



Evaluation of $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ as a Potential Electrode for Symmetrical Solid Oxide Fuel Cells



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ABSTRACT

Structure stability and electrical conductivity of $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ were investigated in air and in hydrogen to explore its potential applications as symmetrical electrodes for solid oxide fuel cells. X-Ray diffraction measurements showed that $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ was essentially stable despite the presence of minor LaSrFeO_4 impurities after heat-treated in humidified hydrogen at 800 °C. $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ -based symmetrical fuel cells fabricated on LSGM electrolyte substrates via screen printing achieved a maximum power density of 224 mW cm⁻². After using a composite electrode (50 wt% $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ -50 wt% $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$), both the anode and the cathode polarization resistances decreased. The maximum power density of symmetrical fuel cells using $\text{LaSr}_2\text{Fe}_2\text{CrO}_{9-\delta}$ - $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ composite electrodes increased to 264 mW/cm² and the corresponding total cell polarization resistance was 0.454 Ω cm² at 800 °C with humidified hydrogen fuels and ambient air oxidants.

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1. Introduction

Solid oxide fuel cells (SOFCs) are solid-state electrochemical devices to convert fuels into electricity with distinctive features of high energy efficiencies, low gas emissions and wide fuel flexibility [1–4]. Traditional SOFCs consist of yttria-stabilized zirconia (YSZ) electrolytes, Ni-YSZ anodes and lanthanum strontium manganite (LSM) cathodes. The new configuration of symmetrical SOFCs utilizes the same and inexpensive oxide materials simultaneously as the anodes and the cathodes [5–8], and has attracted significant interest due to several important advantages over the non-symmetrical counterparts, including minimized interfacial compatibility issues, simplified fabrication procedures, reduced processing costs as well as better tolerance toward coking formation and sulfur poisoning [9]. In order to achieve reasonably good power densities, the symmetrical electrode material should be structurally stable and electrically conductive over a wide range of oxygen partial pressure, and have high catalytic activities for both oxygen reduction and hydrogen oxidation reactions. Currently, most of symmetrical electrode materials are derived from lanthanum chromite perovskite oxides [5,10–12], which have been previously used as the interconnect materials due to their good stability and

acceptable conductivities in both oxidizing and reducing environments. For instances, symmetrical $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ (LCC)-YSZ electrodes showed a total polarization resistances ($R_{p, \tau}$) of 3.142 Ω cm² at 850 °C over YSZ electrolytes [7]. Introducing chromium deficiency in the perovskite oxide resulted in larger electrical conductivities and smaller polarization resistances, e.g., $R_{p, \tau} = 2.17 \Omega \text{ cm}^2$ for symmetrical $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.97}\text{O}_{3-\delta}$ -YSZ electrodes at 850 °C [13].

Alternatively, the symmetrical electrode materials could also be obtained by substituting the common perovskite oxide cathodes with Cr [5,10,11,14,15], Ti [6], Mo [16] and Sc [17,18] that helped to increase their chemical stability in reducing atmospheres. Table 1 lists polarization resistance values for some symmetrical electrode materials. Bastidas *et al.* showed that Cr-doped lanthanum strontium manganite, $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM), were redox-stable and produced polarization resistances of $R_{p, A} = 0.3 \Omega \text{ cm}^2$ in hydrogen and $R_{p, C} = 0.35 \Omega \text{ cm}^2$ in oxygen on YSZ electrolytes at 900 °C [5]. Chen *et al.* reported that Cr-doped lanthanum strontium ferrite, $\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$, exhibited even much smaller polarization resistances when used as symmetrical electrodes on the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolytes, e.g., $R_{p, A} = 0.45 \Omega \text{ cm}^2$ in hydrogen and $R_{p, C} = 0.25 \Omega \text{ cm}^2$ in air at 750 °C [11]. $\text{LaSr}_2\text{Fe}_3\text{O}_9$ is a mixed oxide-ionic and electronic conductor with a rhombohedrally distorted perovskite structure in air, and has been investigated as an oxygen permeation membrane material due to its high ionic conductivities, e.g., 0.34 S cm⁻¹ at 950 °C and 0.14 S cm⁻¹ at 800 °C. Partial substitution of

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Table 1
Polarization resistances for some symmetrical electrodes at open circuits in air and in hydrogen.

Electrode Materials	T/°C	Electrolytes	R _{p,C} (air)	R _{p,A} (H ₂)	R _{p,T}	Ref.
La _{0.7} Ca _{0.3} CrO _{3-δ} -YSZ	850	YSZ	–	–	3.14	7
La _{0.7} Ca _{0.3} Cr _{0.97} O _{3-δ} -YSZ	850	YSZ	0.16	2.01	2.17	13
La _{0.75} Sr _{0.25} Cr _{0.5} Mn _{0.5} O _{3-δ}	900	YSZ	0.35	0.3	0.65	5
	800	YSZ	–	0.28	–	10
	800	YSZ	0.43	–	–	14
La _{0.3} Sr _{0.7} Fe _{0.8} Cr _{0.2} O _{3-δ}	750	LSGM	0.25	0.45	0.7	15
Sr ₂ Fe _{1.5} Mo _{0.5} O _{3-δ}	780	LSGM	0.24	0.27	0.51	16
La _{0.8} Sr _{0.2} Sc _{0.2} Mn _{0.8} O _{3-δ}	850	ScSZ	6.5	0.35	6.85	17
La _{0.6} Sr _{0.4} Fe _{0.9} Sc _{0.1} O _{3-δ}	800	LSGM	0.015	0.29	0.305	18
La _{0.75} Sr _{0.25} Cr _{0.5} Al _{0.5} O _{3-δ}	800	LSGM	1.2	0.45	1.65	14

chromium for ferric in the lattice helped maintain the rhombohedral structure in reducing atmospheres that otherwise changed to an oxygen vacancy-ordered orthorhombic structure [19]. More importantly, partial involvement of oxygen ions coordinated by the chromium dopant in the ion transport mechanism allowed relatively high oxide ionic conductivities at high Cr contents. In particular, the solid solution LaSr₂Fe₂CrO_{9-δ} (LSFCr) exhibited an oxide-ionic conductivity of 0.05 S cm⁻¹ and an electronic conductivity of 100 S cm⁻¹ in air at 800 °C [19]. Due to its promising stability in reducing atmospheres, LSFCr was evaluated for the potential application as an SOFC anode material. Barnett *et al.* showed that the LaSr₂Fe₂CrO_{9-δ}-Gd_{0.1}Ce_{0.9}O_{2-δ} composite anodes could achieve stable polarization resistances of 0.26 Ω cm² in humidified hydrogen at 800 °C [20,21] and good resistances against H₂S poisoning [22]. Note that LaSr₂Fe₂CrO_{9-δ} has rarely been used as the SOFC cathode, even though it did show good mixed conducting behavior in air. In this paper, we explored the application of LSFCr as a potential symmetrical electrode for SOFCs. The polarization behavior was evaluated via impedance measurement on the La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) electrolyte-supported SOFCs exposed to dry air or low humidity hydrogen. Influence of GDC addition into the symmetrical electrodes on the polarization behavior was also discussed.

2. Experimental

LSFCr powders were synthesized using a citric acid-based sol-gel method. Stoichiometric amounts of La(NO₃)₃·6H₂O, Sr(NO₃)₂, Fe(NO₃)₃·9H₂O and Cr(NO₃)₃·9H₂O were dissolved in deionized water. These nitrates were 99% pure and purchased from Sinopharm Chemical Reagent. Ethylene diaminetetra acetic acid (EDTA) was first dissolved in ammonia and then added into the mixed nitrate solution at a 1:1 molar ratio of EDTA to the total metal ions, which was continuously stirred for half an hour to promote chelation of these cations with EDTA. Finally, citric acid was added with the molar ratio of citric acid to the total metal ions at 1.2:1 with the pH value adjusted to around 6 via dropwise addition of ammonia. The solution was then slowly heated on a hot-plate until self-combustion occurred to produce precursor ashes, which were subsequently pulverized and calcinated in air at different temperatures. In order to evaluate the stability of the resultant oxides, some of these powders were thermally treated in humidified hydrogen (3% H₂O) for 10 h at 800 and 750 °C, respectively. The phase structures of air-calcinated and hydrogen-reduced powders were examined at room temperature using an X-ray diffractometer (XRD) (Rigaku-D-Max γA) over a scanning range of 20–100°. As-synthesized LSFCr powders were compacted into rectangular bars and used for measurement of sintering shrinkage behavior in air using a dilatometer (NETZSCH DIL 402 C, Germany) from room temperature to 1200 °C at a ramp rate of 5 °C/min. Green bars were also sintered in air at 1300 °C for 5–20 h to achieve 95% of the theoretical density. The electrical conductivities of LSFCr were measured in

ambient air and humidified hydrogen (3% H₂O) from 500 to 800 °C using a standard four-probe DC method [23].

Electrochemical properties of LSFCr as symmetrical electrodes were evaluated using thick LSGM electrolyte substrates. LSGM powders were synthesized and calcinated at 1000 °C using the citric acid-based sol-gel method, which were uniaxially pressed into disks of 15 mm in diameter under a pressure of 250 MPa and then pre-sintered in air at 1250 °C for 6 h to ensure adequate strength. In order to prevent interfacial diffusion between LSGM electrolytes and LSFCr electrodes [22,24], thin barrier layers of La_{0.4}Ce_{0.6}O_{2-δ} (LDC) powders were coated using the screen printing method onto both sides of LSGM substrates, followed by co-sintering at 1400 °C for 4 h. Similarly, symmetrical LSFCr electrodes were applied and fired at 1200 °C for 3 h. In some cases, GDC was added to the LSFCr electrodes in a weight ratio of 50:50. The working area of symmetrical electrodes was 0.5 cm².

For electrochemical measurements, silver ink was applied on the electrode surface as the current collector and silver wires were attached as the current and voltage leads. Current-voltage curves and electrochemical impedance spectra were obtained using an IM6 Electrochemical Workstation (ZAHNER, Germany) with one side exposed to ambient air and the other to humidified (3% H₂O) hydrogen at a flow rate of 40 mL min⁻¹. The individual electrode polarization resistances were determined by testing such symmetrical fuel cells in the single-chamber mode with humidified hydrogen for the anode and ambient air for the cathode. The microstructure of measured fuel cells was examined using scanning electron microscopy (SEM) in a Hitachi S-4800-II microscope.

3. Results and Discussion

Fig. 1(a) shows the X-Ray diffraction (XRD) patterns of LSFCr powders as synthesized in air at 1200 °C. Notably, a pure perovskite phase was obtained without any minor impurity within the instrument resolution. Refinement of the XRD patterns using the MDI Jade 6.0 software indicated that LSFCr crystallized as a rhombohedral crystal structure with R $\bar{3}c$ space group as consistent with prior reports [18]. In order to examine the chemical stability of LSFCr synthesized in air, some powders were further heat-treated in 97% H₂-3% H₂O for 10 h at 750 and 800 °C with XRD patterns shown in Fig. 1(b) and 1(c), respectively. Comparison with Fig. 1(a) indicates that the rhombohedral crystal structure was well maintained for LSFCr reduced at 750 °C while a small peak appeared at 2θ = 31.37° for LSFCr reduced at 800 °C due to the formation of minor LaSrFeO₄ impurity with a mass fraction of 4.67% as estimated using the MDI Jade 6.0 software. The lattice parameters and lattice volume were obtained from refining these XRD patterns (Table 2), and increased with increasing reduction in hydrogen due to loss of oxygen.

Fig. 2(a) shows the sintering behavior of the green LSFCr bars in air, showing that densification and linear shrinkage started to occur above 1000 °C. Note that the measured density for LSFCr samples sintered at 1200 °C for 6 h was 4.47 g cm⁻³, approximately

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