

Progress in the Application of Electrocatalysts

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Abstract: With the increasing demand for energy and the non renewability of fossil fuels, renewable clean energy is favored by people, among which hydrogen energy has attracted much attention due to its high energy density and abundant raw materials. Electrolysis of water for hydrogen production is an important method for the preparation of hydrogen energy, consisting of OER and HER reactions. However, due to its limited reaction rate, efficient catalysts are required to accelerate the reaction process. Common precious metal catalysts such as Pt based and Ir based catalysts have high activity, good stability, but high cost. Non precious metal catalysts are inexpensive and have abundant reserves, but their stability and performance are slightly inferior to precious metal catalysts. This article starts from the mechanism and introduces the reaction steps and principles of OER and HER. It focuses on the research and development progress of precious metal catalysts and non precious metal catalysts in recent years. By analyzing the recent catalyst improvement methods, it summarizes the common catalyst optimization ideas and makes prospects for the future development direction of catalysts.

Keywords: Hydrogen from electrolyzed water, Electrocatalysis, Precious metal catalysts, Stability, Reaction rate

1. Introduction

In the development process of human civilization, the use of fossil fuels has played a key role. According to the 2024 World Energy Statistical Yearbook released by the Energy Research Institute, the proportion of fossil fuels is still as high as 81%. But with the rapid development of modern society and economy, the demand for energy by humans is increasing. In addition, the non renewability of fossil fuels has led to a decreasing amount of fossil energy stored on Earth. Moreover, fossil fuels release various harmful substances such as sulfur oxides, carbon oxides, volatile organic compounds, and heavy metals during use, which not only pollute the natural environment but also endanger human health. In this context, humanity has to turn its attention to renewable, green, environmentally friendly, and sustainable clean energy. In clean energy, hydrogen energy has attracted widespread attention due to its high energy density per unit mass, low-carbon lifecycle, and unrestricted geographical location. The electrolysis of water for hydrogen production stands out due to its abundant raw materials, high product purity, and flexible production. The electrolysis of water for hydrogen production mainly includes two half reactions, namely cathodic hydrogen evolution reaction (HER) and anodic oxygen evolution reaction (OER). Compared with HER, OER involves four electron transfer and complex intermediate products, and its kinetics is about three orders of magnitude slower than HER, becoming the limiting step of the overall reaction. Therefore, the

development of efficient catalysts is of great significance for the development of electrolysis of water for hydrogen production. The commonly used catalysts currently include precious metal catalysts (platinum based catalysts, iridium/ruthenium catalysts, etc.) and non precious metal catalysts (nickel cobalt iron-based catalysts). Precious metal catalysts have good activity, but high cost and are prone to poisoning; Non precious metal catalysts have low cost, good stability, but low density of active sites and are easily soluble under acidic conditions. These various factors are driving people to continuously explore catalysts for hydrogen production through electrolysis of water. For example, Sun Licheng's team at West Lake University synthesized the NiFe based catalyst CAPist-L1 in a non-uniform nucleated liquid-phase system at room temperature and pressure, achieving stable operation for 19000 hours under high current. This article aims to summarize the current development status of hydrogen production through electrolysis of water and its catalysts. By introducing the principle of hydrogen production through electrolysis of water and comparing the differences between different catalysts, it reveals the current technological bottlenecks, looks forward to future research directions, and provides theoretical basis for the preparation of low-cost and high-efficiency catalysts.

2. Principle reaction mechanism of hydrogen production by electrolysis of water

2.1. Oxygen precipitation reaction

The overall reaction equation for the anodic oxygen evolution reaction (OER) is $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, with four electrons involved in the reaction, and is therefore generally considered a four electron transfer process. The specific process is as follows:

The reaction steps that occur on the surface of the catalyst in an acidic electrolyte are as follows:

Firstly, water adsorbs on the surface of the catalyst, forming adsorbed water molecules. Then, a proton is removed to form an adsorbed hydroxyl group, while releasing an electron, resulting in $\text{H}_2\text{O} + * \rightarrow \text{OH}^* + \text{H}^+ + \text{e}^-$

The adsorbed hydroxyl group removes another proton and releases an electron to form adsorbed oxygen, which occurs as $\text{OH}^* \rightarrow \text{O}^* + \text{H}^+ + \text{e}^-$

Water molecules combine with adsorbed oxygen to form an intermediate product, adsorbed peroxide hydroxyl, which simultaneously releases a proton and an electron, resulting in $\text{O}^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + \text{H}^+ + \text{e}^-$. Finally, the adsorbed peroxide hydroxyl group decomposes, releasing one proton and one electron to form oxygen, which then desorbs from the catalyst surface, resulting in $\text{OOH}^* \rightarrow \text{O}_2 + \text{H}^+ + \text{e}^- + *$

The reaction steps that occur on the surface of the catalyst in alkaline electrolyte are as follows:

Firstly, hydroxide ions adsorb on the surface of the catalyst, releasing an electron to form an adsorbed hydroxyl group, which occurs $\text{OH}^- + * \rightarrow \text{OH}^* + \text{e}^-$. The formed adsorbed hydroxyl group reacts with hydroxide ions to form adsorbed oxygen and water molecules, while releasing an electron, resulting in $\text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + \text{e}^-$

Adsorbed oxygen continues to combine with hydroxide ions to form adsorbed peroxy hydroxyl groups, which release an electron

$\text{O}^* + \text{OH}^- \rightarrow \text{OOH}^* + \text{e}^-$ Finally, the adsorbed peroxide hydroxyl group combines with hydroxide ions to form oxygen and water molecules, releasing an electron. Subsequently, oxygen desorbs from the surface of the catalyst.

In the above formula, * represents the active site of the catalyst. Due to the involvement of multiple OOH^* , OH^* , O^* and other reaction intermediates, as well as multi electron transfer processes, the oxygen evolution reaction is slow. Therefore, developing efficient catalysts can help improve the reaction rate and reduce the overpotential of the reaction.

2.2. Hydrogen evolution reaction

The total reaction equation of cathodic hydrogen evolution reaction (HER) is $2H^+ + 2e^- \rightarrow H_2$, involving two electron transfer processes. Like OER, the reaction pathway is also affected by the acidity or alkalinity of the solution.

The reaction steps of HER in acidic electrolyte are as follows:

Hydrogen ions in the solution adsorb on the surface of the catalyst and obtain electrons to form adsorbed hydrogen, which undergoes the Volmer reaction: $H^+ + e^- \rightarrow H^*$

Adsorbed hydrogen can be generated into hydrogen gas through two pathways:

The Heyrovsky step involves the binding of adsorbed hydrogen with another hydrogen ion to obtain an electron, resulting in the formation of hydrogen gas: $H^* + H^+ + e^- \rightarrow H_2$

Alternatively, through the Tafel step, two adsorbed states of hydrogen can be directly combined to form hydrogen gas: $H^* + H^* \rightarrow H_2 + *$

In alkaline or neutral environments, the amount of hydrogen ions is very small, so the mechanism is different from that in acidic environments, as follows:

Water molecules adsorb on the catalyst surface and combine with an electron to form adsorbed hydrogen and hydroxide ions, undergoing the Volmer reaction: $H_2O + e^- + * \rightarrow H^* + OH^-$

Adsorbed hydrogen can also generate hydrogen gas through two pathways:

Heyrovsky step: Adsorbed hydrogen combines with water molecules and obtains an electron to form hydroxide ions and hydrogen gas: $H^* + H_2O + e^- \rightarrow H_2 + OH^- + *$

Tafel steps: $H^* + H^* \rightarrow H_2 + *$

In general, the HER reaction mechanism can be divided into Volmer Heyrovsky and Volmer Tafel processes under both acidic and alkaline conditions. It should be noted that compared to acidic electrolytes, the dissociation process of water also needs to occur under alkaline and neutral conditions, which usually requires additional energy consumption and affects the overall reaction rate. The efficiency of hydrogen production by electrolyzing water under acidic conditions is about three orders of magnitude lower.

3. Research status of anode oxygen evolution catalysts

Anode oxygen evolution catalyst is the core material for hydrogen production by electrolysis of water, and its performance directly affects energy conversion efficiency and cost. At present, common anode oxygen evolution catalysts include precious metal based catalysts, non precious metal based catalysts, and novel composite catalysts. Precious metal based catalysts are considered to have good performance and extremely high stability, but their high cost and limited reserves severely limit their large-scale application. Non precious metal based catalysts are not only abundant in production, but also inexpensive, only one thousandth of precious metals. After appropriate improvements, they possess high activity and stability, and can even surpass precious metal based catalysts. The new composite catalyst can combine the advantages of different materials to achieve the synergy of precious metals and non precious metals, providing unlimited possibilities for improving the efficiency of anodic oxygen evolution reaction.

3.1. Precious metal based catalysts

Ir based and Ru based catalysts are the main representatives of precious metal catalysts, which have better performance than Pt based and Rh based catalysts and are also one of the few commercial catalysts. The OER overpotential of Ir based and Ru based catalysts is significantly lower than that of non precious metal catalysts, making them highly catalytic active; And Ir based catalysts can exhibit extremely strong corrosion resistance in strong acids, which are the core advantages that make

precious metal catalysts the mainstream catalysts. However, the shortcomings of precious metal catalysts are also evident, as the scarcity of resources and high costs constrain the large-scale production and use of precious metal catalysts.

In recent years, researchers have continuously improved precious metal catalysts. Bertheussen et al. successfully prepared IrRuNi nanoparticle catalysts by introducing nickel (Ni) in the supercritical solvothermal synthesis process, changing the structure of Ir Ru and improving its OER performance by 2.6 times compared to IrRu catalysts without Ni [1]. Simeng Wang et al. synthesized W-IrRuO_x catalyst [2] by sol-gel method doped with non precious metal tungsten (W), which realized the reduction of overvoltage from 305mV of IrRuO_x to 249mV, and the current density reached 51.2mAcm⁻² (7.6 times of IrO₂) at 300mV overvoltage.

3.2. Non-precious etal based catalysts

Non precious metal catalysts are mainly composed of Earth abundant metals such as Fe, Co, Ni, Mn, etc., and their cost is much lower than that of precious metal catalysts. Therefore, the research and development of non precious metal catalysts has become a research direction for many researchers. The mainstream types of non precious metal catalysts are as follows:

3.2.1. Transition metal oxides

With the advantages of low cost, high activity, and multi scenario adaptability, transition metal oxide catalysts have entered people's field of vision. Different types of oxide catalysts, such as single metal oxides and composite metal oxides, have the potential to replace precious metal catalysts. A research team has developed two-dimensional transition metal oxychalcogenides, which regulate the oxygen content in the material and achieve continuous structural evolution from transition metal dichalcogenides to metal oxides. As shown in the left column of Figure 1, the mass activity at 0.5V overpotential is 103000 A g⁻¹, and the right line graph shows that after 24-hour stability testing, the overpotential only increases by 14±3mV [3]. It exhibits extremely high oxygen evolution reaction activity and stability in acidic media.

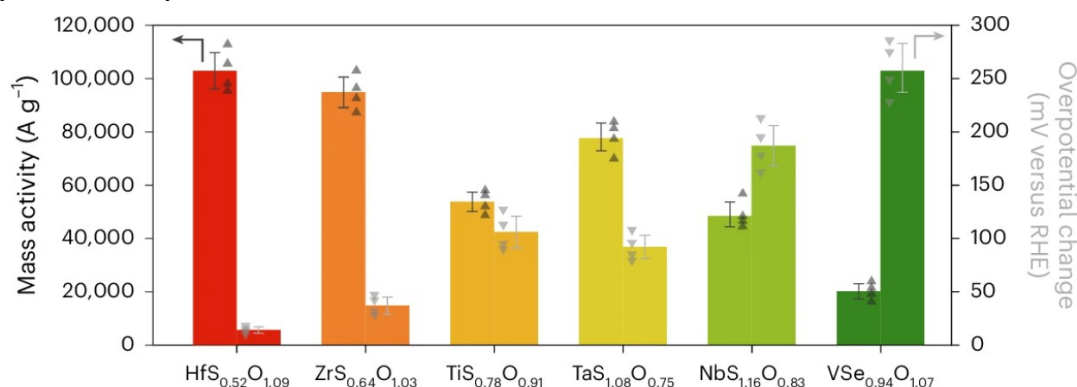


Figure 1: Comparison among different TMOCs of mass activity (left) at the overpotential of 0.5 V versus RHE and potential change (right) after 24h at 50 mA cm⁻². Error bars represent the s.d. of four independent measurements and the data distribution is shown using grey triangles

In addition, the Key Laboratory of New Power Batteries at Nanjing Normal University used plasma assisted strategy to disperse single atom Ce in CoO and construct Ce (4f) — O (2p) — The Co (3d) gradient orbital coupling structure was found to enhance the covalency of Co-O, achieving a Tafel slope of only 75mV dec⁻¹ [4], which outperforms pure CoO catalysts in performance.

3.2.2. Transition metal nitrides

Nitride catalysts with superior conductivity and high corrosion resistance compared to oxides have become highly promising materials in OER catalysts. The Dalian University of Technology team introduced a negatively charged PO_4^{3-} layer on the surface of NiO through low-temperature phosphorylation, achieving an overpotential of 228 mV ($10 \text{ mA}/\text{cm}^2$) and a Tafel slope of 29.9 mV/dec in 1M KOH. The catalyst can operate for 2500 hours.

$1 \text{ A}/\text{cm}^2$ in alkaline seawater with a performance degradation of only 34 mV [5], demonstrating both activity and stability, providing a typical example of high-performance catalyst for industrial seawater hydrogen production. As early as 2022, the laboratory of Nankai University attempted to pyrolyze Ni Mo urea precursor and synthesize NMN-MO-NO ternary composite catalyst to achieve synergistic effects of conductivity optimization, porous structure increasing active sites, and Ni Mo interaction optimizing electronic structure [6], greatly improving the performance of oxygen evolution reaction, as shown in Figure 2

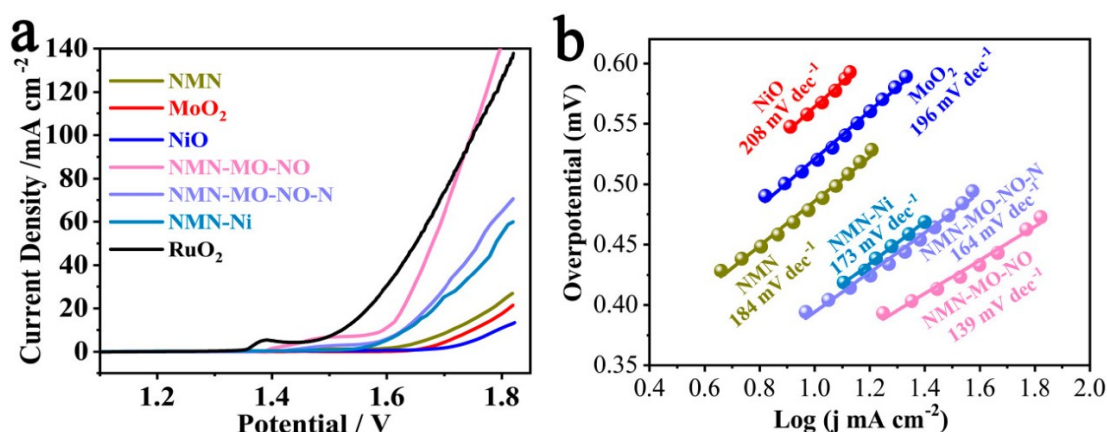


Figure 2: OER performance of different test samples in 1.0 M KOH: (a) LSV polarization curves; (b) tafel slopes

The NMN-MO-NO ternary composite catalyst exhibits excellent performance in alkaline environments compared to materials such as NMN, MoO_2 , and NiO, demonstrating the potential of non precious metal OER catalysts in multiphase composites and surface engineering [7,8].

4. Non precious metal based catalysts

In recent years, inexpensive and abundant non precious metal catalysts have become increasingly popular among people. With the improvement of non precious metal catalysts, they have gradually gained activity and high stability that are not inferior to precious metal catalysts. The non precious metal catalysts widely studied at present are as follows:

4.1. Transition metal alloys

There are various combinations of transition metal alloy catalysts, which utilize the advantages of alloys to regulate the hydrogen adsorption energy on the metal surface, improve catalytic activity, and can significantly reduce research and development costs by adding non precious metal materials. Balancing cost, activity, and stability is an important research direction for HER catalysts. Armin et al. [9] prepared CoCuFeNiMnMo alloy powders using ball milling method, and added five or more elements to form high entropy alloys with high entropy effect. The introduction of Mo can also optimize electron transfer and improve surface active sites. In HER performance testing, the

overpotential was 275mV (10 mA/cm²) in 1M KOH, the Tafel slope was 125 mV/dec, and the stability exceeded 72 hours [10]. Chao Yue Zhang's team found that doping anions (such as sulfur) into metal catalysts can enhance catalytic activity through anion mediated electron transfer. The Co MoS₂ catalyst prepared from this can significantly reduce polarization voltage [11]. This anion electron density model provides new ideas for the development of novel catalysts.

4.2. Transition metal nitrides

The d-band center of transition metal nitrides is close to Pt, and the hydrogen adsorption energy is close to the ideal value, indicating a relatively high catalytic activity [12]. Based on the strategy of eliminating vacancy gaps, the Liming Dai team proposed introducing C atoms into Mo₂N and designed a stoichiometric Mo₂CN. By hybridizing the 2p orbitals of C with the 4d orbitals of Mo, the d-band center of Mo was reduced to optimize the hydrogen desorption/adsorption process. Wenya Zhang et al. found that all doped systems were thermodynamically stable by embedding single transition metal atoms into graphite phase nitrogen doped carbon,

The Rh doped catalyst exhibits the lowest binding energy and the best catalytic performance [12]. This single atom catalyst has low cost, high stability, and HER performance close to noble metal catalysts, making it a highly promising non noble metal catalyst.

5. Conclusion and outlook

This article provides a brief summary of the current development status of OER and HER catalysts by listing and analyzing literature from recent years. For precious metals, common optimization strategies include doping other metal elements such as Co, Ni, Fe, etc. into precious metal catalysts, alloying them, and optimizing the surface adsorption/desorption ability of the catalyst through electronic and synergistic effects. This can reduce the amount of precious metals used, lower costs, and improve the activity and stability of the catalyst; Alternatively, excellent carriers such as metal oxides can be chosen to disperse noble metal nanoparticles, utilizing surface defects to enhance the interaction between the metal and the carrier. Common improvement methods for non precious metal catalysts include doping heteroatoms into the catalyst, introducing oxygen vacancies to provide active sites, and changing the surface electron density of the catalyst; Or by introducing multiple metals to form alloys, high entropy effects can be formed, and the advantages of high entropy alloys can be utilized to improve the performance of catalysts.

Although precious metal catalysts have high activity and stability, they are limited by cost and storage, making it impossible to produce them in industrial quantities. Therefore, how to use as few precious metals as possible to achieve better catalytic effects has become the primary issue. Non precious metal catalysts can achieve the performance of precious metal catalysts through numerous improvement methods, but their stability and safety still need to be verified and are difficult to cycle for a long time. But with the advancement of human technology, we are gradually finding more and more ways to overcome difficulties. We look forward to developing high activity, high stability, and low-cost green catalysts that combine the advantages of precious and non precious metals in the future, providing a solid foundation for sustainable development of clean energy.

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