER volcano diagram, noble metal Pt is still the best catalyst for HER, while the nonprecious metals Fe, Co, and Ni are located in the left branch of the volcano diagram, indicating the strong binding energy between M−H, which is not conducive to the desorption of H atoms. Also, Cu, Au, and Ag metals are located in the right branch of the volcano diagram, indicating the weaker binding energy between M−H, which is not conducive to the catalytic reaction. However, in the actual reaction process, the agglomeration of Pt atoms leads to poor stability in the catalytic reaction process. In addition, the reserves of precious metal Pt are limited, which is not conducive to the long-term development of the alkaline water electrolysis hydrogen production industry. Thus, the design of nonprecious catalysts is critical.

Single atom (SA) catalysts have advantages of unique electronic structures, atomic-scale sizes, surface effects, and maximum atom utilization efficiency, providing high catalytic activity and selectivity. SAs have become the main choice in the field of electrocatalysis.[31−34] To maximize the catalytic activity of noble metal Pt, Zhou et al.[35] prepared single-atom Pt anchored on the surface of NiO/Ni nanosheets by a series of hydrothermal routes, electrodeposition, and electroreduction processes (Figure 2b), and the Ag nanowires were the support for PtSA-NiO/Ni to construct hierarchical three-dimensional morphology for the alkaline hydrogen evolution

Table 2. Comparative Analysis of Three Main Technical Parameters of Electrocatalytic Water Splitting for Hydrogen

|	AWE	PEMFC	SOFC
structure	simple	compact	
temperature (°C)	60−80	50−80	700−1000
electricity consumption (kw·h·N^{-2}·m^{-3})	4.5−5.5	3.7−4.5	2.6−3.6
hydrogen purity	>99.8%	>99.9%	>99.9%
operating characteristics	quick start and stop	quick start and stop	inconvenient to start and stop
dynamic responsiveness	strong	strong	weaker
life cycle	$(55-120) \times 10^3$ h	$(60-100) \times 10^3$ h	$(8-20) \times 10^3$ h
cost of investment (¥·kW^{-1})	3000−9000	8000−13000	>16000
degree of commercialization	full commercialization	preliminary commercialization	basic research
characteristics	mature technology, low cost	good adaptability of renewable energy	high conversion efficiency
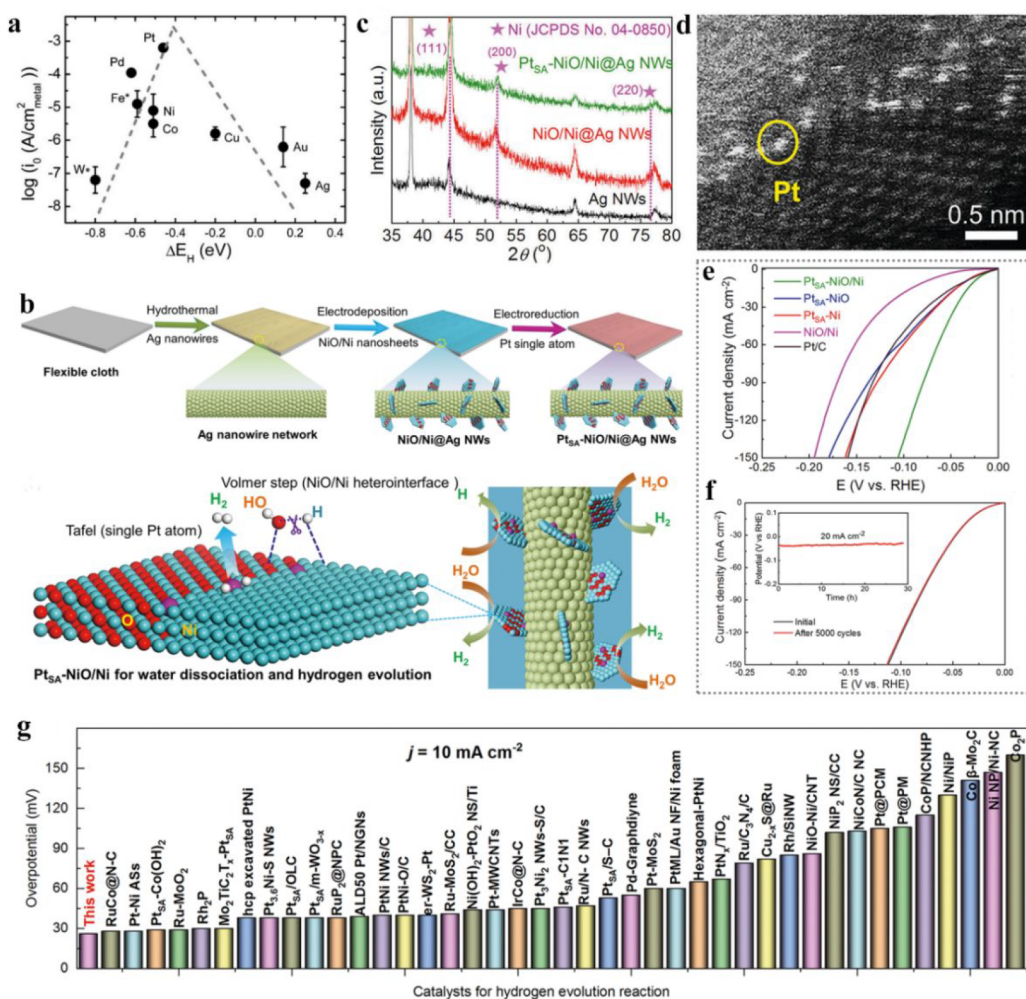
Figure 2. (a) HER volcano plot of single metals under alkaline conditions. Reprinted with permission from ref 30. Copyright 2013 The Royal Society of Chemistry. (b) Synthesis illustration of PtSA-NiO/Ni catalyst. (c) XRD patterns of Ag nanowires, NiO/Ni@Ag, and PtSA-NiO/Ni. (d) HAADF-STEM images of PtSA-NiO/Ni. (e) Comparison of linear scan curves of different catalysts. (f) $V-t$ stability and cyclic voltammetry stability tests. (g) Comparison of HER activities of PtSA-NiO/Ni and reported catalysts. Reprinted with permission from ref 35. Copyright 2021 Springer Nature.

reaction. Meanwhile, such strategy avoids the agglomeration of Pt single atoms. Both the X-ray diffraction (XRD) (Figure 2c) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 2d) patterns show the formation of Pt single atoms without the presence of nanoparticles and clusters. The reason for the excellent HER activity is mainly in the hierarchical interfacial coupling between Pt SAs and NiO/Ni that contributes to the tunable ability of H* and OH*, achieving efficient water molecule adsorption and dissociation processes. Moreover, the presence of 1D Ag nanowires facilitates the efficient electron transfer and mass transport, enabling efficient water molecule adsorption and dissociation processes and obtaining high stability and material activity (20.6 A mg^{-1}), which has surpassed the currently reported Pt-based electrocatalysts (Figure 2e). At the same time, the preparation of single-atom Pt catalysts can also reduce the use of precious metals. Such control of the amount of precious metals helps to reduce cost and further improves the HER performance.

Reducing the amount of noble metal (e.g., Ir, Ru, Rh, and Pd) by synthesizing Pt single atoms can further control the industrial cost. Designing active sites based on physicochemical

methods such as top-down or bottom-up methods is another way, thereby achieving excellent intrinsic activity.[36−40] For example, the coordination environment of noble metals can also be selected and adjusted, for achieving excellent electrochemical interfacial properties by optimizing the interface interaction. It is well-known that two-dimensional MXene possesses abundant surface terminal groups, good electronic conductivity, and natural hydrophilicity, thus, MXene can be use as a support of metal. In 2019, Ramalingam et al.[33] adjusted the coordination environment of MXene; the introduction of N and S contributes to the formation of Ru−N and Ru−S bonds, thereby the Ru SAs were stabilized on the surface of $Ti_3C_2T_x$ MXene (Figure 3a,b). Such an excellent coordination interaction improves the HER activity (Figure 3c). Furthermore, the defects have lower binding energy, so they can be used as anchoring sites to facilitate the interaction between metal and the substrate to accelerate the adsorption−desorption kinetics of H atoms. Therefore, efficient and stable HER activity can be achieved. Zhang et al.[41] prepared $Ti_3C_2O_2$−Pt SAs with an O vacancy catalyst by the rapid thermal shock technique (Figure 3d). The electron paramagnetic resonance (EPR) characterization confirmed the
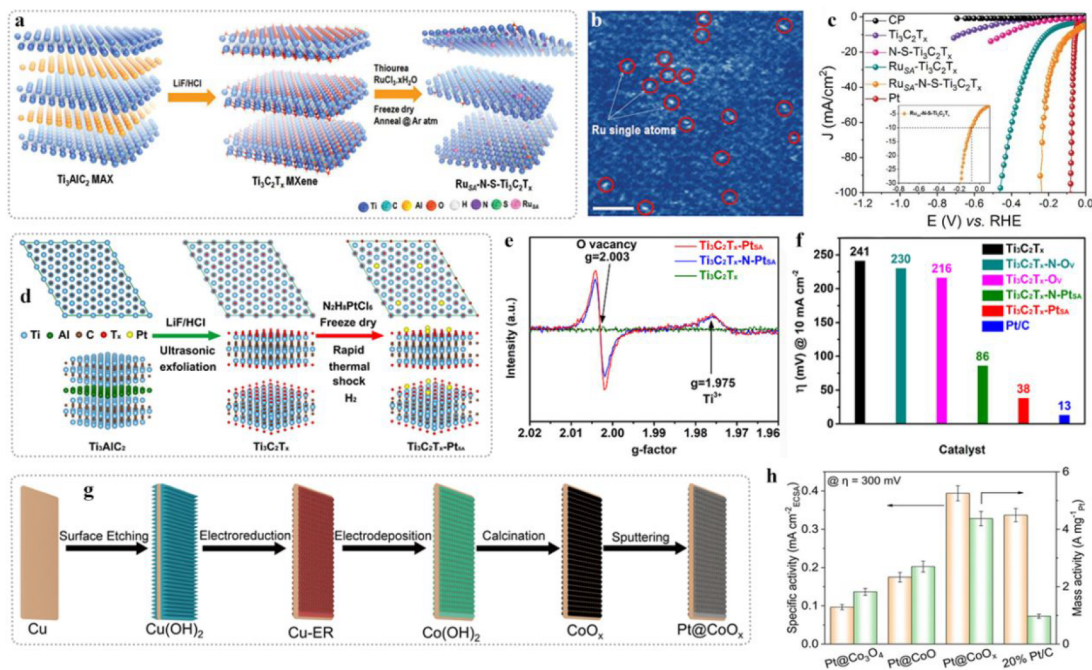
Figure 3. Design of noble-metal-based electrocatalyst. (a) Synthetic route of Ru-based catalysts with Ru−N−S coordination. (b) HAADF-STEM image of Ru−N−S−$Ti_3C_2T_x$. (c) HER curves of Ru-based catalysts. Reprinted with permission from ref 33. Copyright 2019 Wiley-VCH. (d) Synthetic route of Pt−$Ti_3C_2T_x$ with O vacancy. (e) EPR of catalysts. (f) HER activity comparison of catalysts. Reprinted from ref 41. Copyright 2022 American Chemical Society. (g) Synthetic route of Pt@CoOx. (h) Intrinsic activity comparison of Pt-based catalysts. Reprinted with permission from ref 42. Copyright 2022 Wiley-VCH GmbH.
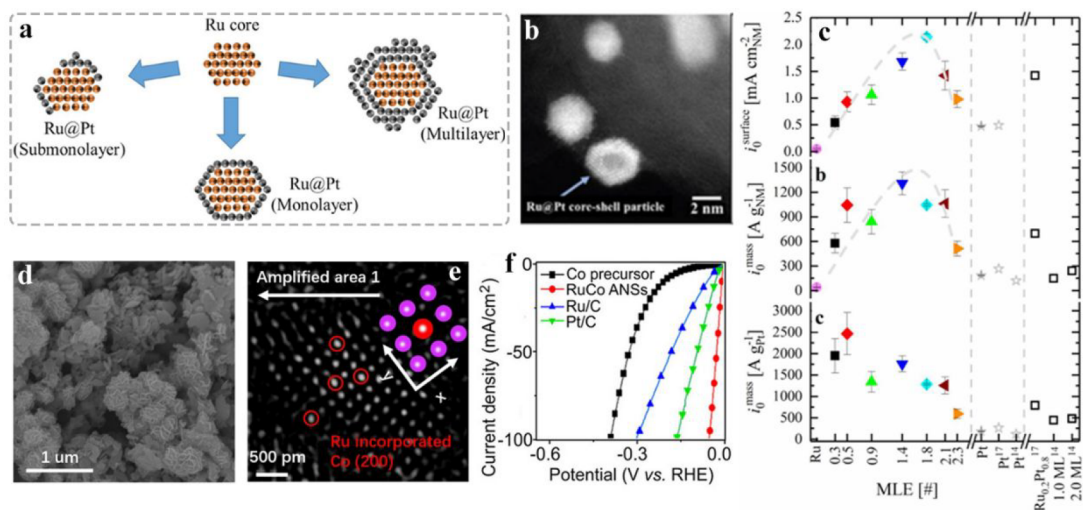

Figure 4. Synthesis and HER performance of noble metal nano alloy. (a) Synthesis route of Ru@Pt core−shell structure. (b) STEM of the Ru@Pt catalyst. (c) HER curve of Ru@Pt catalyst. Reprinted with permission from ref 43. Copyright 2018 ECS. (d) SEM image of RuCo alloy nanosheets. (e) Atomic structure of Ru substituted Co. (f) HER curves of Ru-based catalyst. Reprinted with permission from ref 44. Copyright 2022 Wiley-VCH GmbH.

presence of the O vacancy (Figure 3e). Experiment and density functional theory show that the O vacancy can decrease the binding energy and the hybridization strength of H atom supports, leading to the rapid HER reaction kinetics (Figure 3f).

Controlling the coordination environment of active sites is important for improving HER activity. However, the work function is another important factor. It can affect the surface charge distribution of the catalyst, and such variation of the charge distribution helps to adjust the built-in electric field (BEF), thereby controlling the binding energy between active

sites and H atoms. Zhai et al.[42] explored the HER activity of noble metal Pt on the support of CoOx in the neutral electrolyte (Figure 3g). The larger work function difference of Pt and CoOx induced the charge distribution of the interface, constructing strong BEF, further optimizing the adsorption energy of H (Figure 3h). Therefore, the intrinsic activity of Pt was controlled well. In summary, in experiment, there are many physicochemical methods to control the hydrogen production performance. In turn, it provides a favorable supply for the popularization of hydrogen fuel cell vehicles.
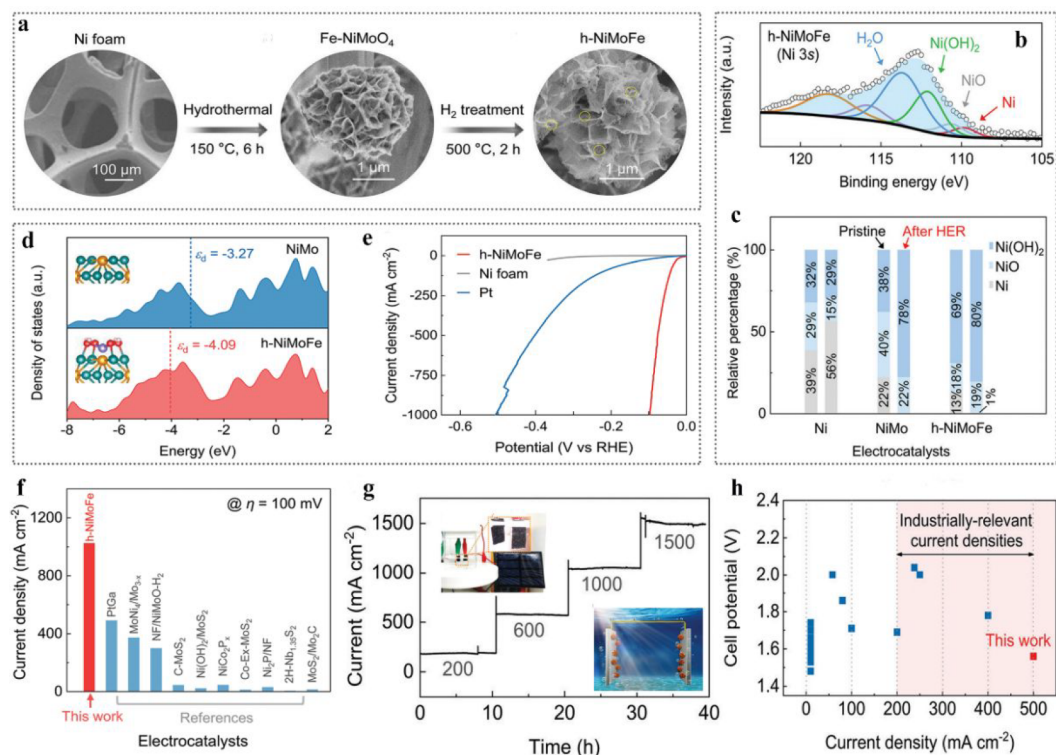
Figure 5. (a) Synthesis illustration of h-NiMoFe catalyst. (b) Ni 3s XPS spectrum of h-NiMoFe showing its surface composition. (c) relative percentage of Ni species on the surface of the Ni, NiMo, and h-NiMoFe sample from 0 to 1000 mA cm^{-2} before and after CV. (d) Partial density of states (PDOS) calculation of Ni in the NiMo (i.e., Ni$_4$Mo$_{(002)}$) plane (top) and h-NiMoFe plane (bottom); the d-band center of Ni (εd) is highlighted with dotted lines. (e) Performance test of different samples. (f) Performance comparison of h-NiMoFe and other catalysts that have been reported in the literature. (g) $I-t$ stability test at different voltages; inset shows a simulation of a commercial photovoltaic cell-driven monolithic water splitting device. (h) Comparison of the voltage of the catalyst composed of the full cell with the reported data. Reprinted with permission from ref 65. Copyright 2021 RSC.

Compared to a single metal catalyst, a noble metal alloy has been researched for exploring HER activity. Pt and Ru have ideal H adsorption Gibbs free energy.[30] However, the Pt−Ru alloy can provide unexpected activity. In 2018,[43] the researchers synthesized a Ru@Pt core−shell nanoalloy (Figure 4a). STEM can excellently show this structure (Figure 4b). The excellent HER performance originated from the electronic structure control of Pt to Ru metal (Figure 4c). In addition to the preparation of noble metal single-atom catalysts, the nanoalloys can also be prepared by introducing nonprecious metals to reduce the amounts of noble metals. Such strategy adjusts the electronic structure of the noble metal surface to achieve optimal surface adsorption and desorption activities. Cai et al.[44] prepared RuCo alloy nanosheets by a rapid co-precipitation method and a mild electrochemical reduction method, which can be demonstrated by scanning electron microscope (SEM) images (Figure 4d). Atomic-level-resolved STEM images and synchrotron radiation structure characterization show that Ru atoms are embedded in the Co substrate, and Ru atoms are isolated active centers with plane-symmetric and Z-direction asymmetric coordination structures. The optimal 4d$_{z^2}$ modulation electronic structure is obtained (Figure 4e). Based on the interaction between Ru−H, the electrochemical tests show that the RuCo alloy nanosheets achieve high stability and an ultralow overpotential of 10 mV at a current density of 10 mA/cm^2 in 1 M KOH solution, which is superior to that of commercial Pt/C (Figure 4f). In addition to the tuning of individual metal elements, noble metal oxides like IrO$_2$ are rarely used for the HER reaction due to their high

Gibbs free energy. However, depositing a small amount of noble metal in the surface tuned the surface electronic structure, optimized the Gibbs free energy of H atoms, and accelerated the reaction process, achieving excellent catalytic activity superior to that of Pt and long-term working stability.[45] In addition, transition metals such as Ni, Mo, and Cu and nontransition metals such as B, N, and P can also be used to tune the electronic structure of noble metals to achieve excellent catalytic activity.

In summary, the excellent catalytic activity and stability can be achieved by optimizing the amount of noble metal elements and the electronic structure of the noble metal or the interfacial interaction between the noble metal and the support, meeting the requirements of industrial production. However, the cost and limited reserves of noble metal elements is main problems that limit the large-scale application of noble-metal-based catalysts. Thus, the current research direction in the field of catalysts is the development of new noble-metal-based catalysts, and the development of nonprecious metal catalysts to replace noble metals is another effective way.

3.2.2. Non-precious-Metal-Based Electrocatalysts. Currently, looking for the low-cost, high-current density and durable electrocatalysts has become a main direction in industry. Compared to commercial Pt electrocatalysts for alkaline hydrogen evolution, the ink-type MoS$_2$-based electrocatalyst and mineral-based catalyst show outstanding hydrogen production performance, stability, and a high current density of 1000 mA cm^{-2}, and the price is far lower than that for Pt catalysts (5 orders of magnitude).[46] This research gives a
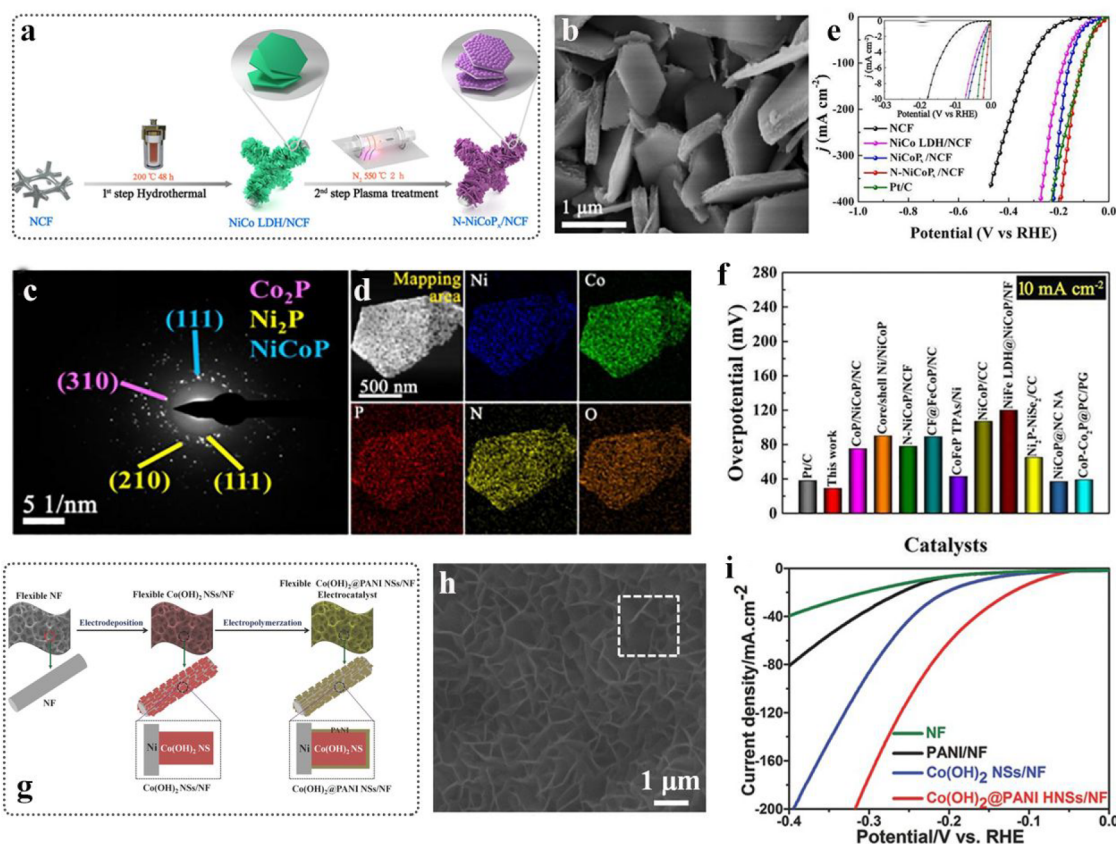
Figure 6. (a) Synthesis routes of N-NiCoP$_x$. (b) SEM of N-NiCoP$_x$. (c) Selected area electron diffraction (SAED) of N-NiCoP$_x$. (d) EDS mapping of N-NiCoP$_x$. (e) HER curves of catalysts. (f) Comparison of N-NiCoP$_x$ with previous reported catalysts. Reprinted with permission from ref 70. Copyright 2020 Elsevier B.V. (g) Synthesis of Co(OH)$_2$@PANI. (h) SEM of Co(OH)$_2$@PANI. (i) HER curves of Co(OH)$_2$@PANI. Reprinted with permission from ref 71. Copyright 2015 Wiley-VCH.

promising direction for acquiring substantiable nonprecious metal-based electrocatalysts. Interestingly, transition group metals (Fe, Co, Ni, Cu, etc.) expected to be substitutes for noble metal catalysts due to the merits of unique d-orbital electronic structures and good electronic conductivity.[47−54] In addition, the interaction between transition group metals and hydrogen atoms is unfavorable to the catalytic reaction based on the description of the HER volcano diagram. The design of transition group metals is necessary for preparing high-performance electrocatalysts. At present, the research about transition-metal-based catalysts mainly in the following ways: (i) The preparation of transition metals single atoms and select suitable supports to avoid single-atom agglomeration and optimize the contact interface achieves the maximum utilization of metal atoms.[55−57] (ii) The combination of transition metals and nonmetal elements can form transition metal phosphides, transition metal carbides, and transition metal sulfides and other compounds.[58−60] (iii) Melting different metal precursors to form alloys at high temperature obtains intermetallic atom electronic structure optimization.[61,62] Reducing the energy consumption during the water electrolysis reaction achieves a current density of greater than 500 mA cm^{-2} and high mechanical stability at high current densities, which is the industrial standard for the production of hydrogen from alkaline electrolysis water.[63]

Ni-based metals are widely used as alkaline water electrolysis catalysts due to their high electrical conductivity, low cost, abundant sources, and high catalytic activity.[64−66] However,

the practical industrial applications of nickel-based catalysts are limited by high energy consumption and high potential. In 2021, Luo et al.[65] prepared a high-performance nickel-based catalyst (h-NiMoFe) with three-dimensional porous morphology under high current conditions through hydrothermal reaction and high-temperature thermal reduction. Such three-dimensional porous morphology facilitates the sufficient contact between the catalytic site and the electrolyte (Figure 5a). The presence of Mo and Fe metal elements, which help to improve the valence of Ni element, leads to the formation of hydroxylation on the Ni surface (Figure 5b). Meanwhile, DFT shows that the introduction of Fe helps to change the d-band center of the Ni site, promoting a weak interaction between Ni−H, thereby optimizing the free energy of hydrogen adsorption (Figure 5c,d). The results show that the over-potential of the h-NiMoFe catalyst at a high current density of 1000 mA cm^{-2} is only 97 mV, which is much higher than that of the commercial noble metal Pt catalyst, and the current density is also much higher than that of the catalysts reported so far (Figure 5e,f). In addition, the h-NiMoFe catalyst was assembled into a catalyst for the full hydrolysis reaction, which only required a low voltage of 1.56 V to achieve a current density of 500 mA cm^{-2}, and obtained a high stability (Figure 5g,h). In addition, the price of the h-NiMoFe catalyst is about 82 US$ m^{-2}, which is similar to the price of commercialized nickel catalyst, but its performance is much higher than that of the commercial nickel catalyst, which has good practical prospects.
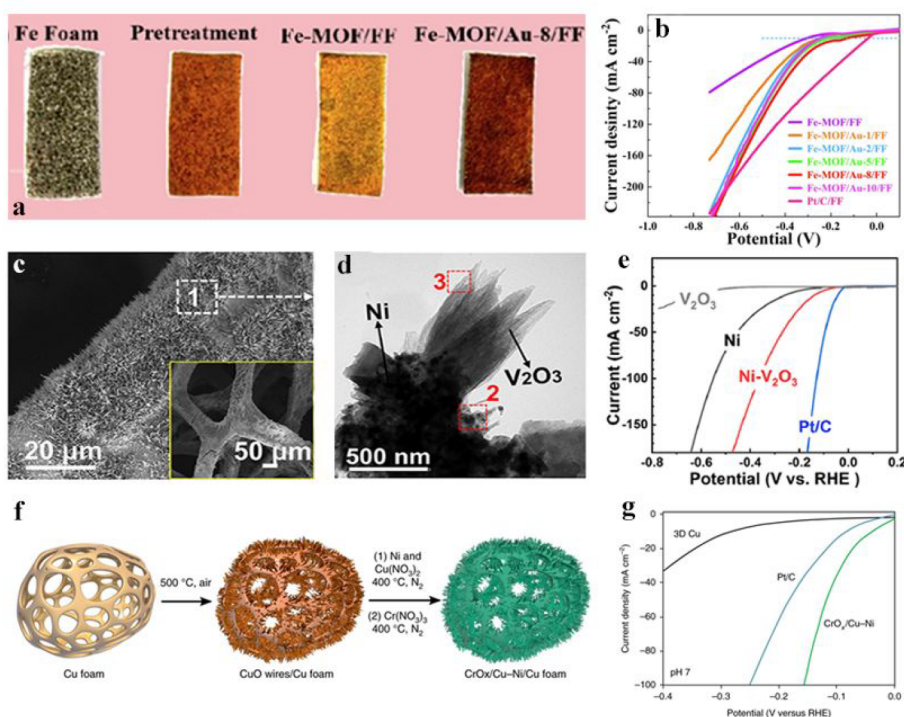
Figure 7. Integrated electrodes without binder and HER performance. (a) Optical photos of Fe foam-based electrocatalyst. (b) LSV curves of different Fe foam-based electrocatalysts. Reprinted with permission from ref 76. Copyright 2022 Elsevier Inc. (c) SEM images of Ni−V$_2$O$_3$. (d) TEM image of Ni−V$_2$O$_3$. (e) LSV curves of Ni-foam-based electrocatalysts. Reprinted with permission from ref 74. Copyright 2020 Elsevier B.V. (f) Synthesis route of Cu-foam-based catalyst. (g) LSV curves of Cu-foam-based catalysts. Reprinted with permission from ref 66. Copyright 2019 Springer Nature.

Non-metal-atom-doped (e.g., N, P, S, Cl) transition metal catalysts can effectively control the electronic structure of the active center.[67−69] Jin et al.[70] prepared N-doped Ni−Co phosphide catalyst by hydrothermal and plasma treatment methods (Figure 6a). The SEM image reveals the NiCo hydroxide nanosheet morphology (Figure 6b). Such morphology has large surface areas and provides abundant catalytic active sites. The component has been characterized by energy-dispersive spectrometry (EDS) (Figure 6d). Furthermore, the HER curves show that the activity of NiCoP (111) (Figure 6c) is analogous to that of commercial Pt/C and previous reports (Figure 6e,f). Therefore, such an electrocatalyst that is environmentally friendly, clean, and efficient is worth being populated. Moreover, for resolving the high stability issue, the composite catalysts have been prepared due to the synergistic effects, especially in transition-metal-based catalysts. Feng et al.[71] synthesized the Co(OH)$_2$@polyaniline composites (Figure 6g). Similar to previous reports, the nanosheet morphology shows excellent HER activity (Figure 6h,i).

In addition, considering the use of binder in powder catalysts will cover the partial active sites, and if the amount of binder is reduced, the catalyst will be peeled off during the catalysis process, resulting in poor stability.[72−75] Such a binder-free catalyst avoids the coverage of active sites, resulting in enhancement of catalytic efficiency. Therefore, the design of integrated electrodes has also become the first choice for electrocatalysts. Three-dimensional self-supporting transition metal supports such as iron-foam-, copper-foam-, and nickel-foam-based electrocatalysts provide abundant specific surface area, high conductivity, high porosity, and rapid gas release. It has also been widely used in non-precious-metal-based electrocatalysts. For example, Xu et al.[76] synthesized Fe-

MOF/Au/Fe foam electrocatalyst (Figure 7a); the Fe foam acts not only as a conductive support but also as a template to control the electronic structure of metal−organic frameworks, for improving the overall water splitting performance (Figure 7b). Meanwhile, the Ni foam[74,77] and Cu foam[66] possess excellent flexibility; they can also be used as a good substrate. Some research has made great progress (Figure 7c−g). Therefore, designing non-precious-metal-based electrocatalysts, except for considering the optimal hydrogen atom Gibbs free energy, the morphology, and dimension of the catalyst are also considered, which is beneficial to the transport of carriers and substances.

Based on the above information, the nonprecious metal catalysts can achieve good or even better activity compared to that of noble metal catalysts, which can effectively reduce production costs and have a good role in promoting the subsequent application of hydrogen.

4. DEVELOPMENT OF ALKALINE ELECTROLYTIC WATER HYDROGEN PRODUCTION TECHNOLOGY

At the present stage, the main methods of hydrogen production at the industrial level are fossil fuel reforming, biomass fuel hydrogen production, photocatalytic hydrogen production, and electrocatalytic hydrogen production. The process of fossil fuel hydrogen production is accompanied by CO$_2$ and other polluting gas emissions, and the hydrogen obtained from the biomass fuel method requires a complex purification process, which are all "gray hydrogen". The industry's recognized development direction should be "green hydrogen", which is produced without pollutants. Among them, photocatalytic hydrogen production mainly relies on the light source as the driving force; however, it is easily affected by

the weather. The alkaline electrolytic water hydrogen production technology is simple; the process is mature and reliable, and the purity of hydrogen production can be over 99%. Therefore, electrocatalytic hydrogen production is expected to achieve large-scale application. Also, the laboratories in universities and research institutes around the world are actively researching electrocatalysts for large-scale hydrogen production, which is expected to become the main way of industrial hydrogen production in the future. Furthermore, the cost and sustainability are discussed for analyzing the advantages of electrocatalytic techniques in the following.

4.1. Costs. The cost of hydrogen production is calculated by the formula of alkaline hydrogen production: cost = electricity price × unit electricity consumption + (annual depreciation + annual operation and maintenance),[78] and combined with the actual production costs, the cost of hydrogen production by electrolytic water is about 30 RMB/ kg, which is much higher than the cost of 8−10 RMB/kg of fossil fuel reforming hydrogen production, which is the lowest cost at present in China.[79] However, the process of hydrogen production from fossil fuels produces a lot of pollution emissions, which is not in line with the requirements of the policy of "double carbon". In order to achieve green hydrogen production, the electrolytic hydrogen production has a wide scope of cost reduction and still is the most promising. For example, Prof. Song Li and Prof. Jiang Jun of the University of Science and Technology of China (USTC) designed a "loose ball structure" catalyst with needle tips, which reduced the amount of platinum metal by nearly 75 times compared to commercial platinum carbon catalysts, while maintaining the same catalytic effect for hydrogen production.[80] This significantly reduces the cost of producing hydrogen from alkaline electrolytic water in industry while also increasing the yield of hydrogen. Therefore, reducing energy consumption by improving catalysts is an economical, practical, and efficient means. Its effective reduction in the cost of hydrogen can lead to a significant reduction in the cost of using hydrogen energy vehicles.

Furthermore, from the perspective of electrolyte, fresh water appears to have lower hydrogen production costs. However, at present, there are more than 100 countries experiencing different degrees of water shortage all over the world, among which 28 countries are classified as water-scarce or severely water-scarce countries.[81,82] For some countries lacking fresh water, it is difficult for life and agriculture to provide sufficient water. Therefore, large-scale hydrogen production from fresh water is basically impossible, which makes the idea of adjusting the energy structure and improving the global environment through green hydrogen empty talk. Moreover, seawater is the most abundant resource in the world (96.5% of the world's water is seawater);[83−86] if seawater desalination can be carried out to produce hydrogen, and cooperate with the advanced wind power, it not only can improve the utilization rate of long-distance wind power generation but also can generate green hydrogen energy and obtain high-purity fresh water.[87,88] As a result, such a combination can achieve the dual purpose of seawater purification and hydrogen production and alleviate the dual crisis of energy and fresh water shortage. However, the high abundance of seawater resources is faced with the dilemma of complex composition and difficult purification.[89] This is due to the presence of a large number of metal ions, microorganisms, and particulate impurities in seawater, which

lead to the formation of competitive side reactions in the process of electrolysis of water for hydrogen production, which is not conducive to the main reaction and may damage the electrolysis device.[90] Therefore, the desalination of seawater to form high-purity fresh water is of great significance for reducing the cost of hydrogen acquisition.

4.2. Sustainability. The main raw material used in domestic hydrogen industry, fossil fuel, is a primary energy source with wide distribution in nature but limited reserves. Thus, the hydrogen production through fossil fuels is unfavorable to the sustainability planning of hydrogen. Electrolytic water splitting mainly uses water as the most reactant; water resources on Earth are widely distributed. Although the currently most efficient Pt metals total only 14,000 tons in the world, its scarce reserves have been a major reason to limit the large-scale application of hydrogen production. With the continuous research on non-precious-metal-based electrocatalysts, the sustainability problem of precious metal catalysts in electrolytic water hydrogen production technology, which is limited by the precious metal reserves, will be further improved.

5. CONCLUSIONS

For achieving the goal of high-current density in industry, it is necessary to discuss the difficulty of hydrogen production by alkaline water electrocatalysis. On the one hand, the amount of electrocatalytic active sites is beneficial for producing more H atoms. On the other hand, the interaction between H atoms and active sites is intrinsically the reason for obtaining high current density. Therefore, it is important to design basic electrocatalysts through physical and chemical methods. As H_2 as an important fuel, it is worthwhile to devote more efforts to exploring the preparation of electrocatalysts. Although there have been many achievements, there are still many challenges to making this technology practically useful.

(1) The cost of hydrogen directly determines the future development of hydrogen fuel cell vehicles in China, and minimizing the cost of hydrogen requires the joint efforts of many aspects and the whole industry chain. Herein, we briefly analyze the new scientific progress of catalysts in industrial alkaline electrolytic water hydrogen production, mainly involving reducing the use of precious metal catalysts, from reducing the size of precious metals to achieve the maximum efficiency of catalyst atom utilization or using nonprecious metals and their compounds to partially or completely replace the precious metal catalysts, thereby optimizing the morphology, electronic structure of catalysts, and surface/interfacial interactions. Thus, the adsorption and desorption strength of hydrogen atoms will be adjusted during the electrocatalytic hydrogen evolution reaction, achieving excellent electrocatalysts with low cost, low-energy consumption, high activity, and high stability. Furthermore, the research and exploration of hydrogen storage, transportation, and filling should also be the focus.

(2) According to market research data, the current hydrogen market mainly coexists with gray hydrogen, blue hydrogen, and green hydrogen. Among all, gray hydrogen is the main way, and the market share exceeds 60%.[91] Green hydrogen technology, developed to achieve carbon neutrality, has a market share of only 1.5% due to its high cost.[92] With the increasing demand for hydrogen energy in various fields, large-scale photovoltaic power generation or wind power generation supporting electrolyzed water production of green hydrogen

will become a trend in the future. In turn, the development of the green hydrogen industry will also promote electrolyzers and the advancement of new energy source equipment. At present, hydrogen production from alkaline water electrolysis is the main force in the development of green hydrogen technology, with mature technology and a market share of 70−80%. While the research on PEMFC and SOFC water electrolysis remains in the laboratory's basic research stage, especially for PEMFC, the market share is only between 5 and 10%.[93,94] Therefore, breaking through the technical bottleneck of hydrogen production from alkaline electrolysis water and speeding up the process of the other two technologies in the research and development period is of great significance for achieving mass production of green hydrogen and accelerating the pace of realizing the zero-carbon market.

(3) Currently, although much progress has been made in optimizing the activity of catalysts, there are still many unaddressed issues. For example, research on cost reduction by completely replacing noble metals with nonprecious metals is still limited. Although it has some advantages in cost, further research is needed to completely replace their highly active performance and explore the mechanism. In addition, current research on catalysts is only limited to basic research in the laboratory, and the large-scale application in industrialized alkaline electrocatalytic hydrogen production remains to be realized.

(4) The development mode of hydrogen fuel cell vehicles in China is not like the standard system in the United States and Japan, which is relatively single. We should rationally learn from relevant foreign technologies and further improve the overall level by combining our national conditions as well as practical problems. Moreover, the production of high energy conversion efficiency and high-purity hydrogen by electrolytic water technology is an effective strategy to promote the further development and application of hydrogen fuel cell vehicles. As the main productive force for China to realize the "automobile power", the development of hydrogen gas directly determines the future development of the hydrogen fuel cell vehicle industry in China. With the continuous progress of science and technology, and the government attention and capital investment, the fuel cell vehicle technology will gradually be maturing, and the problem of lagging construction of related supporting facilities is gradually being solved. With the simultaneous development of hydrogen production technology, it is believed that, in the near future, fuel cell vehicles will definitely form a three-legged situation with fuel cars and pure electric vehicles.

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Notes

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