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Review on the Effect of Manganese Oxides on Oxygen Evolution in Electrolytic Water

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Abstract

Manganese oxides have important research value and application potential in oxygen evolution reaction (OER). As the core reaction of energy technologies such as electrolytic water and metal-air batteries, the kinetic process of OER is slow and overpotential is high, and efficient catalysts are needed to improve the reaction efficiency. Manganese oxide has become the focus of OER catalyst research because of its abundant reserves, low cost, environmental friendliness, controllable electronic structure and electronic structure. In recent years, researchers have significantly improved the OER properties of manganese oxides by means of nanostructure design, doping modification and defect engineering. This paper mainly introduces the research progress of manganese oxides, and summarizes the problems to be solved to enhance the stability of manganese based oxides and improve the hydrogen production rate.

Keywords

Manganese Oxides; Electronic Structure; Electronic Structure.

1. Introduction

With the global transformation of energy structures and increasing emphasis on environmental protection, hydrogen energy, as a clean and efficient energy form, has garnered widespread attention[1]. The primary methods of hydrogen production include chemical, physical, and electrolysis approaches, among which water electrolysis for hydrogen generation has become a research hotspot due to its pollution-free nature, controllable process, and high energy conversion efficiency[2,3]. In the water electrolysis process, the Oxygen Evolution Reaction (OER) is a critical reaction, as its efficiency directly impacts the energy conversion efficiency of the overall process. However, the OER typically requires a high overpotential, and the performance of electrode materials significantly influences its catalytic activity[4,5]. Therefore, the development of highly efficient, stable, and cost-effective catalysts is key to advancing the industrialization of water electrolysis.

Among numerous catalyst materials, transition metal oxides, particularly manganese oxides, have emerged as a focal point of research due to their excellent electrocatalytic properties and low cost. The abundance and low oxidation states of manganese in the periodic table endow manganese oxides with significant economic advantages. Moreover, the catalytic performance of manganese oxides in the Oxygen Evolution Reaction (OER) has garnered considerable attention from researchers. Studies have shown that manganese oxides not only exhibit favorable electrical conductivity, catalytic activity, and stability but also allow for performance optimization through structural modulation and synthesis methods. With ongoing research, the potential of manganese oxides in the OER for water electrolysis has been increasingly unveiled, establishing them as a critical component in the field of water electrolysis catalysts.

Water electrolysis is a process that decomposes water molecules into hydrogen and oxygen using electrical energy, as represented by the following reaction:

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$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

During this process, two half-reactions occur on the surface of the electrodes in the electrolyzer: the reduction reaction at the cathode generates hydrogen, while the oxidation reaction at the anode produces oxygen. The Oxygen Evolution Reaction (OER), as the anode reaction, involves the oxidation of water molecules and is described by the following equation:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

The OER not only requires overcoming the high energy barrier associated with water oxidation but also faces challenges such as the generation of oxygen bubbles and the formation of gas films during electrolysis, which further increase the energy consumption of the reaction[6,7]. Therefore, reducing the overpotential of the OER, enhancing the reaction rate, and improving the stability of catalysts have become central issues in water electrolysis research.

2. Catalytic Mechanism and Structural Characteristics of Manganese Oxides

Manganese oxides, as catalysts for the OER, offer unique advantages. Firstly, they can be synthesized through various methods at relatively low costs. Manganese is an abundant element in the Earth's crust, and its oxides exhibit catalytic performance in water electrolysis that is more economically viable and widely applicable compared to precious metal catalysts such as platinum and iridium. Secondly, manganese oxides possess highly tunable structures, with different oxidation states (e.g., MnO_2, Mn_2O_3, Mn_3O_4) and various crystal forms (e.g., α-MnO_2, β-MnO_2, γ-MnO_2), which significantly influence their catalytic properties[8]. Additionally, the catalytic activity and stability of manganese oxides can be further enhanced through methods such as doping and alloying.

2.1. Catalytic Mechanism of Manganese Oxides

The catalytic mechanism of manganese oxides is relatively complex and is generally believed to be closely related to their crystal structure, changes in oxidation states, and the processes of surface oxygen adsorption and desorption. In the Oxygen Evolution Reaction (OER), manganese oxides release oxygen by altering their oxidation states (e.g., Mn(III)/Mn(IV)), a process considered the primary driving force for the OER. Notably, MnO_2, compared to other transition metal oxides such as iron oxides and cobalt oxides, exhibits lower overpotential and higher stability. Additionally, manganese oxides possess high electrical conductivity, which facilitates efficient electron transfer, thereby improving the energy conversion efficiency of the water electrolysis process.

Despite the promising catalytic performance of manganese oxides in the OER, their practical application faces several challenges. Firstly, manganese oxides suffer from relatively poor stability, particularly under high current densities and potentials, where structural degradation or loss of activity during redox cycling may occur. Therefore, enhancing the durability and stability of manganese oxides to prevent performance degradation during electrolysis is a critical research focus. Secondly, although manganese oxides exhibit high catalytic activity, they still demonstrate certain overpotentials under specific reaction conditions, leading to energy efficiency losses. Reducing overpotentials and further improving catalytic activity remain key challenges in optimizing the performance of manganese oxide catalysts.

To enhance the application performance of manganese oxides in the OER for water electrolysis, researchers have proposed various modification strategies. For instance, doping with other transition metals (e.g., iron, cobalt) can modulate the electronic structure and catalytic activity

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of manganese oxides, improving their stability. Utilizing catalyst supports such as carbon materials or conductive polymers can enhance the electrical conductivity of manganese oxides, promoting electron transfer. Furthermore, nanostructured manganese oxides can provide more active sites, thereby further boosting catalytic performance. Nevertheless, the application of manganese oxides still faces numerous technical challenges. Future research will focus on catalyst structural design, stability enhancement, and cost control to advance their widespread use in industrial water electrolysis.

2.2. Changes in Oxidation States of Manganese Oxides

The catalytic activity of manganese oxides is closely related to the variation in their oxidation states. In oxides, manganese typically exists in three oxidation states: Mn(II), Mn(III), and Mn(IV). During the Oxygen Evolution Reaction (OER), the oxidation state of manganese undergoes dynamic changes, with the transition between Mn(III) and Mn(IV) being considered a critical step in the OER. Specifically, manganese oxides facilitate the adsorption of water molecules and their subsequent oxidation through redox cycling, releasing oxygen in the process.

In the OER, the Mn(III) and Mn(IV) sites on the surface of manganese oxides participate in electron transfer. Mn(III) is oxidized to Mn(IV), releasing electrons in the process. The higher oxidation state, Mn(IV), reacts with oxygen atoms from water molecules to form oxygen gas, which then desorbs from the catalyst surface. This transformation of oxidation states and the interplay between oxygen species adsorption and desorption are key driving forces of the reaction.

The catalytic performance of manganese oxides is also closely tied to their surface structure. Different crystal structures of manganese oxides, such as α-MnO_2, β-MnO_2, and γ-MnO_2, exhibit distinct pore structures and active sites. Manganese oxides with high specific surface areas and open pore structures can provide more active sites, enhancing the reaction rate. Additionally, the exposed manganese ion sites on the surface play a significant role in catalytic performance. During the OER, oxygen atoms on the surface of manganese oxides strongly interact with oxygen atoms from water molecules, promoting the generation of oxygen gas.

MnO_2, a common manganese oxide, typically exhibits a distribution of oxidation states (e.g., Mn(III) and Mn(IV)) on its surface. The interconversion of these oxidation states endows MnO_2 with excellent catalytic activity and stability in the OER. The electron transfer process during the catalytic OER is crucial. In the reaction, oxygen atoms from water molecules are adsorbed onto the catalyst surface and oxidized to form oxygen gas under the influence of electrons. During this process, surface oxygen atoms of manganese oxides gradually release oxygen through electron transfer while maintaining the stability of the catalyst.

In summary, the catalytic mechanism of manganese oxides involves multiple aspects, including oxidation state changes, surface structure modulation, and electron transfer. By tuning the structure and oxidation states of manganese oxides, the overpotential of the OER can be effectively reduced, and the reaction efficiency improved. This is a key reason why manganese oxides are considered promising catalysts for water electrolysis.

3. Practical Application of Manganese Oxides and Problems to Be Solved

3.1. Catalytic Mechanism of Manganese Oxides

In practical applications, manganese oxides primarily leverage their unique redox properties to facilitate the oxidation of water molecules, generating oxygen. Studies have shown that manganese oxides such as MnO_2, Mn_3O_4, and Mn_2O_3 exhibit relatively low overpotentials and high stability in various water electrolysis systems, making them widely used as anode catalysts. To further enhance their catalytic performance, researchers have optimized manganese oxides

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through methods such as alloying, doping, and nanostructuring. For instance, doping with elements like iron or cobalt can modulate the electronic structure of manganese oxides, improving their electrical conductivity and reaction activity.

Moreover, manganese oxides have been applied in high-efficiency water electrolysis devices, particularly in small- to medium-scale hydrogen production, demonstrating promising industrial potential as an economical and sustainable alternative catalyst. Nevertheless, the long-term stability of manganese oxides remains a challenge. Future research will focus on improving their durability and optimizing catalytic performance to enable broader industrial adoption.

3.2. Manganese Oxides Need to Be Solved

Although manganese oxides have demonstrated excellent catalytic performance in the Oxygen Evolution Reaction (OER) for water electrolysis, their practical application still faces several challenges, primarily related to stability, catalytic activity, and corrosion resistance.

Firstly, the stability of manganese oxides remains a significant issue under high potentials and prolonged operation, particularly at high current densities. Manganese oxide catalysts are prone to dissolution, structural degradation, or loss of activity during redox cycling, leading to a decline in catalytic efficiency. Enhancing the durability of manganese oxides and extending their operational lifespan are critical research priorities. Secondly, the catalytic activity of manganese oxides still exhibits relatively high overpotentials under certain conditions, especially at high current densities, resulting in lower reaction efficiency. Although improvements have been made through doping and alloying, further reducing overpotentials and enhancing catalytic efficiency remain pressing challenges.

To address these issues, three main strategies have been proposed to improve the performance of manganese oxides: Nanostructuring, Porosity, and Surface Design: Nanostructuring and creating porous architectures can significantly increase the specific surface area and active sites of manganese oxides, thereby improving the efficiency of catalytic reactions. By controlling the size and morphology of nanomaterials, the electronic structure of the catalyst can be optimized, enhancing its stability and reaction rate under high current densities. Doping and Composite Catalyst Construction: Doping with other transition metals (e.g., iron, cobalt, copper) or constructing composite catalysts can further modulate the electronic structure and catalytic performance of manganese oxides[7,9–11]. Multimetal catalysts not only improve catalytic activity but also enhance stability and corrosion resistance. This multi-element co-catalysis strategy has been proven to significantly boost the electrocatalytic performance of manganese oxides. Surface Modification Techniques: To improve the stability of manganese oxides, researchers are exploring various surface modification techniques, such as applying coatings, encapsulation, or protective layers to prevent catalyst dissolution or corrosion. These strategies can effectively extend the catalyst's lifespan and enhance its durability in practical applications.

4. Conclusion and Prospect

Manganese oxides have demonstrated significant potential as efficient and cost-effective catalysts for the Oxygen Evolution Reaction (OER) in water electrolysis. Their unique redox properties, tunable oxidation states, and diverse crystal structures enable them to facilitate the OER with relatively low overpotentials and high catalytic activity. However, challenges such as limited stability under high current densities, susceptibility to corrosion, and the need for further overpotential reduction remain critical barriers to their widespread industrial application.

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To overcome these limitations, advanced strategies such as nanostructuring, doping with transition metals, and surface modification have been employed to enhance the performance and durability of manganese oxide catalysts. These approaches have shown promising results in increasing active sites, optimizing electronic structures, and improving corrosion resistance. Despite these advancements, further research is needed to fully realize the potential of manganese oxides in practical water electrolysis systems.

Prospects for Future Research:

1)Stability Enhancement: Developing innovative approaches to improve the long-term stability of manganese oxides under harsh operational conditions, such as high potentials and current densities, will be critical for their industrial adoption.

2)Catalytic Activity Optimization: Further reducing overpotentials and improving reaction kinetics through advanced material design, such as multi-element doping and hybrid catalyst systems, will enhance energy efficiency.

3)Scalability and Cost-Effectiveness: Exploring scalable synthesis methods and low-cost raw materials will be essential to make manganese oxide catalysts economically viable for large-scale hydrogen production.

4)Mechanistic Studies: Deeper insights into the catalytic mechanisms, particularly the role of oxidation state transitions and surface interactions, will guide the rational design of next-generation catalysts.

In conclusion, manganese oxides hold immense potential as sustainable and efficient catalysts for water electrolysis. With continued advancements in material design and engineering, they are poised to play a pivotal role in the global transition toward clean energy and green hydrogen production.

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