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Dear Mr Liu:

Manuscript ID: NR-REV-07-2025-003118.R1
TITLE: Acid-Stable Oxygen-evolving Catalysts: Progress in Non-Precious Material Engineering and Scalability Barriers

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ARTICLE

Acid-Stable Oxygen-evolving Catalysts: Progress in Non-Precious Material Engineering and Scalability Barriers

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As the cornerstone of proton exchange membrane water electrolyzers (PEMWE) systems, oxygen-evolving electrocatalysts play a decisive role in governing both energy conversion efficiency and cost-effectiveness. In recent years, non-precious metal-based oxygen-evolving catalysts have garnered significant attention as promising alternatives to noble metal counterparts. This review comprehensively explores the fundamental principles of acidic oxygen evolution reaction (OER) catalysis mediated by non-precious metal systems, with particular emphasis on the dynamic interplay between their activity and stability. Furthermore, it systematically analyzes degradation mechanisms within key components of PEMWE and outlines corresponding mitigation strategies. Specific advancements in diverse categories of non-precious metal catalysts and their associated design strategies are elaborated in detail. Finally, an in-depth discussion addresses the remaining barriers hindering the industrialization of non-precious catalysts. By integrating fundamental insights with practical engineering considerations, this work aims to guide the development of cost-effective yet robust catalysts for next-generation green hydrogen technologies.

1. Introduction

Rapidly growing energy needs coupled with urgent ecological priorities have accelerated the global shift to renewable energy infrastructures, particularly wind and photovoltaic technologies [1-3]. These clean energy sources not only alleviate the overreliance on fossil fuels but also align with carbon neutrality goals by contributing to the vision of achieving zero carbon emissions [4-6]. To address the intrinsic variability of renewables and maintain grid stability, advanced energy storage solutions and conversion platforms are essential [7-11]. In this context, electrolytic hydrogen generation has emerged as a key enabler, transforming excess renewable electricity into transportable fuel while providing carbon-neutral alternatives for hard-to-decarbonize industries like aviation and freight logistics [12-18].

As the core component of water electrolysis technology, proton exchange membrane water electrolyzers (PEMWE) exhibit significant competitiveness in dynamic power adaptability due to their rapid response characteristics, low ohmic losses, and high-purity hydrogen production [19, 20]. The inherently slow kinetics of the anodic oxygen evolution reaction (OER), a complex four-electron transfer process, continue to be the primary efficiency constraint in dual-electrode electrolysis systems [21]. Although currently employed iridium/ruthenium-based noble metal catalysts can sustain reaction efficiency, their scarcity and prohibitive costs severely hinder the large-scale application of PEMWE technology [22, 23]. Consequently, developing non-precious catalysts (NPCs) with high activity and robust stability has become an urgent requirement for advancing the green hydrogen industry.

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Several insightful reviews have laid a solid foundation for understanding OER catalysis. For instance, previous works have comprehensively outlined the general stability challenges across various electrolytes [24], delved into the complex mechanistic aspects of the reaction [25], and summarized engineering strategies for acidic OER catalysts [26]. While these reviews provide invaluable broad perspectives, a dedicated and systematic treatise that seamlessly connects fundamental mechanistic insights, material-specific design strategies for NPCs, and their practical integration within the PEMWE system—particularly addressing the critical issue of dissolution-induced cross-component degradation—is still urgently needed.

This review aims to fill this gap by offering a focused and critical analysis of the path forward for NPCs in acidic OER. We move beyond a general discussion to provide a targeted examination of the most promising NPC families for PEMWE applications. Our overarching goal is to bridge the gap between fundamental research on catalyst materials and the practical engineering requirements of industrial electrolyzer systems.

Recent breakthroughs in materials science have provided multidimensional strategies for novel catalyst design [27, 28]. Leveraging structure engineering to optimize active site exposure and composition modulation guided by theoretical calculations, significant progresses have been achieved in systems such as transition metal oxides, phosphides, chalcogenides, and carbon-based composites [29-31]. Notably, in the field of cobalt-based oxides, precisely tailored catalytic materials have yielded high-performance NPCs [32]. Some of these materials now demonstrate stable operation at industrial-level current densities of 1000 mA cm^{-2} for over 600 hours, rivalling the catalytic performance of noble metal benchmarks [33]. Nevertheless, key challenges remain unresolved for industrial deployment, particularly concerning long-term stability in acidic environments and scalable fabrication processes.

This review systematically outlines the reaction mechanisms of non-noble metal catalytic systems in acidic media, emphasizing breakthroughs in cobalt-centric material architectures. It also