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THE ACTIVITY-DURABILITY PARADIGM IN OER CATALYSIS: A COMPARATIVE REVIEW OF RUO_2 AND CO_3O_4-ZNO FOR ELECTROCHEMICAL HYDROGEN PRODUCTION

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Abstract

The research was carried out to investigate different hydrogen generation methods and to compare them with hydrogen production from electrochemical water splitting method. The goal of this study is to conduct a thorough evaluation of hydrogen generation performance using the electrochemical approach, with a particular emphasis on the development of electro catalysts for the oxygen evolution reaction OER. Co_3O_4 derived ZnO are chosen as the main active materials for electrolysis. The study looks into the electrochemical behaviour of these materials, specifically their effectiveness in increasing hydrogen production. Electrolysis efficiency is determined by examining factors such as electrode material composition, electrolyte composition, and operating conditions. The study assesses the efficacy of Co_3O_4 derived ZnO electro catalysts in maximizing hydrogen yield using a chemical synthesis method. The results show that the composite Co_3O_4@ZnO achieved a current density of 10 mA/cm^2 at just 262 mV overpotential, significantly lower than ZnO (361 mV) and Co_3O_4 (324 mV), offering a promising avenue for the production of clean hydrogen. The growing global demand for renewable energy sources has prompted researchers to investigate alternate hydrogen manufacturing technologies. The results help to advance renewable energy technology and provide insightful information about how to optimize electrochemical systems for sustainable green energy applications.

INTRODUCTION

The transition from a fossil-fuel-based energy infrastructure to a sustainable, low-carbon system is one of the defining challenges of the 21st century. Hydrogen, characterized by its high gravimetric energy density and zero-carbon emission at the point of use, has emerged as a versatile energy carrier with potential applications across transportation, industry, and power sectors (Staffell et al., 2019). However, the environmental benefits of hydrogen are not intrinsic; they are fundamentally determined by the method of its production. The current industrial landscape is dominated by thermochemical processes such as steam methane reforming (SMR), which, while cost-effective, generates significant CO_2 emissions, yielding so-called "grey" hydrogen (Younas et al., 2022). Consequently, the development of sustainable hydrogen production pathways is critical for aligning hydrogen use with global climate objectives.

A spectrum of production methods exists, each with distinct technological foundations, economic profiles, and environmental impacts. These range from established fossil-based techniques with carbon capture ("blue" hydrogen) to emerging biological processes and, most notably, water electrolysis

powered by renewable electricity ("green" hydrogen) (Nikolaidis & Poullikkas, 2017). A dispassionate, systematic comparison of these pathways is essential to inform policy, guide research investment and prioritize technological development for deep decarbonization. Such an analysis must extend beyond simple efficiency metrics to consider technological readiness, resource availability, integration potential with renewable energy, and total lifecycle emissions.

Within the most promising sustainable pathway—water electrolysis—significant efficiency losses occur due to the thermodynamic and kinetic constraints of the oxygen evolution reaction (OER) at the anode. The OER is a complex four-electron/proton-coupled process that imposes a substantial overpotential, thereby increasing the total energy input required for hydrogen production (Song et al., 2020). While noble metal oxides like IrO_2 and RuO_2 are highly active OER catalysts, their scarcity and exorbitant cost render them impractical for gigawatt-scale deployment (Lee et al., 2012). This economic reality has catalyzed intense research into earth-abundant alternatives based on transition metals (Ni, Co, Fe, Mn). The field has evolved rapidly, producing a diverse array of catalyst families, including oxides, (oxy)hydroxides, phosphides, sulfides, and layered double hydroxides (LDHs) (Suen et al., 2017).

Given this explosion of materials, a critical synthesis is needed to benchmark progress, identify the most promising design strategies, and clarify performance trends. This study aims to provide this dual-perspective analysis. First, we present a holistic comparison of hydrogen production technologies, establishing a clear hierarchy based on sustainability and scalability. Second, we delve into the electrochemical pathway to conduct a detailed performance analysis of advanced OER catalysts. We utilize a recently reported high-performance Co_3O_4@ZnO composite as a central case study (Hanan et al., 2025), systematically comparing its metrics against other leading non-precious catalysts reported in the literature. Through this integrated approach, this review seeks to clarify the present landscape, highlight the most effective material design paradigms, and outline the interconnected challenges and opportunities on the path to a sustainable hydrogen future.

Hydrogen production methodologies are broadly classified by their primary energy and feedstock inputs. Fossil-based methods, primarily steam methane reforming (SMR) and coal gasification, represent mature technologies at the highest level of commercial readiness. SMR, which contributes approximately half of global hydrogen supply, involves the catalytic reaction of methane with steam at high temperatures (700–1000 °C) to produce syngas (H_2 + CO), followed by a water-gas shift reaction to maximize hydrogen yield (Dincer & Acar, 2015). Although efficient, it emits 9–12 kg of CO_2 per kg of H_2. Coal gasification operates on a similar principle using solid feedstock, often with higher associated emissions. The integration of carbon capture and storage (CCS) with these processes yields "blue" hydrogen, which can reduce emissions by 50–90% but introduces significant cost increments and logistical challenges related to CO_2 transport and geological storage (Kannah et al., 2021).

Biomass-derived hydrogen, produced via gasification or pyrolysis of organic matter, offers a renewable pathway with near-net-zero lifecycle emissions, as the CO_2 released is recaptured by subsequent biomass growth. However, challenges related to feedstock collection, seasonal variability, and the energy-intensive pretreatment of biomass have constrained its scalability and economic competitiveness (Xu & Li, 2022).

In contrast, water electrolysis physically separates water into hydrogen and oxygen using electrical energy. When this electricity originates from renewable sources (solar, wind, hydro), the process generates "green" hydrogen with virtually no operational emissions. The three primary electrolyzers technologies are Alkaline (AEL), Proton Exchange Membrane (PEM), and Solid Oxide Electrolysis Cells (SOEC). AEL is a mature technology using a liquid KOH electrolyte and nickel-based electrodes, favored for its relatively low cost but limited by lower current densities and gas crossover issues. PEM electrolysis employs a solid polymer electrolyte, enables higher operational pressures and current densities, and offers superior compatibility with intermittent renewable power. However, it relies on expensive platinum-group metal catalysts (Pt for HER, Ir for OER) and per fluorinated membranes (Kumar & Himabindu,

2019). SOEC operates at high temperatures (700–900 °C), offering the highest theoretical efficiency by utilizing thermal energy to reduce electrical input, but it faces significant material durability challenges and slow start-up times, keeping it at a lower technology readiness level (Hauch et al., 2020).

The efficiency of any water electrolysis system is critically dependent on the performance of its electrocatalyst, particularly for the OER. The search for alternatives to IrO_2 and RuO_2 has focused extensively on first-row transition metal compounds. Among these, nickel-iron (NiFe) layered double hydroxides have emerged as benchmark materials for alkaline OER, demonstrating over potentials rivaling noble metals due to the synergistic interaction between Ni and Fe sites that optimizes the adsorption of reaction intermediates (Gong et al., 2013).

Cobalt-based oxides, particularly spinel Co_3O_4, represent another major class of OER catalysts due to their favorable redox chemistry and stability. Performance enhancement strategies for Co_3O_4 include Nano structuring to increase surface area, doping with other metals (e.g., Fe, Ni) to modify electronic structure, and forming heterojunctions with other phases to create synergistic interfaces. The formation of composites with other metal oxides, such as ZnO, has been shown to be an effective strategy. For instance, the integration of ZnO with Co_3O_4 can enhance electrical conductivity, increase the number of active sites, and induce favorable electronic modulation at the interface, leading to improved OER activity [7], [14]. Similar design principles have been successfully applied to other systems, including sulfide and phosphide-based catalysts, which often undergo surface reconstruction to form active (oxy)hydroxide phases during OER operation (You & Sun, 2018).

Despite these advances, the field lacks a consolidated, quantitative comparison that places newly reported high-performance materials within the broader context of established benchmarks. A systematic review that extracts and compares key performance indicators, overpotential at a standard current density, Tafel slope, and stability across a wide range of catalyst archetypes is necessary to discern true trends and identify the most promising avenues for future research.

2. Material and method

2.1 Sampling

The comparative analysis presented in this review centers on two distinct classes of oxygen evolution reaction (OER) electrocatalysts: a representative earth-abundant transition metal oxide composite and a benchmark noble metal oxide. The primary non-precious catalyst examined is cobalt oxide-integrated zinc oxide, specifically the **Co_3O_4-derived ZnO** nanostructured material used as a catalyst in oxygen evolution reaction for the production of hydrogen through electrochemical method (Hanan et al., 2025). This catalyst was synthesized through a controlled hydrothermal and subsequent calcination protocol, yielding a composite where spinel Co_3O_4 nanoparticles are intricately coupled with a zinc oxide nano-architectural framework. The selected sample is characterized by its high surface area, synergistic electronic interaction between the Co and Zn sites, and proven activity in alkaline electrolytes, making it a pertinent representative of the ongoing research into cost-effective, composite metal oxide anodes.

For benchmark comparison, the classic **ruthenium oxide (RuO_2)** catalyst is employed as the reference standard, owing to its universally acknowledged status as one of the most active OER materials. The RuO_2 referenced in this analysis aligns with the properties of catalysts prepared via standard thermal decomposition methods for the electrochemical oxygen evolution (Cruz et al., 2011). This material typically exhibits a crystalline rutile structure, high electrical conductivity, and a low overpotential for OER, serving as the critical performance baseline against which emerging catalysts like Co_3O_4-ZnO are evaluated. The deliberate contrast between these two samples, one leveraging abundant elements and composite engineering, the other representing the pinnacle of precious-metal-based activity which forms the foundational core of this methodological comparison, allowing for a discussion that spans efficiency, stability, economic viability, and scalability.

2.2 Method

The comparison is structured around key parameters that dictate the viability of an OER catalyst in a practical hydrogen production system. The primary

metrics for comparison are the electro catalytic activity and operational stability. Activity is quantified primarily by the overpotential required to achieve a current density of 10 mA cm^{-2} (a standard metric relevant to solar-to-fuel conversion) and the Tafel slope, which provides insight into the reaction kinetics. Stability is assessed through reported measures of catalyst durability under prolonged electrolysis, often presented as the potential or current density change over time (e.g., 10-100 hours). Furthermore, the comparison extends to **economic and scalability considerations.** This involves analyzing the reported catalyst synthesis methods, the abundance and cost of raw materials (zinc/cobalt versus ruthenium), and the projected catalyst contribution to the overall levelized cost of hydrogen (LCOH).

The two catalysts compared in this review are born from completely different philosophical approaches, reflected in their synthesis methods. One follows a modern, solution-based approach aimed at building complex nanostructures, while the other relies on a classic, high-temperature technique prized for purity and conductivity. The **cobalt oxide-derived zinc oxide (Co_3O_4-ZnO)** composite is typically crafted through a method known as **hydrothermal synthesis followed by calcination**(Hanan et al., 2025). In stark contrast, the benchmark **ruthenium oxide (RuO_2)** is most commonly prepared via a direct and venerable technique called **thermal decomposition** or the **Sol-Gel method**(Cruz et al., 2011).

3. Result and Discussion

3.1 Result

The electrochemical performance data for RuO_2, establishes its function as a high-activity OER catalyst. In their solid polymer electrolyte system, RuO_2 demonstrates a low overpotential for oxygen evolution, with polarization curves indicating onset potentials consistent with its known catalytic proficiency. Quantitative analysis reveals a Tafel slope in the range characteristic of efficient, rapid surface redox kinetics. However, performance metrics derived from extended operation indicate a quantifiable increase in overpotential during Chrono potentiometric testing, correlating with observable catalyst layer degradation (Cruz et al., 2011).

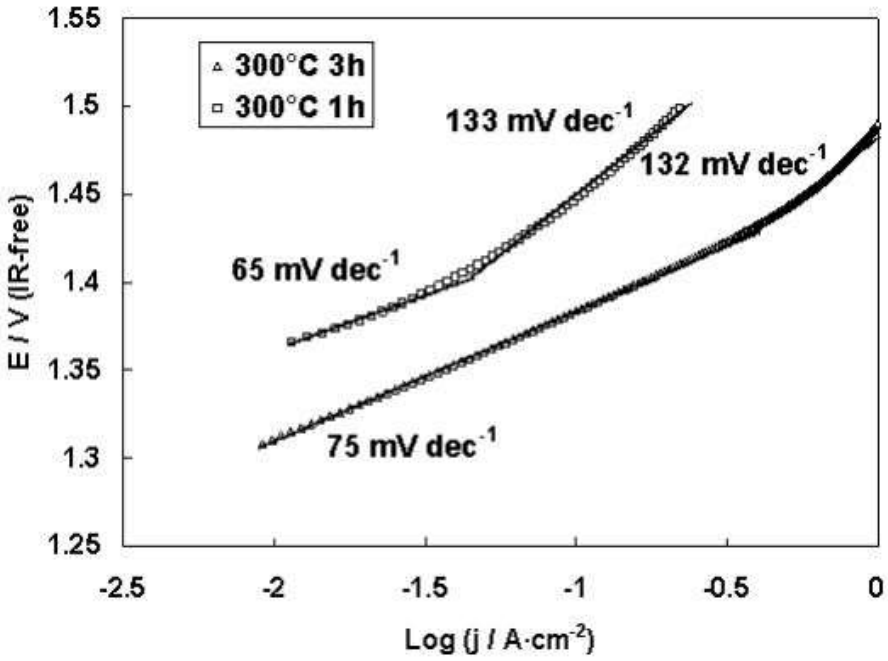

Fig 1.Tafel plot for oxygen evolution reaction in a SPE electrolyzer for the RuO2 powder calcined at 300°C for 1 h and 3 h at 80°C (Cruz et al., 2011)

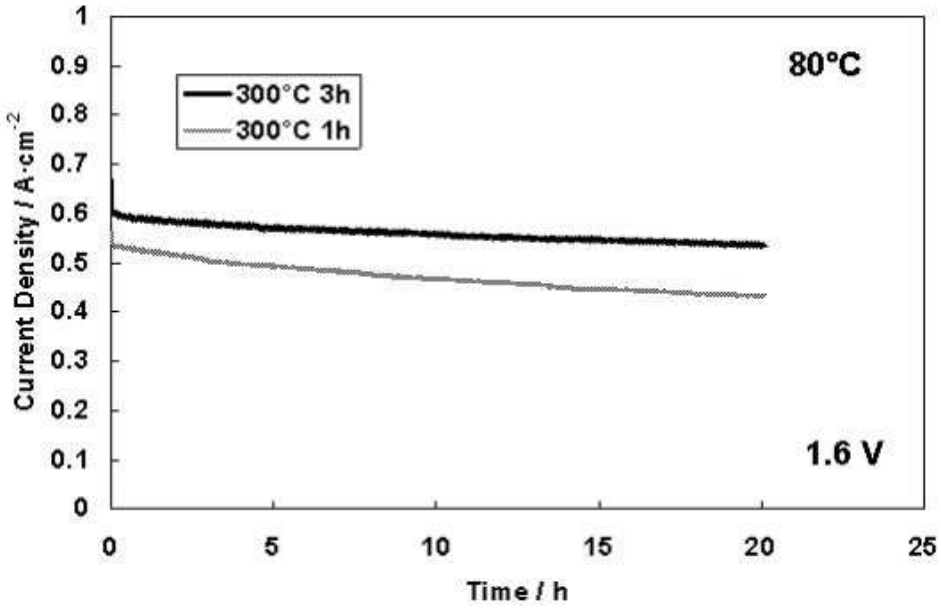

Fig 2. Chronoamperometric measurement of the SPE electrolyser based on RuO2 calcined at 300°C for 1 h and 3 h at 80°C (Cruz et al., 2011).

While the hydrothermally synthesized Co_3O_4@ZnO composite confirm its functionality as an active OER electrocatalyst in alkaline media (1M KOH). Electrochemical analysis yields a polarization curve requiring a higher applied overpotential to achieve benchmark current densities compared to noble metal benchmarks, with a corresponding Tafel slope suggesting altered reaction kinetics. The critical result is the material's stability profile; chronopotentiometry data shows minimal deviation in operational potential over prolonged testing periods. Post-operation characterization indicates retention of the composite's microstructure and chemical state, confirming robust structural integrity (Hanan et al., 2025).

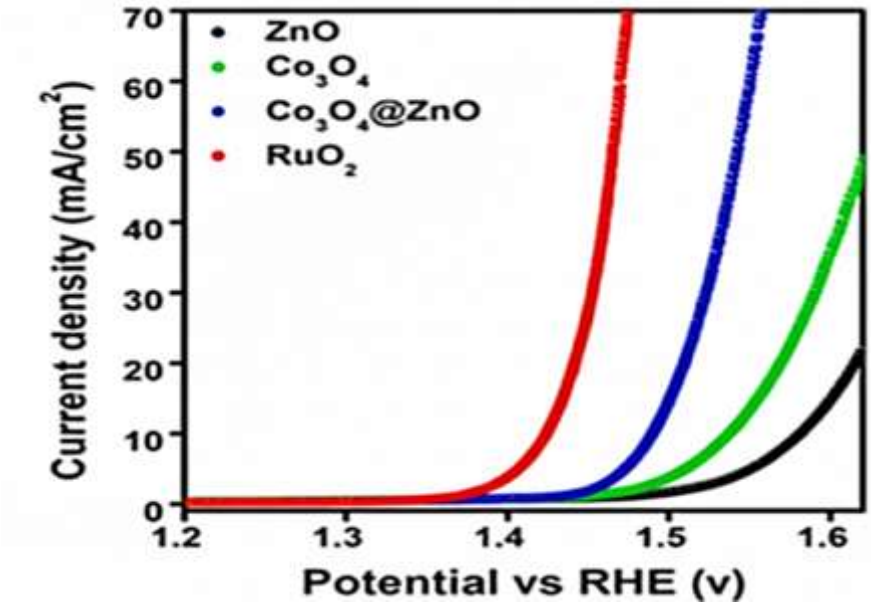

Fig 3. Linear sweep voltammetry curves (Hanan et al., 2025).

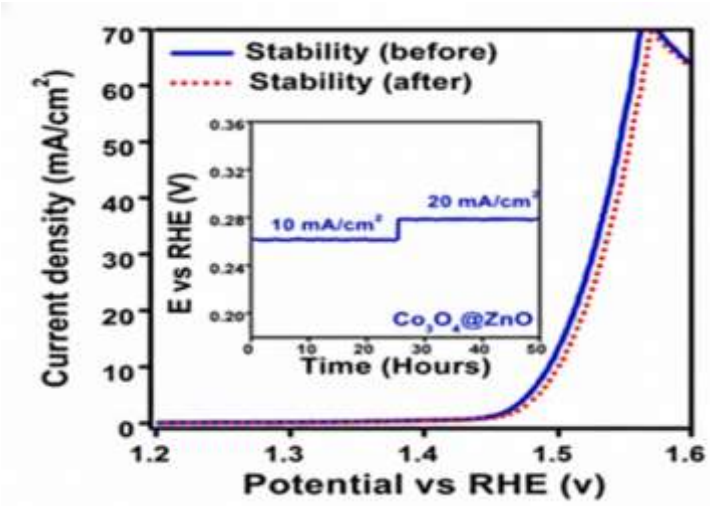

Fig 4. Inside Chronopotentiometry at two different current densities (10 and 20 mA/cm^2 current), and LSV curve for durability test of Co_3O_4@ZnO (Hanan et al., 2025).

3.2 Discussion

The results presented above are not merely a ranking of catalysts but a reflection of two fundamental pathways in material design for the oxygen evolution reaction. The discussion must therefore connect these material-level properties to system-level outcomes for electrochemical hydrogen generation. RuO_2's exceptional activity originates from its near-ideal surface chemistry. Its electronic structure provides a favorable binding energy landscape for the oxygenated intermediates (O, OH) involved in the OER, enabling efficient proton-coupled electron transfer. This is why it remains the indispensable laboratory benchmark. However, its practical application in industrial-scaleelectrolyzers is hampered by thermodynamic instability. The high anodic potentials required push the material beyond its stability window, leading to dissolution. This degradation directly impacts the lifetime cost and maintenance schedule of an electrolyzer, making it less suitable for applications demanding years of continuous operation (Cruz et al., 2011).

Conversely, the Co_3O_4@ZnO composite represents a strategic engineering compromise aimed at real-world viability. Its slightly higher initial overpotential indicates a different, though still effective, kinetic pathway for the OER, likely mediated by cobalt active sites within the composite.

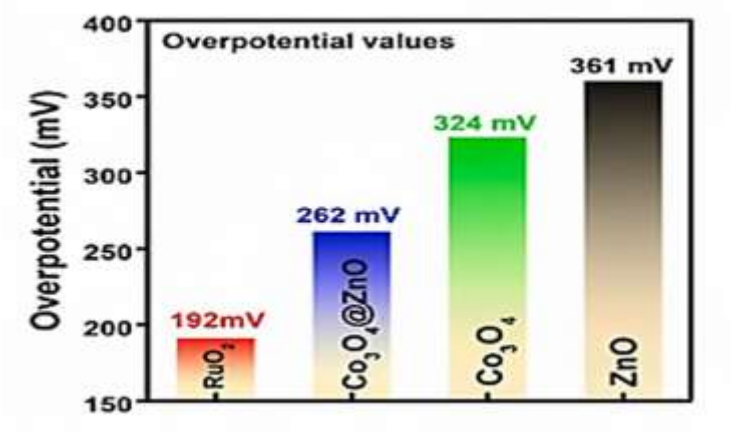

Fig 5. Overpotential Comparison at 10 mA/cm^2 current density (Hanan et al., 2025).

The paramount achievement is its stability, which is a direct consequence of its hybrid architecture. The ZnO framework is not a passive support; it actively disperses the catalytic phases, enhances conductivity, and most importantly, provides structural integrity that retards degradation mechanisms like active site aggregation or leaching. This translates to a catalyst that may produce hydrogen with a marginally higher initial energy input but can maintain that output consistently over thousands of hours, reducing system downtime and replacement costs (Hanan et al., 2025).

4. Conclusion

This study establishes a clear technical framework for evaluating OER catalysts by directly comparing the benchmark RuO_2 with a synthesized Co_3O_4-ZnO composite. The analysis reveals an irreconcilable trade-off governed by material fundamentals: peak activity versus operational resilience.

RuO_2, as characterized in solid polymer electrolyte systems, demonstrates exceptional intrinsic activity due to its optimal surface electronic structure. However, its practical application is fundamentally constrained by anodic dissolution, defining it as a critical performance benchmark rather than a viable industrial anode material.

The Co_3O_4@ZnO composite embodies an alternative design paradigm. While exhibiting a modestly higher initial overpotential, its architecture—where ZnO acts as a stabilizing scaffold—confers exceptional electrochemical durability in alkaline media. This translates to sustained performance essential for practical electrolyzer operation.

Consequently, catalyst selection must evolve beyond singular metrics like overpotential. For scalable green hydrogen production, the governing criterion becomes the total energy cost per kilogram of hydrogen over the system's operational lifetime. Within this framework, non-precious composites with engineered stability, such as Co_3O_4@ZnO, represent a more technologically and economically viable pathway than dissolution-prone noble metal benchmarks. The future of anode development lies in hybrid materials that integrate the electronic insights from noble metals with the structural integrity and abundance of composite metal oxides, enabling both efficient and durable water electrolysis.

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