Proceedings of CONF-MCEE 2026 Symposium: Advances in Sustainable Aviation and Aerospace Vehicle Automation
DOI: 10.54254/2755-2721/2026.KA29033

Research Progress of Novel Metal Oxide-Based Cathode Materials in High-Temperature CO_2 Electrolysis

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Abstract. To achieve carbon neutrality,the high-temperture CO_2 electrolysis technology using solid oxide electrolysis cells (SOECs) has attracted much attention.However,their traditional Ni-based cathodes have become a promising alternative due to their excellent stability and anti-coking properties. This paper first analyzes the performance enhancement mechanisms such as oxygen vacancy regulation and interface engineering. Then, it reviews the research progress of fluoride-based materials (GCO, Fe-SDC), perovskite and derivative materials (SFMC, HE-PSCFMMN), and composite structure materials (Ru-modified SDC), including their material characteristics, modification methods, and case studies. Currently, these materials suffer from issues such as insufficient activity at medium and low temperatures. Future research should focus on dynamic interface regulation and other directions to promote the industrialization of SOECs.Moreover, exploring multi-element doping strategies to tailor the electronic conductivity and ionic diffusion pathways of cathode materials could effectively bridge the activity gap across temperature ranges. Additionally, integrating in-situ characterization techniques to track the structural evolution of materials during long-term electrolysis will provide critical insights for optimizing their durability in practical industrial environments.

Keywords: Solid oxide electrolysis cell (SOEC), high-temperature CO2 electrolysis, perovskite, oxygen vacancy

1. Introduction

Driven by the dual pressures of global warming and energy structure transformation, carbon neutrality has become a core strategic goal for sustainable development in various countries. In this process, achieving efficient conversion and resource utilization of carbon dioxide (CO_2) has emerged as a critical issue to be addressed in the fields of energy and environment. As a highly promising low-carbon technology, solid oxide electrolysis cells (SOECs) can directly electrolyze CO_2 into high-calorific-value fuels such as carbon monoxide (CO) by virtue of their unique high-temperature operation advantage (typically between 600-1000 ℃). With an energy conversion efficiency exceeding 80%, SOECs can also form deep coupling with intermittent renewable energies like solar and wind power, constructing a closed-loop carbon cycle system of "power generation - electricity storage - fuel utilization". This provides an innovative solution to the dual challenges of energy storage and carbon emission reduction, as reported by Song et al. [1].

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DOI: 10.54254/2755-2721/2026.KA29033

To achieve carbon neutrality, high-temperature CO_2 electrolysis using solid oxide electrolysis cells (SOECs) has emerged as a promising technology, with metal oxide-based cathode materials gaining increasing attention due to their superior stability and anti-coking properties compared to traditional Ni-based cathodes. Among these, fluoride-based materials, such as gadolinium-doped ceria (GCO) and Fe-doped Sm_2O_3-CeO_2 (Fe-SDC), have demonstrated excellent performance by regulating oxygen vacancies through doping, enhancing CO_2 adsorption and activation, as reported by Shaur et al. and Song et al. [2,3]. Perovskite and derivative materials, including Co-doped $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMC) and high-entropy layered perovskite HE-PSCFMMN, have shown remarkable long-term stability via in-situ crystallization of metal-oxide interfaces and high-entropy effects, as reported by Lv et al. [4] and Wang et al. [5]. Composite structure materials like Ru single-atom modified $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) further optimize catalytic activity through interface engineering, forming covalent bonds that reduce reaction energy barriers, as reported by Song et al. [3].

However, the commercial application of SOECs is still limited by performance bottlenecks of core components, among which the stability and catalytic activity of cathode materials are particularly crucial. Although traditional nickel (Ni)-based cathodes exhibit high initial catalytic activity, they have two unavoidable shortcomings, first, in the reducing atmosphere of CO_2 electrolysis, Ni tends to react with carbon to form carbon deposits, leading to blockage of reaction sites and a sharp decline in electrolysis efficiency; second, long-term high-temperature operation can cause agglomeration and sintering of metallic Ni particles, significantly reducing the specific surface area and the number of active sites of the material, thus severely shortening the battery life. These defects have greatly restricted the industrialization process of SOECs, making the development of high-performance alternative cathode materials a top priority in current research.

In recent years, metal oxide-based cathode materials have gradually become a core research direction to replace traditional Ni-based materials due to their excellent chemical stability, anti-coking performance, and high-temperature tolerance. According to differences in material structure and performance regulation mechanisms, the currently studied metal oxide-based cathodes can be mainly divided into three categories, fluoride-based materials focus on precise regulation of oxygen vacancies, introducing more active sites through doping modification, which significantly enhances CO_2 adsorption and activation capacity, showing outstanding performance in catalytic activity; perovskite and derivative materials form stable metal-oxide heterogeneous interfaces through lattice structure regulation and in-situ crystallization technology, effectively inhibiting particle agglomeration and demonstrating excellent long-term operation stability; composite structure materials optimize electron orbital arrangement and charge transfer efficiency through interface engineering, synergistically improving catalytic activity and stability, achieving a leap in catalytic performance.

This paper will first systematically elaborate on the performance enhancement mechanisms of metal oxide-based cathode materials in the process of CO_2 electrolysis, including core principles such as oxygen vacancy regulation, interface effect, and electronic structure optimization. Then, it will classify and detailedly introduce the composition characteristics, typical modification methods, electrolysis performance, preparation methods, and characterization technologies of fluoride-based, perovskite and derivative materials, and composite structure materials, while comparing and analyzing the advantages and application limitations of various materials. Finally, combined with current research hotspots and technical bottlenecks, it will look forward to the future development directions of metal oxide-based cathode materials, providing theoretical reference and technical guidance for the design of high-efficiency and long-life SOECs.

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2. Performance enhancement mechanisms

The performance enhancement of metal oxide-based cathode materials in high-temperature CO_2 electrolysis relies on three core mechanisms. Oxygen vacancy regulation, primarily achieved through doping, increases active sites by elevating oxygen vacancy concentrations, thereby promoting CO_2 adsorption, activation, and ion diffusion. Interface engineering, via single-atom modification or alloy precipitation, constructs metal-oxide interfaces to optimize electronic structures and reduce reaction energy barriers, enhancing catalytic kinetics. The high-entropy effect, induced by multi-element doping, increases configurational entropy, inhibits element segregation, and improves ionic conductivity, while facilitating oxygen vacancy formation and reaction interface expansion. These synergistic mechanisms collectively boost catalytic activity, stability, and ion transport efficiency, underpinning the superior performance of these cathode materials.

2.1. Oxygen vacancy regulation

Oxygen vacancies, as "active sites" formed by the absence of oxygen ions in materials, can provide a basis for electrolysis reactions by adsorbing and activating CO_2. Doping is the main means to increase oxygen vacancies, when Fe is doped into Sm_2O_3-CeO_2 (Fe-SDC), the introduction of Fe increases the proportion of Ce^{3+} from 15.6% to 20.2%, and the oxygen vacancy concentration increases by 133%. Song et al. reported through theoretical calculations that the increase in oxygen vacancies reduces the CO_2 dissociation energy barrier and accelerates oxygen ion diffusion, resulting in an 88% increase in current density compared to the undoped sample under the same working conditions [3].

2.2. Interface engineering

Constructing metal-oxide interfaces through single-atom modification or alloy precipitation can optimize the electronic structure and reduce reaction energy barriers. For example, when Ru single atoms modify $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC), Ru-O-Ce covalent bonds are formed, reducing the CO_2 adsorption energy to -0.61 eV. Song et al. confirmed via X-ray absorption characterization that this interface effect reduces the energy barrier of the rate-determining step of CO_2 reduction by 30%, and the current density is 54% higher than that of the unmodified sample [3].

2.3. High-entropy effect

High-entropy materials formed by multi-element doping can increase configurational entropy, inhibit element segregation, and enhance ionic conductivity. Zhang et al. reported that the high-entropy layered perovskite HE-PSCFMMN has a configurational entropy of 1.39R due to the synergistic effect of multiple elements, and its oxygen ion diffusion coefficient is twice that of traditional perovskites [6,7]. Meanwhile, the high-entropy effect promotes the formation of oxygen vacancies, and the in-situ precipitated CuFe@FeO_x core-shell particles further expand the reaction interface, significantly improving activity and stability.

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3. Cathode materials

Metal oxide-based cathode materials for high-temperature CO_2 electrolysis must exhibit high electrocatalytic activity, mixed ionic-electronic conduction, strong anti-coking properties, and long-term stability. Their preparation involves diverse methods, sol-gel for fluoride-based materials (ensuring uniform doping), solid-phase reaction for perovskites (suitable for large-scale production), and in-situ reduction (enhancing interface effects via in-situ nanoparticle precipitation). Characterization technologies such as XPS, in-situ XRD, and EIS analyze chemical states, real-time structural changes, and electrochemical kinetics. Research spans fluoride-based materials (abundant oxygen vacancies), perovskites and derivatives (tunable via doping), and composite structures (synergistic interface effects), collectively advancing the development of high-performance SOECs.

3.1. Material characteristics and performance requirements

Metal oxide-based cathode materials for high-temperature CO_2 electrolysis need to possess specific characteristics and meet key performance requirements, they should have high electrocatalytic activity to efficiently adsorb and activate CO_2 (e.g., Fe-SDC with increased oxygen vacancies shows 88% higher current density, and Ru-modified SDC reduces energy barriers via covalent bonds), good mixed ionic-electronic conduction for rapid charge transport (e.g., GCO with mixed conduction mechanism and perovskites optimized via lattice structure), strong anti-coking property to avoid carbon deposition in reducing atmospheres (a key advantage over Ni-based cathodes), and long-term stability to maintain structure under high temperatures without particle agglomeration (e.g., SFMC with reversible redox cycles and HE-PSCFMMN using high-entropy effects).

3.2. Preparation methods

The preparation methods of cathode materials are tailored to their structural and performance requirements. The sol-gel method, suitable for fluoride-based materials like Fe-SDC, involves dissolving metal precursors (e.g., $Sm(NO_3)_3$, $Ce(NO_3)_3$, $Fe(NO_3)_3$) in solvents (e.g., citric acid) to form a sol, which gels, dries, and is calcined at 600-800 ℃ to form crystalline powders, ensuring uniform doping and controlled particle size. The solid-phase reaction, widely used for perovskites such as SFMC, mixes stoichiometric raw materials (e.g., $SrCO_3$, Fe_2O_3) via ball milling, followed by high-temperature calcination (1000-1200 ℃) to form the ABO_3 structure, which is simple and suitable for large-scale production. In-situ reduction, often used for composite or perovskite materials like SFMC, involves treating the pre-formed perovskite in a reducing atmosphere (e.g., H_2/Ar) at 700-900 ℃ to reduce transition metal ions (e.g., Co^{2+}, Fe^{3+}) and precipitate metal alloy nanoparticles (e.g., CoFe) in-situ, enhancing interface effects and avoiding agglomeration.

3.3. Characterization technologies

X-ray photoelectron spectroscopy (XPS) analyzes element chemical states and concentrations, such as determining Ce^{3+} proportion in Fe-SDC (from 15.6% to 20.2% with Fe doping, reflecting increased oxygen vacancies) and verifying covalent bonds like Ru-O-Ce in Ru-modified SDC. In-situ X-ray diffraction (XRD) monitors real-time structural changes during redox cycles, as seen in Lv et al.'s study on SFMC, which confirmed reversible crystallization/dissolution of CoFe

DOI: 10.54254/2755-2721/2026.KA29033

nanoparticles and evaluated thermal stability via lattice parameter changes. Electrochemical impedance spectroscopy (EIS) assesses charge transfer resistance and ion diffusion kinetics, for example, showing that Fe doping in Fe-SDC reduces charge transfer resistance, corresponding to improved catalytic activity.

3.4. Research progress of cathode materials

To address the performance limitations of traditional Ni-based cathodes in high-temperature CO_2 electrolysis using SOECs, extensive research has been conducted on novel metal oxide-based cathode materials. These materials are designed to overcome issues such as carbon deposition, particle agglomeration, and insufficient stability, while enhancing catalytic activity and ion/electron transport efficiency. Based on their structural characteristics, modification mechanisms, and performance advantages, the current research on metal oxide-based cathodes mainly focuses on three key categories, fluoride-based materials, perovskite and derivative materials, and composite structure materials. Each category adopts distinct design strategies—ranging from oxygen vacancy regulation and lattice structure tuning to interface engineering—to optimize their performance in CO_2 adsorption, activation, and reduction reactions. The following sections will systematically review the material composition, modification methods, typical performance data, and application prospects of each category, providing a comprehensive overview of the latest research progress in this field.

3.4.1. Fluoride-based materials

Fluoride-based materials, centered on doped cerium oxide, have abundant oxygen vacancies and mixed ionic-electronic conduction, exhibiting good stability and anti-coking performance in reducing atmospheres. They enhance CO_2 adsorption and activation by regulating oxygen vacancies through doping (e.g., Gd or Fe doping to adjust lattice structure and increase vacancies) and form mixed conduction mechanisms for efficient charge transport. Typical cases include GCO, which at 800°C and 1.5 V achieves a current density of 1.51 $A \cdot cm^{-2}$ with no attenuation after 300 hours and nearly 100% Faraday efficiency [2], and Fe-SDC, where Fe doping increases oxygen vacancies, leading to a current density of 2.26 $A \cdot cm^{-2}$ at 800°C and 1.5 V (88% higher than undoped samples) with no obvious carbon deposition [3].

3.4.2. Perovskite and derivative materials

Perovskite and derivative materials have ABO_3 or derivative structures, with flexibly adjustable performance via element doping; in reducing atmospheres, they in-situ crystallize to form metal-oxide interfaces, balancing activity and stability. Their enhancement mechanisms include structural regulation to stabilize frameworks, in-situ crystallization of high-activity nanoparticles, and reversible redox cycles improving long-term stability. Modification methods involve doping elements like Co and Mo (e.g., SFMC) or constructing high-entropy structures (e.g., HE-PSCFMMN), and rare-earth doping (e.g., Pr) to improve ionic conductivity. Typical cases are SFMC, which in-situ precipitates CoFe alloy nanoparticles, showing a current density of 1.2 $A \cdot cm^{-2}$ at 800°C and 1.6 V with a decay rate of 0.17 $mA \cdot h^{-1}$ over 230 hours [4]; HE-PSCFMMN, achieving 1.95 $A \cdot cm^{-2}$ at 800°C and 1.5 V with a decay rate of 0.05 $mV \cdot h^{-1}$ over 200 hours [8]; and Pr-doped lanthanum perovskites, showing improved conductivity and stability over 500 hours [7].

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3.4.3. Composite structure materials

Composite structure materials, composed of two or more components (e.g., single-atom-oxide, alloy-oxide), have significant interface effects, synergistically optimizing catalytic activity and charge transport. They regulate electronic structures via interface engineering to reduce CO_2 adsorption/dissociation energy barriers, and improve active site utilization through dispersed single atoms or nanoparticles. Modification methods include single-atom modification (e.g., Ru-modified SDC), alloy-oxide composites, or multi-phase design (e.g., zirconia-based composites). Typical cases are Ru single-atom modified SDC, where Ru forms Ru-O-Ce covalent bonds, increasing oxygen vacancies by 40% and achieving a current density of 2.39 $A \cdot cm^{-2}$ at 800℃ and 1.6 V (54% higher than unmodified samples) with excellent anti-coking property [3]; zirconia-based composite cathodes with tailored oxygen vacancies, reaching 1.8 $A \cdot cm^{-2}$ at 800℃ and 1.6 V [9]; and dual-atom modified ceria, where Ru and Fe co-doping lowers CO_2 dissociation energy barriers [10].

4. Conclusion

Metal oxide-based cathode materials have emerged as promising alternatives to traditional Ni-based cathodes in high-temperature CO_2 electrolysis using SOECs, demonstrating superior anti-coking properties, stability, and catalytic activity. Fluoride-based materials like GCO and Fe-SDC, with their abundant oxygen vacancies, excel in CO_2 activation and long-term operation; perovskites and derivatives such as SFMC and HE-PSCFMMN leverage doping and high-entropy effects to balance activity and structural robustness; and composite structures like Ru-modified SDC harness interface engineering to synergistically enhance performance. These advancements have significantly driven forward the development of SOECs, bringing them closer to practical applications in carbon recycling and renewable energy storage.

However, critical challenges persist, hindering their widespread industrialization. A primary limitation is insufficient catalytic activity at medium and low temperatures (below 600 ℃). For example, fluoride-based materials like GCO exhibit sharply reduced ionic conductivity at lower temperatures, while perovskites such as SFMC show diminished CO_2 dissociation kinetics, restricting their adaptability to flexible operating conditions required for coupling with intermittent renewable energy sources. Additionally, long-term stability remains a concern, composite materials, despite their high initial activity, face risks of nanoparticle agglomeration or interface degradation during prolonged high-temperature operation, leading to gradual performance decay. Moreover, the cost and scalability of synthesis methods—such as the complex sol-gel processes for fluoride-based materials or the energy-intensive calcination steps for perovskites—need optimization to meet industrial production demands.

To overcome these hurdles, future research should focus on targeted strategies. Dynamic interface regulation, such as designing stimuli-responsive core-shell structures that enable reversible precipitation and dissolution of active nanoparticles, could adaptively adjust reaction sites under varying temperatures, enhancing both low-temperature activity and stability. Multi-element synergistic engineering, inspired by high- and medium-entropy materials, offers another avenue, fine-tuning elemental compositions (e.g., incorporating rare-earth elements or transition metals) can optimize electronic structures and oxygen vacancy distributions, promoting CO_2 adsorption and reducing reaction energy barriers across a broader temperature range. Furthermore, integrating advanced in-situ characterization techniques—such as operando X-ray absorption spectroscopy and environmental transmission electron microscopy—will provide real-time insights into dynamic

DOI: 10.54254/2755-2721/2026.KA29033

changes in material structures and reaction intermediates, guiding the rational design of more durable and efficient cathodes.

By addressing these challenges through interdisciplinary efforts in material science, electrochemistry, and engineering, metal oxide-based cathodes are poised to unlock the full potential of SOECs, accelerating their role in achieving carbon neutrality and building a sustainable, closed-loop carbon cycle system.

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