



Copper oxide as a synergistic catalyst for the oxygen reduction reaction on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite structured electrocatalyst



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H I G H L I G H T S

- CuO is used as synergistic catalyst for oxygen reduction reaction on LSCF.
- Enhanced rate is attributed to CuO surface and LSCF-CuO-gas boundaries.
- The contribution of CuO to incorporated oxygen could reach 78%.
- The reduced resistance of LSCF is related to oxygen surface process.
- LSCF and CuO could remain chemical compatible in testing condition.

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This work presents the effect of dispersed copper oxide (CuO) nanoparticles on the oxygen reduction reaction (ORR) on a typical solid oxide fuel cell (SOFC) electrocatalyst, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). The ORR kinetics were enhanced by a factor up to 4 at 750 °C as demonstrated by electrical conductivity relaxation measurements used to determine the chemical surface exchange coefficient, k_{chem} . The value of k_{chem} increased from $2.6 \times 10^{-5} \text{ cm s}^{-1}$ to $9.3 \times 10^{-5} \text{ cm s}^{-1}$ at 750 °C when the LSCF surface was coated with submicron CuO particles. The enhanced k_{chem} was attributed to additional reactions that occur on the CuO surface and at the LSCF-CuO-gas three-phase boundaries (3PBs) as suggested by the k_{chem} dependence on CuO coverage and 3PB length. This enhancement was further demonstrated by the introduction of CuO nanoparticles into LSCF electrodes. CuO infiltrated electrodes reduced the interfacial polarization resistance from $2.27 \Omega \text{ cm}^2$ to $1.5 \Omega \text{ cm}^2$ at 600 °C and increased the peak power density from 0.54 W cm^{-2} to 0.72 W cm^{-2} at 650 °C. Electrochemical impedance spectroscopy indicated that the reduced resistance was due to the shrinkage of the low frequency arc, which is associated with the electrochemical surface exchange reaction.

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1. Introduction

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) is a mixed ionic and electronic conductive (MIEC) perovskite oxide which has demonstrated excellent catalytic activity for the oxygen reduction reaction (ORR) in addition to high level of ion/electron conductivities which have attracted considerable attention for applications including solid

oxide fuel cell (SOFCs) cathodes, oxygen sensors, and oxygen separation membranes [1–3]. While significant progress has been made on LSCF based electrocatalysts, there is still room for improvement in order to achieve enhanced chemical-to-electrical conversion efficiency [4,5]. Efforts have been made to develop nano-scale and nano-structured electrodes, which are usually achieved by an impregnation or infiltration method. The unique structure of nanoparticles on the surface of submicron LSCF grains results in an enlarged surface area for three-phase boundaries (3PBs) where the electrode catalyst, electrolyte and gas phases

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meet and catalytic reaction occur [6,7]. Traditionally, costly precious metals such as Ag [8,9], Pd [10] and Rh [11] were used as nanoparticles to enhance the activity, i.e. reduce the interfacial polarization resistance of LSCF based cathodes used in SOFCs. Due to concurrent issues of the high cost of Pt and performance degradation associated with metal particle coarsening, alternative catalysts based on non-precious metals and metal-free materials are being actively pursued. Recent examples are the infiltration of oxides such as doped ceria $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (SDC) [12] and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) [13] which have been reported to improve the ORR catalytic activity. The performance improvements observed in doped ceria which has high levels of oxygen ion conductivity have been attributed to the enlarged 3PB where ORR principally occurs [14]. Hu et al. [15,16] have used an electrical conductivity relaxation (ECR) method to determine the ORR kinetics at the LSCF-SDC boundary. It was found that the oxygen incorporation at the LSCF-SDC-gas 3PB was more facile than on the LSCF surface. Estimates for the individual contributions of 3PB and LSCF surface indicated that the 3PB zones contribute 70% of the total ORR on the dense LSCF-SDC composite. In addition active metals and oxygen ion conductive oxides, materials such as Co_3O_4 and BaCO_3 have been tried as nanoparticle coatings to improve ORR activity through synergistic effects [17,18]. For example, BaCO_3 nanoparticles were recently demonstrated as excellent synergistic catalytic materials resulting in significant improvements in the ORR reaction in intermediate-temperature SOFCs. The performance improving factors of BaCO_3 nanoparticles were found to be even higher than those reported for precious metals [19]. Subsequent work revealed that the enhanced electrochemical performance is mainly associated with the surface exchange process [20].

Transition metal oxides such as CuO are often considered as optimal catalysts for CO oxidation [21–23]. This material has not attracted much attention for the reduction reaction because of the perceived limited catalytic abilities towards ORR. Chang et al. have reported the application of CuO as the cathode materials for $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{2-\delta}$ (YSZ) electrolyte [24] and proposed that CuO may possess requisite levels of oxygen vacancies needed to serve as a MIEC. CuO has also been used as a sintering aid to reduce the electrode calcination temperature [25]. In this work, it was found that 2 mol% CuO added to a LSCF-SDC composite, reduced the calcination temperature from 1000 °C to 800 °C and resulted in a 67% higher performance with an area specific resistance is $0.05 \Omega \text{ cm}^2$ at 700 °C.

This work reports on an investigation of the synergistic catalytic effect of CuO for ORR on LSCF electrodes. An ECR method was employed to investigate CuO effect on the ORR kinetics, i.e. the chemical surface oxygen exchange coefficient k_{Chem} . Combined with the surface microstructure analysis, we reveal the relationship between k_{Chem} and CuO surface morphology data and quantify the contribution of CuO to the overall oxygen incorporation rate. The performance of dispersed copper oxide (CuO) nanoparticles on LSCF electrodes was evaluated to verify the enhanced surface reaction process.

2. Experiment

2.1. Powder preparation

LSCF ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) powder was prepared with citric-EDTA method [26]. Stoichiometric amounts of precursors $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sino-pharm Chemical Reagent Co. Ltd) were dissolved in distilled water. Citric acid was then added to the solution at a mole ratio of 1:1:1 for metal ions: citric: EDTA and the pH value of the solution was controlled in 7 by using ammonia water at last. The precursor solution was subsequently heated on a hot plate until self-combustion occurred. The resulting ashes were calcined at 800 °C for 2 h to remove possible organic residues and to form the desired perovskite structure. SDC ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$) and NiO powders were prepared with the glycine-nitrate process and followed by heating the ashes at 600 and 850 °C for 2 h, respectively. To test the chemical compatibility of LSCF with the CuO, LSCF powders were mixed with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ at the weight ratio of 1:1 and sintered at 800 °C for 10 h.

2.2. Cell fabrications

Symmetrical cells were composed of dense SDC electrolyte substrates and porous LSCF electrodes decorated with CuO particles. The SDC powders were die-pressed at 250 MPa to form green substrates with a diameter of 13 mm and subsequently sintered at 1300 °C for 5 h. LSCF slurries were prepared by mixing the LSCF powders with an organic binder (α -terpineol as solvent and ethyl cellulose as the binder). The slurries were then printed onto both sides of the substrates. After drying under an infrared lamp, the samples were heated at 1000 °C for 2 h to form symmetrical cell structures. In order to infiltrate CuO particles, a solution was prepared with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolved in a mixture of water and ethanol (2:1, v/v) at a metal ions concentration of 0.3 mol L^{-1} . The infiltrating process was carried out by placing a drop of the solution on the top of the porous LSCF, letting the solution soak into the porous structure, drying, and heating the sample at 800 °C in air for 1 h to form metal oxide particles. The sample mass before and after each impregnating-drying-heating cycle was measured to estimate the CuO loading, which was expressed as the mass ratio of the infiltrated oxides to the porous LSCF.

Single cells were fabricated with the configuration of NiO-SDC anode substrates, SDC film electrolytes, and LSCF cathodes. The anode powders consisting of 65 wt% NiO and SDC were combined, and 20 wt% graphite was added as the pore forming-agent followed by pressing at 30 MPa. SDC powder as the electrolyte was subsequently added on the top of the pre-pressed anode pellet and co-pressed at 180 MPa to form a green bi-layer structure. The green bodies were sintered at 1300 °C for 5 h to densify the electrolyte layer. Cathodes were fabricated on the electrolytes with the same process used for symmetrical cell fabrication previously described.

Table 1
Characteristics for CuO particles on LSCF surfaces.

Sample code	Sputter time (s)	Processing temperature (°C)	θ_{CuO}	$L_{3\text{PB}} (\mu\text{m}^{-1})$	k_{eff} at 750 °C ($\times 10^{-5} \text{ cm s}^{-1}$)
Bare LSCF	0	—	0	0	2.6
CuO40	40	800	0.00792	1.13576	4.0
CuO60	60	800	0.02809	2.6102	5.8
CuO80	80	800	0.054	5.22519	7.23
CuO100	100	800	0.1279	12.6139	9.05
CuO120	120	800	0.1354	14.74012	9.3

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