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Research Progress on Ruthenium-based Electrocatalysts for Oxygen Evolution Reaction in Water Electrolysis

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Abstract

Water electrolysis, as a green hydrogen production technology, involves both the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER). Researchers have been dedicated to developing high-activity, low-cost electrocatalytic materials for water electrolysis. Among these, ruthenium (Ru)-based OER materials stand out due to their exceptional catalytic activity, universality, and relatively low cost within the precious metal family, making them highly promising for future development. This paper provides a comprehensive review of recent advances in Ru-based catalytic materials, including ruthenium oxides, ruthenium nanoparticles, and ruthenium single atoms. Finally, the challenges faced by Ru-based catalysts in OER and the potential future developments are discussed.

Keywords

Ruthenium; Water Electrolysis; Oxygen Evolution Reaction.

1. Introduction

With the over-exploitation and use of traditional fossil fuels, the emission of carbon dioxide has intensified, exacerbating the greenhouse effect and leading to global extremes, which pose significant challenges to the sustainable development of human society. As fossil fuels are depleting due to their limited resources, the development of sustainable, clean alternative energy sources has become a global issue that must be addressed. Hydrogen energy is a secondary clean energy source with broad availability, abundant reserves, zero carbon emissions, high calorific value, high conversion efficiency, high energy density, and extensive applications [1]. It can also be used as an excellent energy storage carrier, offering an effective solution for large-scale inter-regional and inter-seasonal transportation and storage [2]. Experts and scholars consider it one of the ideal renewable energy carriers to replace traditional fossil fuels in the future.

The water electrolysis process for hydrogen production is highly regarded due to its low cost and zero carbon emissions. The only reactant is water, and hydrogen is produced without any pollution or environmental issues. The water electrolysis process includes the anode oxygen evolution reaction (OER) and the cathode hydrogen evolution reaction (HER) [3]. In electrochemical cells, water splitting occurs through the HER at the cathode and the OER at the anode. Various electrocatalytic materials have been developed for OER, including precious metal materials, transition metal materials, and heteroatom-doped materials. While many non-precious metal materials have been developed for OER, precious metal catalysts still exhibit the highest activity under acidic conditions. For example, Pt/C is widely used as the benchmark for HER, while IrO_2/RuO_2 serves as the benchmark for OER [4,5]. Thus, precious metal catalysts remain promising materials.

According to the volcano plot of oxygen intermediate binding energies, ruthenium (Ru) and iridium (Ir)-based OER catalysts are currently known to exhibit reasonable activity and

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stability under acidic conditions [6-8]. While Ir exhibits lower activity, it is more stable under acidic conditions; however, the higher cost of iridium compared to ruthenium remains a limitation. Iridium's relatively high loading (greater than 2.0 mg cm^{-2}) is one of the main constraints on the large-scale development of PEM-based hydrogen production technologies. As the least expensive member of the Pt-related precious metal family, ruthenium-based materials, compared to Ir-based catalysts, provide relatively superior OER activity [9].

In this review, we discuss the research progress of ruthenium-based catalytic materials for acidic oxygen evolution in water electrolysis. The different types of ruthenium-based catalytic materials include ruthenium oxides, ruthenium nanoparticles, ruthenium single atoms, and ruthenium-doped materials.

2. Research Progress on Ruthenium-based Electrocatalytic Materials for Water Electrolysis

The ruthenium-based catalytic materials developed to date have been widely utilized in oxygen evolution reaction (OER) for water electrolysis. These materials include ruthenium oxides, ruthenium nanoparticles, ruthenium single atoms, and ruthenium-doped materials. The following summarizes the various ruthenium-based materials and their performance.

2.1. Ruthenium Oxides

Weijie Zhu et al. [10] developed a modified Co_3O_4 spinel electrocatalyst, where ruthenium atoms (Ru) substituted into the Cooct sites (subsequently named RuCoOx). The highly symmetric Ru_oct−O−Cooct synergistic coordination, driven by strong electronic coupling effects, significantly reduced the spatial distance between Ru_oct and Co_oct, making direct oxygen radical coupling more favorable. Both experimental and theoretical evidence confirmed that the thermodynamically favored heterogenous DOM (Dual Occupation Model), driven by the Ru_oct−O−Cooct synergistic coordination, is superior to the more commonly discussed, theoretically limited AEM (Anion Exchange Mechanism) and structurally unstable LOM (Ligand Occupancy Model). Importantly, the strong interaction resulting from the Ru_oct−O−Cooct synergistic coordination was well maintained during acidic OER, as it facilitated the capture of electrons from the surrounding electron-rich tetrahedral Co (i.e., Cotet) atoms through bridging oxygen bonds. Yunxing Zhao et al. [11] developed a stable Ru-based OER catalyst by dispersing chlorine-oxidized ruthenium active species onto a solid MnOx support material. In this design, Ru serves as the actual active site, while the doping/chemical adsorption of Cl promotes the dispersion of Ru, thereby providing abundant active structural defects. Yunzhou Wen et al. [12] synthesized a Ru-W binary oxide catalyst, achieving atomic-level uniform metal dispersion through a sol-gel method. Compared to the original RuO_2, the optimized catalyst exhibited a 20-fold increase in intrinsic OER activity. Furthermore, it demonstrated remarkable stability during continuous electrolysis for over 550 hours, with a degradation rate of only 0.014 mV h^{-1}.

2.2. Ruthenium Nanoparticles

Jinchang Fan et al. [13] achieved highly efficient and unprecedentedly robust acidic OER performance by employing self-assembly engineering and phase modulation of Ru_3Ir nanocrystals. By controlling the nucleation sequence and generating gas/liquid interfaces in situ during synthesis, they synthesized quasi-two-dimensional (2D) Ru_3Ir nanocrystals with an unconventional face-centered cubic (fcc) phase. This catalyst exhibited excellent acidic OER activity, with a low overpotential of 190 mV at a current density of 10 mA cm^{-2}. Additionally, it showed negligible activity degradation over 400 hours or 10,000 potential cycles, demonstrating remarkable stability. Figure 1 illustrates the OER performance of the material. Shi Chen et al. [14] designed ultrasmall Mn-doped RuO_2 nanocrystals as excellent OER electrocatalysts in acidic electrolytes, with the scheme shown in Figure 1. The doping of Mn

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ions in RuO_2, as calculated using density functional theory (DFT), increased the gap between the p-band center of oxygen (O) and the d-band center of ruthenium (Ru), thus optimizing the energy levels. This optimization enhanced the oxygen evolution performance.

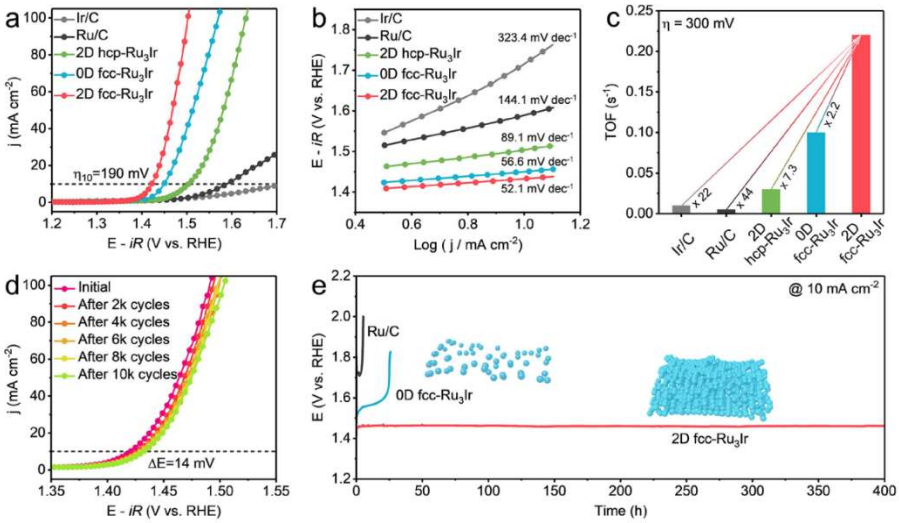

Figure 1. The OER performance of the material [13].

2.3. Ruthenium Single Atoms

Chengli Rong et al. [15] developed an atomically dispersed Ru–Co dual-site catalyst to modulate the intermediate species affinity on the Ru surface, enabling the high-activity bifunctional catalyst to perform water splitting under both acidic and alkaline conditions. Through pyrolysis of Ru/Co co-doped UiO-66-NH_2 and acid etching, RuN_4 and CoN_4 sites were separated and uniformly distributed on a nitrogen-carbon support (Ru/Co-N-C-800°C). Thanks to the unique atomic isolation structure and synergistic effect between the Ru–N_4 and Co–N_4 sites, Ru/Co-N-C-800°C exhibited excellent catalytic performance for OER, HER, and overall water splitting across a wide pH range.

2.4. Ruthenium Doping

Jing He et al. [16] successfully synthesized a metal intermetallic compound Ru_1Ir_1Ox nanocatalyst by introducing Ru into IrOx. Utilizing the electronic properties between Ru and Ir atoms, the metal intermetallic Ru_1Ir_1Ox catalyst exhibited a low overpotential (η) of 204 mV at a current density of 10 mA cm^{-2} (geo) in acidic electrolytes, outperforming IrOx, RuOx, and other Ru_mIr_nOx nanocatalysts with different molar ratios.

3. Conclusion

Hydrogen energy is a novel, clean, and efficient energy source. Unlike traditional petrochemical hydrogen production methods, water electrolysis for hydrogen production is not only green and simple but also zero-carbon-emission, offering vast potential for large-scale applications. However, issues such as the high cost, scarcity, and instability of platinum-based electrode materials remain bottlenecks for industrial development. Ruthenium-based materials are excellent alternatives. This paper focuses on summarizing Ru-based catalysts with superior OER performance under acidic conditions. More importantly, ruthenium excels over other precious metals in terms of electrochemical stability and cost. Various strategies, such as ruthenium oxides and ruthenium single atoms, have been developed to enhance performance. In conclusion, with a deeper understanding of Ru-related materials and other catalysts, we believe that more efficient electrocatalysts will be developed for industrial applications in the future.

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