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Research Progress on Electrocatalytic Materials for Water Electrolysis

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Abstract

Firstly, the application prospect of electrolytic water reaction is introduced, and then the relevant mechanisms of hydrogen evolution reaction and oxygen evolution reaction of electrolytic water are described. The research status of catalysts for hydrogen and oxygen evolution from electrolyzed water, mainly acid oxygen evolution catalyst and basic hydrogen evolution catalyst, was introduced. Finally, a summary and prospect of the water electrolysis catalyst are given.

Keywords

Hydrogen Evolution Reaction; Oxygen Evolution Reaction; Electrocatalysis.

1. Introduction

The increasing depletion of fossil fuels and environmental pollution have accelerated global research and development of new energy sources. Among these, hydrogen energy has garnered widespread attention due to its high energy density and environmentally friendly characteristics. Hydrogen can be produced through water electrolysis. The hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) occur at the cathode and anode, respectively, in the water electrolysis process. Both HER and OER are uphill reactions, requiring efficient catalysts to reduce the reaction barriers and enable the industrial-scale production of hydrogen. For OER catalysts, their high working potential and the highly alkaline or acidic reaction environment significantly impact the stability and longevity of electrolysis devices. The electrochemical catalysis process involves the adsorption of reactants on active sites, their conversion, and the desorption of products. Therefore, constructing highly active catalysts requires tuning the electronic structure of active sites to facilitate the mild adsorption and transformation of electrochemical reactants, thereby enhancing the intrinsic catalytic activity of the catalyst. Additionally, controlling the morphology of the catalyst can expose more active sites, improving its utilization and enhancing the apparent catalytic activity. To ensure the stability of catalysts, particularly OER catalysts, strong electronic interactions and confinement effects must be employed to inhibit the electrochemical dissolution of active sites at high potentials, thus improving catalyst stability. Currently, the most commonly used cathode catalyst in industry is platinum, while precious metal oxides such as RuO_2 and IrO_2 are typically employed as anode catalysts. However, because the water electrolysis reaction usually takes place in highly acidic or alkaline environments with working voltages ranging from 1.4 to 2.0 V, the stability of the catalysts is severely challenged. At the same time, considering the cost requirements for industrial-scale production, there is a pressing need for higher catalytic efficiency. As a result, the development of efficient and stable catalysts has become a hot research topic in the field of water electrolysis.

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2. Overview of Water Electrolysis Reaction

Figure 1 illustrates the schematic diagram of water electrolysis. As shown in the figure, the water electrolysis device mainly consists of the electrolyte, cathode, and anode. The water electrolysis reaction comprises two half-reactions: the reduction reaction at the cathode and the oxidation reaction at the anode. Specifically, the reduction reaction at the cathode corresponds to the hydrogen evolution reaction (HER), while the oxidation reaction at the anode corresponds to the oxygen evolution reaction (OER). The overall reaction equation is expressed as follows: $2H_2O \rightarrow O_2 + 2H_2$.

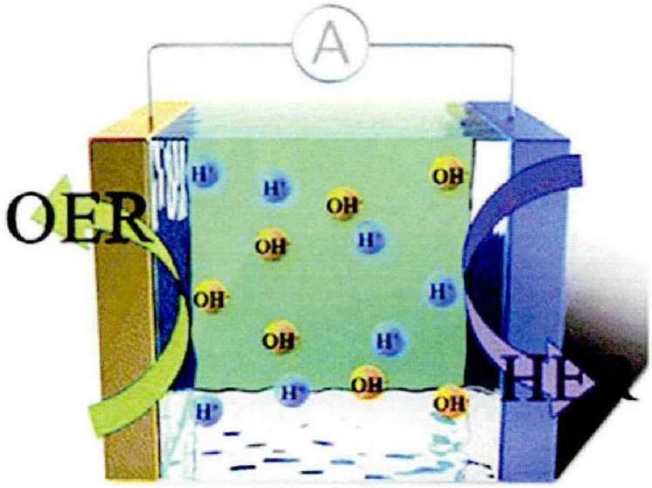

Figure 1. Schematic of electrolyzed water.

3. Electrocatalytic Materials for Water Electrolysis

Both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) in water electrolysis are heterogeneous reaction processes. In Proton Exchange Membrane (PEM) electrolysis and Alkaline Water Electrolysis (AWE) cells, the electrolyte is in solution form, making these two half-reactions solid-liquid interface electrocatalytic processes. The three primary factors that influence the catalytic performance of electrocatalytic materials are the active sites, reaction kinetics, and conductivity. In recent years, numerous researchers have made significant efforts to develop electrocatalytic materials for water electrolysis. The following section briefly outlines the research progress in the field of water electrolysis catalysis materials.

3.1. Acidic Electrolyte Oxygen Evolution Materials

For solid-liquid interface electrocatalytic reactions, the intrinsic catalytic activity of electrocatalysts for water splitting and oxygen evolution is primarily determined by the binding energy between the catalyst surface active sites and the reaction intermediates in the oxidized state. An optimal binding energy allows for a dynamic process of both adsorption and desorption of the intermediates. When the binding energy of the intermediates is too low, these reaction intermediates are difficult to activate; conversely, when the binding energy is too high, the intermediates will occupy all the active sites and fail to desorb, causing surface poisoning and catalyst deactivation [1]. In the case of oxygen evolution in water electrolysis, the main active metal components can be classified into two categories: one consisting of precious metals such as Ru, Ir, and Pt, and the other consisting of non-precious metals such as Co, Ni, and Mn.

Currently, research on anode catalysts for oxygen evolution in acidic water electrolysis remains largely focused on precious metal catalysts. Among these, RuO_2 has been widely used as a

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commercial electrocatalyst to enhance the efficiency of electrocatalytic water splitting for oxygen evolution reactions [2]. However, there are still significant barriers to the large-scale industrialization of RuO_2, mainly due to its high cost as a precious metal and its poor stability. To address these issues, many research groups have conducted extensive studies. To improve the utilization of ruthenium atoms, efforts have been made to enhance the morphology of RuO_2 by synthesizing catalysts at the nanoscale, thus increasing the exposure of ruthenium atoms [3]. Regarding stability, research has focused on doping the surface of RuO_2 with heteroatoms such as Mn and Pb to optimize its electronic structure [4,5], or developing perovskite-type ruthenium catalysts (which may include elements like Sb, Ba, or Y) to slow down the dissolution rate of ruthenium to some extent [6].Zhengxin Qian and colleagues reported an electrochemical lithium (Li) intercalation method to enhance the acidic oxygen evolution reaction (OER) activity and stability of RuO_2. In this approach, Li ions are inserted into the RuO_2 lattice, which not only induces electron transfer but also causes local structural distortions. As a result of electrochemical Li intercalation, the oxidation state of Ru is reduced, and a stable Li-O-Ru local structure is formed. This weakens the covalent bonding of the Ru-O bond, thus inhibiting the dissolution of Ru and significantly improving the durability of the catalyst. Additionally, the inherent lattice strain causes the surface structure of $LixRuO_2$ to distort, activating the oxygen-bridging bonds (O*) near the Ru active sites. This facilitates the stabilization of the OER intermediate OOH*, leading to a substantial improvement in catalytic activity [7]. Iridium-based electrocatalysts remain the only relatively practical anode catalysts for proton exchange membrane (PEM) water electrolysis due to their exceptional stability under acidic oxygen evolution reaction (OER) conditions. However, their high cost and limited availability present significant limitations. In response to this, Luo Yu and colleagues proposed a nickel-stabilized ruthenium dioxide (Ni-RuO_2) catalyst as a potential alternative to iridium. This Ni-RuO_2 catalyst has demonstrated high activity and durability in the acidic OER of PEM water electrolysis, offering a promising solution to reduce reliance on expensive iridium-based catalysts [8].

3.2. Alkaline Electrolyte Hydrogen Evolution Materials

Compared to the oxygen evolution reaction (OER) that involves a four-electron transfer process, the hydrogen evolution reaction (HER) in water electrolysis involves only a two-electron transfer, making its reaction mechanism simpler and more well-defined. In the case of the hydrogen evolution reaction, the main active metal components are precious metals such as Pt and Ir, as well as non-precious metals such as Fe, Co, and Ni.

For hydrogen evolution in water electrolysis, much of the research has focused on transition metal compounds, such as metal sulfides, selenides, phosphides, and nitrides [9,10]. Breakthrough studies have also been made regarding the hydrogen evolution reaction (HER) in alkaline environments. For instance, the research group of Sim reported the electrocatalytic hydrogen evolution performance of nickel sulfide nanoparticles in an alkaline environment, with the catalytic activity following the trend Ni_3S_2 > NiS_2 > NiS [11]. Among these, the Ni_3S_2 material achieved a hydrogen evolution overpotential of η_{10} = 335 mV and a Tafel slope of 97 mV dec^{-1}. Similarly, optimizing the morphology and structure of catalyst materials can further enhance their electrocatalytic hydrogen evolution performance. For example, in the 2014 study by Jin's group, CoS_2 catalytic materials with different morphologies, including film-like, micron-scale linear arrays, and nano-scale linear arrays, were grown on graphite substrates [12]. The corresponding electrocatalytic hydrogen evolution overpotentials for these different morphologies were η_{10} = 190 mV, η_{10} = 158 mV, and η_{10} = 145 mV, respectively. Compared to the film-like CoS_2 catalyst, the array-structured CoS_2 catalysts required a lower overpotential, with the enhanced electrolysis performance attributed to the optimized morphology. Carbon materials, with their diverse structural morphologies, remain highly suitable for electrocatalytic water splitting, particularly for hydrogen evolution reactions (HER). Dan Li and

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colleagues designed a novel hybrid electrocatalyst consisting of single Pt atoms fixed on partially amorphous NiRu hydroxides (NiRu-OH) with abundant functional groups (referred to as Pt/NiRu-OH) [13]. The formation of functionalized NiRu-OH and the fixation of Pt atoms both occur in an alkaline three-electrode system, where Pt serves as the counter electrode. The synthesized Pt/NiRu-OH exhibited high catalytic activity for HER under alkaline conditions, with an overpotential (η) of 10 mA cm^{-2} and high intrinsic catalytic activity. This study demonstrated that NiRu-Layered Double Hydroxides (LDH) can transform into partially amorphous NiRu-OH during the OER process, generating a large number of functional groups for fixing single Pt atoms. This low-Pt-loading hybrid catalyst provides a promising pathway for achieving efficient HER catalysis in alkaline media.

4. Conclusion

To enhance the efficiency of hydrogen production via water electrolysis, researchers have developed numerous efficient, stable, and cost-effective composite electrode materials using various methods and materials, achieving significant progress and breakthroughs in large-scale applications. The realization of large-scale, efficient, and rapid hydrogen production is not only related to the electrode materials but also heavily influenced by other factors such as electrolyzer design and operational conditions. In the field of catalytic hydrogen production, the research and development of efficient, stable, and low-cost composite electrode materials hold significant practical value. Therefore, theoretically designing electrode materials with higher catalytic activity and long-term stability remains a critical task and direction for future research efforts.

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