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# Effects of cerium doping on the performance of LSCF cathodes for intermediate temperature solid oxide fuel cells

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## ABSTRACT

In this paper, effects of Ce substitution of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF) on the crystal structure have been investigated by XRD Rietveld refinement and results show that Ce doping at La-sites leads to lattice expansion without changing centrosymmetric cubic space group of LSCF. The electrochemical results suggest that the electrocatalytic activity of LSCF cathodes is enhanced by Ce doping. The values of oxygen surface exchange coefficient of LSCF, LCSCF03, LCSCF06, measured by electrical conductivity relaxation (ECR) method, are  $5.6 \times 10^{-4} \text{ cm s}^{-1}$ ,  $1.0 \times 10^{-3} \text{ cm s}^{-1}$ ,  $3 \times 10^{-3} \text{ cm s}^{-1}$  at 750 °C respectively, implying that oxygen surface exchange coefficients are increased by Ce doping compared with that of LSCF. The enhancement of electrochemical performance of LSCF cathodes can be ascribed to the increase of the concentration of oxygen vacancies obtained from the thermogravimetric results, which results in faster kinetics of oxygen transport by Ce doping.

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## Introduction

Solid oxide fuel cells (SOFCs) are promising devices which can convert the chemical energy directly into electrical energy and heat as long as sufficient fuels such as hydrogen or natural gas are supplied [1–3]. Nowadays, many researchers devote efforts to intermediate temperature SOFC (IT-SOFC) using metal interconnectors because of their better long time stability, low-cost compared with high temperature SOFC (HT-SOFC) [4–6]. Although the other components such as anode and

interconnect have issues such as coarsening of nickel and interactions between cathode and interconnect, a great challenge originates from cathodes [7].

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM) [5,8] and  $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_3$  (LSCF) [9–14] are accepted as two promising cathode materials worldwide. Though the satisfied performance can be achieved at high operation temperature (~1000 °C), high operation temperature will cause faster degradation rate and higher requirement for components. Lowering temperatures from ~1000 °C to 600–800 °C for commercial application of SOFC decreases the performance of LSM cathodes since their poor

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catalytic activities for oxygen reduction reaction [15,16], while more attentions were attracted by LSCF cathode due to their excellent mixed ionic and electronic conductivities [17,18], catalytic activities for oxygen reduction reaction [11,19,20] and better stability than LSM [15,21].

Many studies have adopted various methods such as changing microstructure, impregnation, doping elements to improve the electrocatalytic activities of LSCF-based cathodes. Zhao et al. studied the performance of LSCF fiber which had high electrocatalytic activity due to their high porosity and the facile gas diffusion [22]. Our previous study proved that impregnating palladium on LSCF-GDC cathode decreased the polarization resistance [23]. Zhang et al. found that infiltration CaO to porous LSCF electrodes can increase the oxygen reduction reaction (ORR) catalytic activity [24]. Lakshminarayanan et al. demonstrated that B-site doping of LSCF with Zn, Ni and Cu enhanced the oxygen vacancy generation properties significantly, while LSCF still maintaining a stable perovskite structure [16]. Huang et al. clarified that adding Cu, Ag and Pt to LSCF could take in more oxygen from the gas phase because of higher oxygen affinity of the metals [25]. Mastrikov et al. concluded that Pd doping on LSCF could decrease oxygen vacancy formation energy, forming more oxygen vacancies [26]. Naumovich et al. confirmed that partial substitution by copper in B sublattice of LSCF resulted in a higher electrical conductivity below 800 °C [27]. Longo et al. reported Ni dopant on LSCF stabilized the oxygen vacancies in LSCF and delayed their formation [28]. Chen et al. found that Nb and Pd co-doped LSCF exhibited better electrocatalytic activity and excellent operation stability than that of LSCF [29]. All the work mentioned above enhanced the performance of LSCF cathodes. Up to now, cation doping is regarded as an effective strategy to develop high performance perovskite-type SOFC cathode materials. But most elements for doping are noble metal, which are expensive and not suitable for commercial use of SOFC.

Recently, materials containing cerium have exhibited excellent catalytic activities for oxygen reduction reaction and hydrocarbon reformation. Chaudhari et al. investigated the catalytic activity of Ce-doped  $\text{Sm}_2\text{CuO}_{4+\delta}$ , and results demonstrated that  $\text{Sm}_{1.9}\text{Ce}_{0.1}\text{CuO}_4$  showed higher catalytic activity than that of  $\text{Sm}_2\text{CuO}_{4+\delta}$  [30]. Song et al. explored A-site ceria-substituted  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$  and studied the catalytic activities for  $\text{H}_2$  oxidation and  $\text{H}_2\text{S}$  reformation, determining that  $\text{La}_{0.75}\text{Sr}_{0.125}\text{Ce}_{0.125}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$  exhibited better redox properties [31]. Bian et al. studied Ce-doped  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$  in direct-methane solid oxide fuel cells and concluded that cerium doping enhanced methane reforming activity of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$  [32]. Therefore, Ce doping may enhance the performance of LSCF cathodes and its mechanism should be investigated in detail.

The present study focused on effects of Ce doping on electrochemical properties of LSCF cathodes. In this work, LSCF,  $\text{La}_{0.57}\text{Ce}_{0.03}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LCSCF03) and  $\text{La}_{0.54}\text{Ce}_{0.06}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LCSCF06) electrodes were synthesized and their performances were investigated. X-ray diffraction (XRD), Electrochemical impedance spectroscopy (EIS) and Electrical conductivity relaxation (ECR) were employed to evaluate the enhanced mechanisms of electrochemical catalytic activities of LSCF cathodes by Ce doping.

## Experimental

### Preparation of cathodes and cells

LSCF, LCSCF03, LCSCF06,  $\text{La}_{0.51}\text{Ce}_{0.09}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LCSCF09) powders were synthesized by sol-gel method. Stoichiometric amount of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.9%),  $\text{Sr}(\text{NO}_3)_2$  (99.5%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98.5%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (98.5%) and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.5%) (Sinopharm Chemical Reagent Co. Ltd.) were dissolved in deionized water simultaneously, followed by the addition of citric acid (CA). The ethylenediamine-tetra-acetic acid (EDTA) was dissolved with ammonia. Both of solutions above were then mixed together. The mole ratio of the total metal ions: CA: EDTA = 1:1.25:1.25. Ammonia aqueous was applied to adjust the pH value of the solution to 6–7. The mixture was heated in an oil bath at 80 °C until it became a transparent gel. The obtained gel was then fired at 200 °C for 5 h. A subsequent heat treatment was performed at 900 °C for 6 h in air in order to obtain the final powders.  $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$  (GDC) powders (Ningbo SOFCMAN Energy Technology Co. Ltd, China) were die pressed and then sintered at 1550 °C for 5 h to form the dense GDC electrolyte pellets. The electrode powders were mixed with cellulose binder in a weight ratio of 5:5 to obtain the electrode slurries, which then was coated onto the GDC electrolyte. The cathode will be obtained after sintering at 1050 °C for 2 h. Pt was used as counter and reference electrode. Pt was also applied to paint on the working electrode as the contact layers for current collection after sintering at 900 °C for 2 h.

### Characterization measurements

EIS measurements of LSCF, LCSCF03 and LCSCF06 cathodes were carried out by using a Gamry Interface 1000 Potentiostat in air under the condition of open circuit. The temperature of electrochemical measurements ranged from 650 to 800 °C with an interval of 50 °C. Impedance data were recorded in a frequency range from 0.1 Hz to 100 KHz with an excitation voltage of 10 mV. The value of electrode polarization resistance ( $R_p$ ) was equal to the differences between the high and low frequency intersections of the impedance spectrum in the first quadrant on the real axis (Zreal axis). DRT (Distribution of relaxation times) was used to fit the impedance data, which turned impedance data into a distribution of the time constants involved in the considered system. The numbers of peaks represent the amount of sub-processes and the area of peaks represented the polarization resistance related to the main limiting sub-processes involved in ORR processes of cathodes.

The values of the oxygen surface exchange coefficient  $K$  were achieved with ECR results by changing the oxygen partial pressure from 0.21 (21% $\text{O}_2$ +79% $\text{N}_2$ ) to 1 (100% $\text{O}_2$ ) atm. Four silver threads wrapped around the ends of strip dense samples of LCSCF03 and LCSCF06, two of which acted as current leads while two other silver threads acted as voltage probes. The silver paste was coated on the silver threads to ensure good contact. Then the data acquired by a digital multimeter (Keithley Model 2000) were dealt with a program written by the LabVIEW software.

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