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# Electrochemical performance of (La,Sr)(Co,Fe)$O_{3-\delta}$–(Ce,Sm)$O_{2-\theta}$–CuO composite cathodes for intermediate temperature solid oxide fuel cells

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ABSTRACT

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\theta}$–CuO composite cathodes were studied for the potential application in intermediate temperature solid oxide fuel cells. $Ce_{0.8}Sm_{0.2}O_{2-\theta}$ electrolyte with porous $Ce_{0.8}Sm_{0.2}O_{2-\theta}$ interlayer was successfully prepared by one-step sintering process. The effect of interlayer between cathode and electrolyte and CuO on the electrochemical performance of the composite cathodes was investigated by AC impedance spectroscopy. The application of interlayer decreased the area specific resistance of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\theta}$ cathode. The addition of CuO to $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ reduced the phase formation temperature of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ by 150 °C and the addition of CuO to $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\theta}$ cathode reduced the optimal calcination temperature of the cathode to 800 °C. The composite cathode with 2 mol% CuO calcined at 800 °C exhibited the lowest area specific resistance of 0.05 $\Omega$ $cm^2$ at 700 °C in air, which was reduced by 67% compared with that of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{2-\theta}$ cathode. The studies of the corresponding single cell performance, thermal expansion and thermal cycling behaviors further indicated that the composite cathode with 2 mol% CuO could be a promising cathode material.

## 1. Introduction

Recently, much attention has been focused on decreasing the operating temperature of solid oxide fuel cells to intermediate temperature (600–800 °C) [1,2]. However, the reduction of operating temperature enhanced cathodic polarization and resulted in cell performance decline. The electrochemical performance of cathode was closely related to its ionic conductivity, three phase (cathode/electrolyte/oxygen) boundary (TPB) area and electro-catalytic activity for oxygen reduction reaction (ORR) [3–5]. Consequently, it is necessary to develop the cathode with high ionic conductivity, large TPB area and outstanding electro-catalytic activity.

Noble metals [6], predominant electronic conductors [7,8] and mixed ionic–electronic conductors (MIECs) [9–11] have been studied for the potential application in intermediate temperature solid oxide fuel cells (IT-SOFCs). Due to the high cost for noble metals and the insufficient ionic conductivity for predominant electronic conductors, their applications were restricted and MIECs attracted extensive attention. MIEC $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) has been proposed primarily as cathode material owing to its high electrical conductivity and rapid surface exchange kinetics. Because the ionic conductivity of LSCF was relatively low and yet that of $Ce_{0.8}Sm_{0.2}O_{2-\theta}$ (SDC) was relatively high [12], LSCF-SDC cathode (with 30 wt% SDC) was prepared to improve the electrochemical performance of LSCF cathode [13]. For the SOFCs using YSZ electrolyte, the interfacial chemical reactions between LSCF cathode and YSZ electrolyte resulted in remarkable decline of cathode performance, thus YSZ electrolyte with dense GDC or SDC interlayer was prepared by two-step sintering process to prevent the undesirable reactions [14–17]. Nevertheless, for the IT-SOFCs using SDC electrolyte, cathode performance can be greatly affected by the TPB area, so we attempted to apply porous SDC interlayer between LSCF-SDC cathode and SDC electrolyte to enlarge the TPB area.

The electro-catalytic activity of cathode directly determined the ORR rate. As cathode had to be calcined at relatively high temperature (about 1000 °C) to form good adhesion to electrolyte [18–20], the electro-catalytic activity of cathode decreased greatly because of remarkable grain growth. It is an effective way to modify the cathode component to decrease its calcination temperature and increase its electro-catalytic activity. CuO was an effective sintering aid of ceramics and a good catalyst for chemical reactions as well [21–25]. Accordingly, CuO was considered to be added to LSCF-SDC cathode to increase the electro-catalytic activity of the cathode.

In this work, SDC electrolyte with porous SDC interlayer was prepared by one-step sintering process. LSCF-SDC-CuO composite cathode materials were prepared by mixing LSCF-SDC powder with

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copper nitrate in different molar ratio. The effect of interlayer and CuO on the electrochemical performance of LSCF-SDC-CuO composite cathodes was studied in detail. The composite cathode with the best electrochemical performance was determined by AC impedance spectroscopy. The corresponding single cell performance, thermal expansion and thermal cycling behaviors were further evaluated to determine the feasibility of using the composite cathode in IT-SOFCs.

## 2. Experimental

The $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) precursor powder was synthesized by glycine-nitrate process. The analytical reagent (AR) $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water in the stoichiometric ratio. Designed amount of glycine (AR) was then added to the above solution with constant stirring. A transparent sol was formed via continuous heating at 80 °C and then heated until it was ignited to form precursor powder. The precursor powder was calcined for 2 h at 800 °C in air. The $Ce_{0.8}Sm_{0.2}O_{2-\theta}$ (SDC) powder was synthesized by the same method. The SDC electrolyte was prepared by pressing SDC powder into pellet under 100 MPa and sintering the pellet at 1400 °C for 4 h. To prepare electrolyte with porous interlayer, SDC slurry made by ball-milling SDC powder, ethyl cellulose and terpineol was brushed on both surfaces of SDC green pellet and then sintered at 1400 °C for 4 h. The CuO powder was prepared by calcining copper nitrate at 750 °C for 2 h. The samples for the characterization of chemical compatibility were prepared by mixing LSCF powder with SDC/CuO powder thoroughly in the same weight ratio, followed by calcining for 2 h at 750–1100 °C. The phase composition was characterized by X-ray diffraction (XRD) with Cu K$\alpha$ radiation at room temperature.

The area specific resistances of cathodes were measured by AC impedance method using symmetric electrodes. The LSCF powder was mixed with 30 wt% SDC powder and then ball-milled for 10 h in ethanol using agate grinding media to obtain even mixture (denoted as LSCF-SDC). LSCF-SDC powder was mixed with 2 mol% solid copper nitrate to prepare LSCF-SDC-2CuO(S) powder. LSCF-SDC powder was also mixed with 0–3 mol% copper nitrate solution to prepare LSCF-SDC-$x$CuO ($x$ = 0, 0.5, 1, 2, 3) powders. LSCF-SDC-2CuO(S) and LSCF-SDC-$x$CuO powders were mixed with ethyl cellulose and terpineol followed by milling thoroughly in an agate mortar to prepare slurries. The slurries were brushed symmetrically on both surfaces of electrolytes (10.4 mm in diameter and 1 mm in thickness) with/without interlayer and then calcined for 2 h at 750–900 °C (LSCF-SDC slurry was calcined at 1050 °C) to form symmetric electrodes. The single cell was constructed based on the SDC electrolyte (26.5 mm in diameter and 1 mm in thickness). NiO powder was mixed with SDC powder thoroughly in the same weight ratio to prepare NiO-SDC power, which was then mixed with ethyl cellulose and terpineol to prepare slurry. NiO-SDC slurry was brushed on the one side of the SDC electrolyte as the anode and then calcined for 2 h at 1200 °C. Cathode slurry was brushed on the other side of the SDC electrolyte and then calcined at the corresponding optimal calcination temperature. LSCF-SDC, LSCF-SDC-$x$CuO ($x$ = 0.5–3) and SDC powders were pressed into bars (68 mm × 7 mm × 4 mm) under 220 MPa followed by sintering for 4 h at 1250, 1100 and 1400 °C respectively to form dense ceramics for thermal expansion measurements.

The electrochemical performances of cathodes were characterized in air using electrochemical workstation (PARSTAT 2273). The area specific resistances were measured at open circuit voltage (OCV) with the signal amplitude of 20 mV and the frequency range of 0.1–$10^6$ Hz. The single cell attached to one end of an alumina tube with the anode inside by using glass O ring as sealant followed by sealing in a specialized designed quartz tube with a sealant. The 40 $cm^3$ $min^{-1}$ of $H_2$ with 3% $H_2O$ and $O_2$ were supplied to the anode and cathode side, respectively. The single cell performance was tested using the same electrochemical workstation. The thermal cycling behavior was tested by increasing cell temperature to 700 °C and then decreasing to 30 °C repeatedly. The thermal expansion measurements were conducted in air between 25 °C and 700 °C by a dilatometer (RPZ-01, Luoyang, China). The microstructures of samples were examined using scanning electron microscope (SEM, JEP, JSM-5900).

## 3. Results and discussion

XRD analysis indicated that all the samples of LSCF, SDC and CuO powders were single phase and no secondary phases occurred except the peak shifts in the pattern of LSCF-SDC (1100 °C) compared to the corresponding patterns of single phase, shown in Fig. 1. The peaks of SDC shift towards low-angle while the peaks of LSCF shift towards high-angle. It may result from the interdiffusion of La ions in LSCF and Sm ions in SDC at 1100 °C, which induced the expansion of SDC lattice and the contraction of LSCF lattice. Furthermore, the addition of CuO to LSCF made the phase formation temperature of LSCF decrease from 900 °C to 750 °C, as presented in the pattern of LSCF-CuO (750 °C). It can be caused by the catalysis of CuO, which made the activation energy of the formation reaction of the perovskite phase reduced. Neither secondary phases nor peak shifts occurred in the pattern of LSCF-SDC-CuO (950 °C). Additionally, the content of CuO in the cathode was actually much lower and the operating temperature of the cathode was 600–800 °C. Thus LSCF-SDC cathode exhibited good chemical compatibility with CuO at the working temperature.

In order to enlarge the TPB area, porous interlayer was applied between cathode and electrolyte. Fig. 2 shows the impedance spectra of LSCF-SDC/SDC/LSCF-SDC symmetrical cells (calcined at 1050 °C) with/without interlayer measured at 700 °C. The polarization resistances ($R_p$) of cathodes were determined by fitting the impedance spectra using the equivalent circuit shown in Fig. 2. $L$ is the inductance caused by leads. $R_s$ is the overall ohmic resistance, including the electrolyte, electrodes and contact resistances. It corresponds to the intercept of the impedance arc with the real axis at high frequency. ($R_1$, $CEP_1$) at high frequency and ($R_2$, $CEP_2$) at low frequency represent the processes of charge transfer and oxygen diffusion respectively. $R_p$ is the sum of $R_1$ and $R_2$. The area specific resistance (ASR) can be deduced from the relation: ASR = $R_p$ × surface area/2.

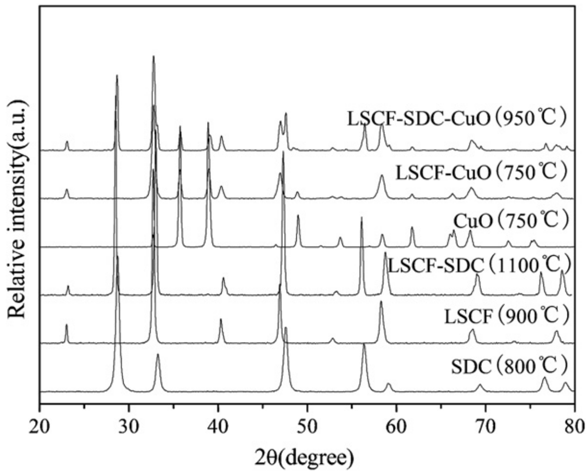

**Fig. 1.** XRD patterns of samples.