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Short communication

# A cobalt-free electrode material $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ for symmetrical solid oxide fuel cells

Jun Lu, Yi-Mei Yin *, Jingcheng Li, Lei Xu, Zi-Feng Ma **

*Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

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ABSTRACT

Cobalt-free perovskite oxide $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFC) was applied as both anode and cathode for symmetrical solid oxide fuel cells (SSOFCs). The LSFC shows a reversible transition between a cubic perovskite phase in air and a mixture of $SrFeLaO_4$, a $K_2NiF_4$-type layered perovskite oxide, metallic Cu and $LaFeO_3$ in reducing atmosphere at elevated temperature. The average thermal expansion coefficient of LSFC in air is $17.7 \times 10^{-6}\ K^{-1}$ at 25 °C to 900 °C. By adopting LSFC as initial electrodes to fabricate electrolyte supported SSOFCs, the cells generate maximum power output of 1054, 795 and 577 mW $cm^{-2}$ with humidified $H_2$ fuel (~3% $H_2O$) and 895, 721 and 482 mW $cm^{-2}$ with humidified syngas fuel ($H_2$:CO = 1:1) at 900, 850 and 800 °C, respectively. Moreover, the cell with humidified $H_2$ fuel demonstrates a reasonable stability at 800 °C under 0.7 V for 100 h.

## 1. Introduction

Tremendous efforts have been devoted to reduce the cost and prolong the lifetime of solid oxide fuel cells (SOFCs) to promote their commercialization [1,2]. Recently, a simplified single cell configuration using the same initial materials as both anode and cathode, denoted as symmetrical SOFCs (SSOFCs), has been catching increasing attention due to its remarkable advantages in problem-solving and cost reduction [3–6]. In SSOFCs, such problems as coke formation and sulfur poisoning over the anode using carbon containing fuels can be easily solved by simply reversing the gas flow. Moreover, the same initial composition of the electrodes allows the cell to be fired in a simpler step compared to the conventional SOFCs; therefore, not only reducing the cell fabrication costs but also slowing down the coarsening of particles in electrodes. Thus the reliability of SSOFC systems will be enhanced.

However, developing efficient electrode materials for SSOFC is a serious challenge, because the materials are required to have not only appreciable electrocatalytic activity for both oxygen reduction and fuel oxidation, but also high electronic conductivity in both oxidizing and reducing atmospheres to decrease ohmic losses. Limited materials have been reported to be effectively used as both anode and cathode for SSOFCs [7]. Conventional ceramic anode materials as electrodes for SSOFC showed poor cathode performance, and consequent low fuel cell output [4,8–11], Cobalt-iron based typical cathode materials with single phase were then used as SSOFC electrodes, for example, $Ln_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (Ln = La, Ce)[12–14] and $SrFe_{0.75}M_{0.25}O_{3-\delta}$ (M = Ti, Zr, V, Nb, Cr, Mo and W) [15]. Although these materials demonstrate considerable activity for hydrogen or methane oxidation, their structure stability in reducing atmospheres is still a significant concern [16]. Alternatively, several partially reducible cathodes were reported to display promising properties and performance as electrodes of SSOFC, such as $(Ln_{0.4})_xSr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\delta}$ (Ln = Pr, La) [17,18]. These materials can be partially reduced to $K_2NiF_4$-type layered perovskite oxides and metallic particles at anode which show excellent activity for fuel oxidation and good electronic conductivity. However, the high price of cobalt and praseodymium will raise the cost of the materials; furthermore, cobalt in these materials results in high thermal expansion coefficients (TECs) in air which will be detrimental to their thermal compatibility with electrolyte and the long term stability of fuel cells.

$La_{1-x}Sr_xFe_{1-y}Cu_yO_{3-\delta}$ ($LSFC_{x/y}$) perovskite oxides are affordable cobalt-free perovskite oxides with excellent cathode performance for SOFCs [19], and copper–iron containing perovskite oxides have been reported to show catalytic activity for oxidation reactions of CO or methane [20,21]. Furthermore, copper can effectively decrease the TEC and the calcining temperature of the materials [22,23]. Nevertheless, they have never been reported, to the best of our knowledge, as anode of SOFC. Therefore, in this work, the potential of LSFC used as SSOFC electrodes will be assessed by examining its redox property, thermal compatibility with electrolyte, and single cell performance.

## 2. Experimental

$La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFC) precursor (eg. 0.1 mol) was synthesized using a conventional solid-state reaction method with $La_2O_3$ (0.025 mol), $SrCO_3$ (0.05 mol), $Fe_2O_3$ (0.04 mol) and CuO (0.02 mol)

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* Corresponding author. Tel.: +86 21 34206255; fax: +86 21 54741297.
** Corresponding author. Tel.: +86 21 54742894; fax: +86 21 54741297.
*E-mail addresses:* yimei@sjtu.edu.cn (Y.-M. Yin), zfma@sjtu.edu.cn (Z.-F. Ma).

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powders as starting materials and mixed by ball milling for 24 h [21]. The LSFC powders were obtained by calcining the precursor in air at 1100 °C for 10 h. X-ray diffraction (XRD) measurements were performed on an X-ray diffractometer (XRD, Rigaku D/max-2200/PC) with a Cu Ka radiation, $\lambda = 0.15415$ nm; And TEC values were determined with a horizontal pushrod Netzsch DIL 402 PC dilatometer from room temperature (RT) to 900 °C.

Electrolyte-supported single cells with the LSFC|SDC|ScSZ|SDC|LSFC configuration (SDC: $Sm_{0.2}Ce_{0.8}O_{1.9}$; ScSZ: Sc-doped $ZrO_2$, 10Sc1CeSZ) were prepared by screen-printing method. SDC interlayer was inserted between LSFC electrode and ScSZ electrolyte to prevent reactions between LSFC and ScSZ as confirmed by XRD measurements (data not shown). The current density–voltage (I–V) and current density–power density (I–P) curves of the single cells were tested by four-probe configuration. The anode side is fed by humidified hydrogen or syngas ($50\%H_2 + 50\%CO$) with 3 vol.% $H_2O$ at the flow rate of 60 ml $min^{-1}$, while the cathode is exposed to stationary air as oxidants. The cell was heated to 900 °C and held for 1 h to ensure a stable output to be reached. Detailed test processes and instruments setup can be found in our previous reports [24–26].

Electrochemical impedance spectra (EIS) of the SSOFCs were collected via AC impedance method using Autolab PGSTAT 302 N electrochemical workstation in temperature range of 700–900 °C at 50 °C interval. An AC signal with 10 mV amplitude and a frequency range from 0.01 Hz to $10^6$ Hz was applied as stimuli. The cells were stabilized at each testing temperature for 15 min before the EIS records were collected.

## 3. Results and discussion

To investigate the redox behavior of LSFC in air and reducing atmospheres, the LSFC powders were reduced in $5\%H_2$–Ar and humidified $H_2$ at 900 °C for 10 h, respectively, and the $H_2$ reduced sample was followed by a sequential re-oxidization in air at 900 °C for 2 h. Fig. 1A shows the XRD patterns of those samples. Cubic perovskite phase (space group *Pm-3m*) was well indexed for LSFC prepared in air (A1), which is consistent with previous reports for $La_{0.2}Sr_{0.8}Fe_{1-x}Cu_xO_{3-\delta}$ ($x = 0.1$–$0.2$) [27]. After the mild reduction in $5\%H_2$–Ar, a secondary $K_2NiF_4$-typed minor phase of $SrFeLaO_4$ and metallic Cu can be observed in pattern A2. A further structure transition for the LSFC occurs after the deep reduction in humidified $H_2$ as shown in pattern A3. The reduced products, denoted as R-LSFC, are mixture of $SrFeLaO_4$, metallic Cu, minor phase of $LaFeO_3$ and the perovskite phase. A similar reduction had been reported for $La_{0.5}Sr_{0.5}FeO_3$ perovskite oxide after heating in $90\%$ $H_2/10\%N_2$ at

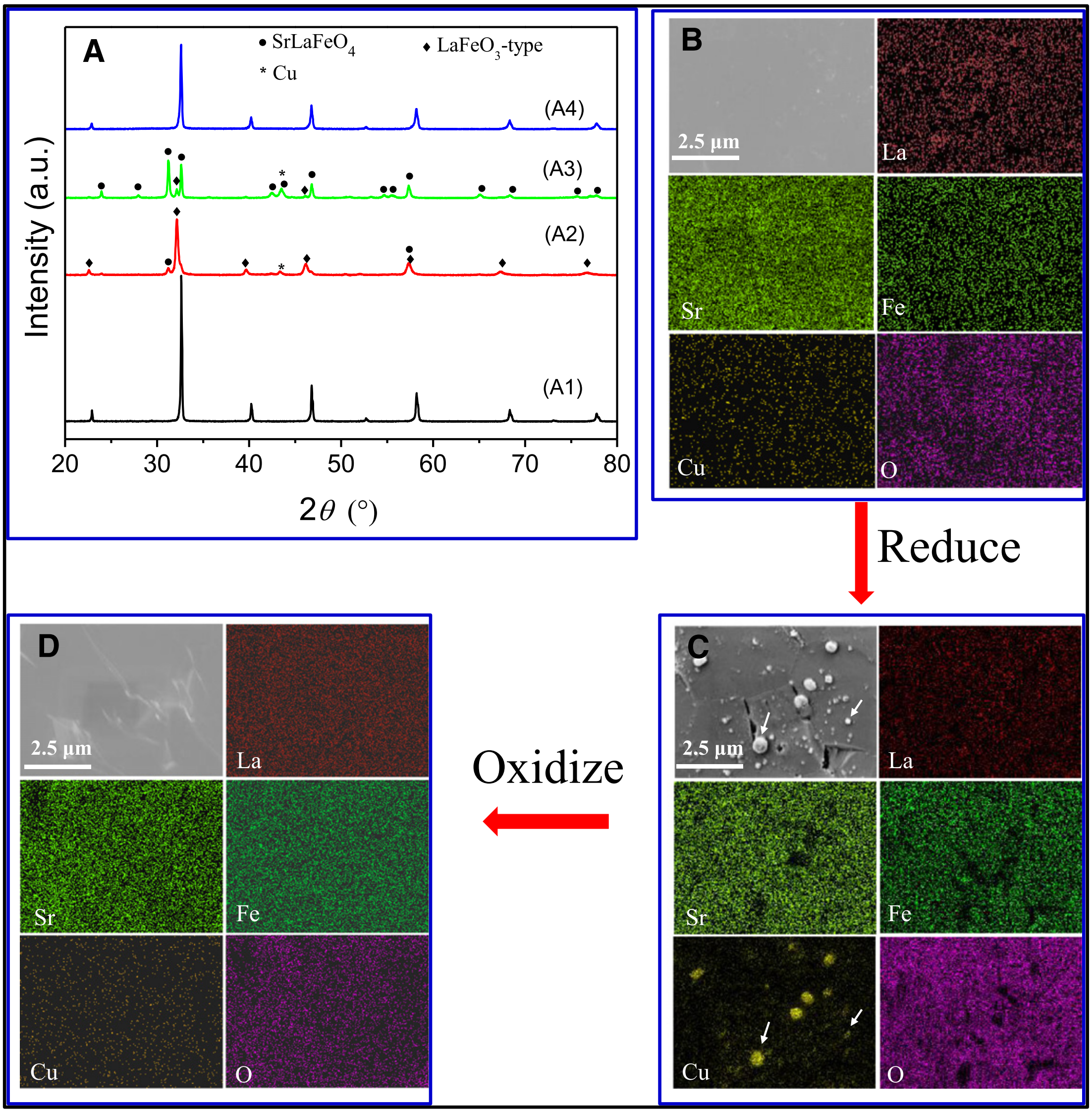

**Fig. 1.** XRD patterns of LSFC powders (A1), reduced LSFC samples in $5\%H_2$–Ar (A2) and humidified $H_2$ (A3), respectively, at 900 °C for 10 h, and re-oxidized A3 sample in air at 900 °C for 2 h (A4). SEM images and EDX mapping analysis of LSFC bars (B) sintered in air at 1200 °C for 5 h, (C) reduced in humidified $H_2$ at 900 °C for 10 h and (D) re-oxidized in air at 900 °C for 2 h.