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La_{0.7}Sr_{0.3}Fe_{0.7}Ga_{0.3}O_{3-δ} as electrode material for a symmetrical solid oxide fuel cell

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In this research, La_{0.7}Sr_{0.3}Fe_{0.7}Ga_{0.3}O_{3-δ} (LSFG) perovskite oxide was successfully prepared using a microwave-assisted combustion method, and employed as both anode and cathode in symmetrical solid oxide fuel cells. A maximum power density of 489 mW cm⁻² was achieved at 800 °C with wet H₂ as the fuel and ambient air as the oxidant in a single cell with the configuration LSGF|La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-δ}|LSFG. Furthermore, the cells demonstrated good stability in H₂ and acceptable sulfur tolerance.

Symmetrical solid oxide fuel cells (SSOFCs), using the same materials for both anode and cathode, have attracted much attention because they can be easily assembled, minimizing problems with the diffusion between cell components and suppressing possible problems with sulfur poisoning and carbon deposition.^{1,2} For SSOFCs, however, the requirements of electrode materials are rather limiting because they need to be operated in both oxidizing and reducing environments. The electrode must demonstrate good chemical and structural stabilities in both environments and maintain an ideal electrocatalytic performance for oxygen reduction and fuel oxidation.³ Many methods have been introduced to modify the conventional electrode to achieve better performance and stability. For example, Chen *et al.* reported a novel design for enhancing the coking resistance of a solid oxide fuel cell (SOFC) anode while maintaining good performance.⁴ Ding *et al.* found that surface modification through infiltration drastically enhanced the electrocatalytic activity and stability of the cathode.^{5,6} However, those modifications increase the system complexity.

Recently, different types of perovskite materials, such as Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ},¹ La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM),^{2,7} La_{0.8}Sr_{0.2}Sc_{0.8}Mn_{0.2}O_{3-δ} (LSSM),⁸ La₄Sr₈Ti_{12-x}Fe_xO₃₈,⁹

Pr_{0.7}Ca_{0.3}Cr_{1-y}Mn_yO_{3-δ}¹⁰ and La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-δ},¹¹ have been investigated as electrodes for SSOFCs. However, the cell performance of SSOFCs is normally lower than that of traditional SOFCs, which can be attributed to the narrow selectivity of the electrode materials. For example, the cell with the configuration of LSCM|yttria-stabilized zirconia (YSZ)|LSCM showed a peak power density of 300 mW cm⁻² when using hydrogen (H₂) as the fuel at 900 °C.⁷ Shao *et al.* obtained the highest power density of 310 mW cm⁻² when operating on wet H₂ at 900 °C by applying LSSM as cathode and anode.⁸ Most of the previously mentioned materials show a moderate performance. Therefore, it is urgent that new symmetrical electrodes for application in SSOFCs are developed.

La_{0.7}Sr_{0.3}Fe_{1-y}Ga_yO_{3-δ} (LSFG) perovskite-type oxides have been investigated as oxygen permeating materials because of their mixed ionic and electronic conductivity.^{12,13} In addition, they also show a very good stability against reduction over a wide range of oxygen partial pressures (*P*_{O₂}).¹² Furthermore, LSFG has been proven to be an active catalyst with thermal stability for the catalytic combustion of methane, which is attributed to the active surface oxygen species with high reducibility and oxygen mobility,¹⁴ which means that LSFG could be a potential anode for SOFC. On the other hand, according to the studies of Ishihara *et al.*¹⁵ and Vivet *et al.*,¹⁶ LSFG shows a higher oxygen permeation rate than that of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}, a conventional cathode for SOFC.

In this research, LSFG was evaluated for use as the electrodes for SSOFCs with a La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-δ} (LSGM) electrolyte. The phase behavior, thermal expansion behavior and electrical conductivity of LSFG in both oxidizing and reducing atmospheres were studied, and the output performance of the single cell was investigated.

LSFG powder was prepared by a citric nitrate process with a microwave-assisted combustion method in air, as reported in our previous paper.¹⁷ The microwave-assisted method of oxide synthesis is gaining popularity because of its high rate of reaction, efficient heat transfer, and environmentally friendly

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nature. Solutions of lanthanum nitrate ($\text{La}(\text{NO}_3)_3$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3$), gallium nitrate ($\text{Ga}(\text{NO}_3)_3$) and strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) were used as metal precursors. Polyvinyl alcohol (PVA) and citric acid were used as the fuel and citric acid also had an additional function to adjust the pH value. The mole ratio of citric acid and total metal ions was controlled at 2 : 1. The four metal precursors in a stoichiometric ratio were dissolved in hot deionized water together with PVA, resulting in a dark reddish suspension. Citric acid was then added gradually to the suspension and a clear dark reddish solution (precursor) was eventually obtained. The precursor was then transferred to a larger beaker and moved into a microwave oven for combustion. The combustion ash was collected and sintered at 600 °C for 2 h to remove the organic residue. Subsequently, the powder was pressed into pellets before calcination at 1100 °C for 2 h. The powder was then reduced in a flowing wet (3 vol% H_2O) H_2 at 800 °C and 900 °C for 12 h before X-ray diffraction (XRD) analysis. The 1100 °C-sintered powder was pressed into several rectangular bars (48 mm × 6 mm × 2 mm) at 200 MPa and the bars were then sintered at 1350 °C for 5 h in air before electrical conductivity and thermal expansion measurements.

LSGM powder was synthesized using a solid state reaction method. LSGM powders were uniaxially pressed into pellets of 15 mm in diameter at 600 MPa and then sintered at 1450 °C for 10 h to obtain a dense LSGM electrolyte. The ink of LSGF was then screen printed on the two sides of LSGM. The anode and cathode were co-sintered with the electrolyte in air at 1100 °C for 2 h. The thicknesses of the electrode and electrolyte was about 30 μm and 320 μm , respectively. The cathode area was about 0.33 cm^2 . To avoid a potential catalytic influence on fuel oxidation, the gold paste was printed on the anode surface while the platinum paste was printed on the cathode surface.

The powder XRD patterns were recorded on a Rigaku D/MAX-3C X-ray diffractometer with graphite-monochromatized $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scanning rate of 2° min^{-1} in the 2θ range of 20–80°. The total electrical conductivity of LSGF in a rectangular bar shape was measured in air and wet 5% H_2 using the standard four-probe direct current method. The temperature of the bar was reduced to 800 °C for 12 h before a conductivity test in 5% $\text{H}_2/95\% \text{ N}_2$ was performed. Thermal expansion coefficients of the samples were measured using a Netzsch DIL 402 C dilatometer with an aluminium oxide reference over the range of 200–1200 °C. A heating rate of $5^\circ \text{ C min}^{-1}$ and a flow control of 40 sccm were applied during these tests. Button cells were sealed to one end of an alumina tube with a ceramic paste (Aremco Ceramabond-552). The fuel flow rate was controlled at 40 sccm. Ambient air was used as the oxidant. The electrochemical impedance spectra were typically measured in the frequency range from 0.01 Hz to 1 MHz using Zahner IM6 and Zennium electrochemical workstations.

The synthesis of LSGF is quite challenging. It is reported that a secondary phase, such as $\text{SrLaGa}_3\text{O}_7$ or SrLaGaO_4 , is typically formed in a $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Ga}_y\text{O}_{3-\delta}$ system when $x > 0.2$ and $y > 0.3$.¹⁸ As shown in Fig. 1, a single perovskite phase can be obtained by a citric acid microwave combustion method (Fig. 1(a₁)), while the $\text{SrLaGa}_3\text{O}_7$ phase is very easy to form in the

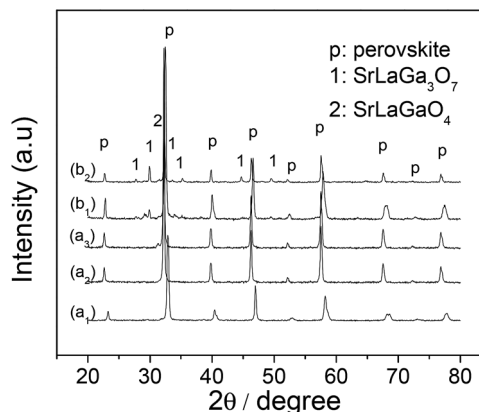


Fig. 1 XRD patterns of (a₁) LSGF powder obtained after 1100 °C calcination for 2 h in air (prepared by a citric acid microwave-assisted combustion method); (a₂) as-prepared LSGF after treatment at 800 °C in wet H_2 for 12 h; (a₃) as-prepared LSGF after treatment at 900 °C for 12 h; (b₁) LSGF powder obtained by the GNP method; (b₂) as-prepared LSGF powder after treatment at 800 °C in wet H_2 .

powder prepared by the glycine–nitrate process (GNP) method (Fig. 1(b₁)).

Therefore, it might be considered that the citric acid microwave combustion method with a lower heat treatment temperature can lead to a better crystallized LSGF than LSGF obtained with the GNP method.¹⁹ Indeed, the nature of the combustion reagent may be the key aspect for this method because it can strongly influence parameters such as gelation time, porosity, and particle shape and size.²⁰ The average crystallite size of the powders, calculated by the Scherrer formula from the XRD data, is around 26.8 nm and 35.1 nm, which corresponds to the results for the powders obtained by a citric acid microwave combustion method and GNP method, respectively. After treatment in wet H_2 at 800 °C for 12 h, LSGF maintains the perovskite phase without any secondary phase (Fig. 1(a₂)). However, SrLaGaO_4 can be detected in the main perovskite phase after treatment in wet H_2 at 900 °C for 12 h (Fig. 1(a₃)).

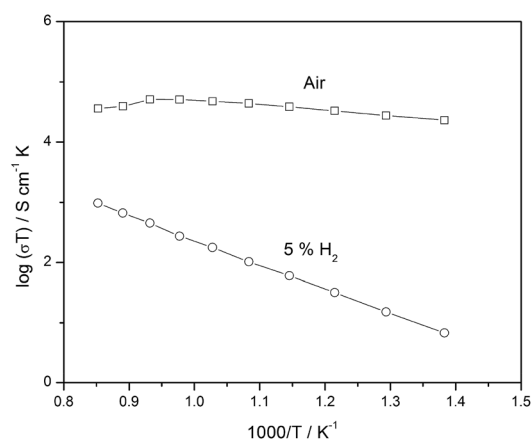


Fig. 2 Temperature (T) dependence of total conductivity (σ) of LSGF in air and 5% H_2 .

Conductivity is another important requirement for electrode materials. Fig. 2 shows the dependence of the conductivity of LSGF on temperature in reducing and oxidizing atmospheres. Electrical conductivity values of 30–50 S cm⁻¹ were obtained for samples measured at 450–900 °C in air. The sample showed a metal-like behavior of conductivity at over 800 °C, which was in agreement with results from other papers.^{12,13} The conductivities at 800 °C are about 47.45 and 0.422 S cm⁻¹ in air and 5% H₂, respectively, which are comparable to those of LSCM.²¹

Fig. 3 shows the thermal expansion behavior in air and 5% H₂. It can be seen that thermal expansion coefficients (TECs) for LSGF were 13.79 × 10⁻⁶ K⁻¹ in air and 13.88 × 10⁻⁶ K⁻¹ in 5% H₂ in the temperature range of 200–800 °C. The TEC closely matched with that obtained for the conventional SOFC electrolyte materials such as Ce_{0.8}Gd_{0.2}O_{1.95} and La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-δ}.^{22,23} The removal of oxygen from the material in a reducing atmosphere causes cell expansion, because of both cationic repulsion and reduction of Fe⁴⁺ (0.58 Å) to Fe³⁺ (0.64 Å). The difference between the TECs of LSGF in reducing and oxidizing atmospheres is very small, indicating that the ceramic is quite stable in these two atmospheres.

The cross-sectional view of a single cell is presented in Fig. 4. The dense electrolyte with a thickness of about 320 μm adheres well to the electrode. The thicknesses of the porous anode and cathode are about 30 μm. The presence of pores in the electrodes will facilitate mass transport to the three-phase boundary area, which would decrease concentration resistance.

Fig. 5 presents the *I*-*V* and *I*-*P* curves of a cell with the configuration LSGF|LSGM|LSFG at different temperatures when using wet H₂ (3 vol% H₂O) as the fuel and air as the oxidant. The cell maximum power densities (*P*_{max}) are as high as 133, 267 and 489 mW cm⁻² at 700 °C, 750 °C and 800 °C, respectively.

Fig. 6 shows the impedance spectra of a cell measured at different temperatures under open-circuit conditions. The polarization resistances of the symmetrical cell are 2.38, 1.02 and 0.43 Ω cm² at 700 °C, 750 °C and 800 °C, respectively. It can be seen that the cell performance is comparable to that of a conventional cell (nickel-YSZ cermet as the anode, YSZ film as

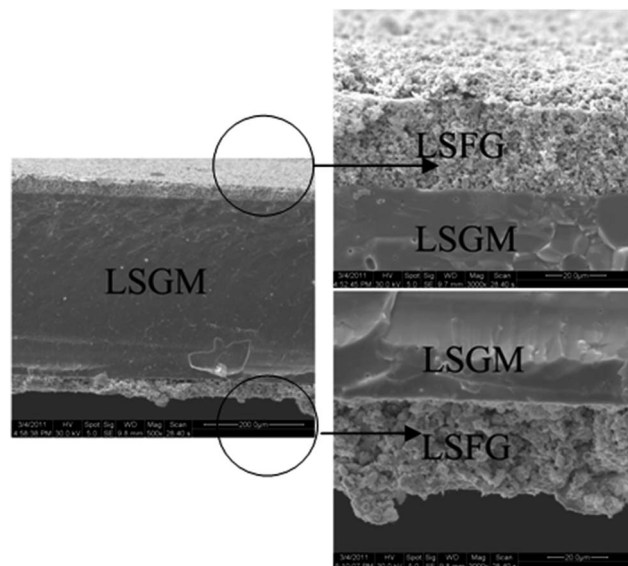


Fig. 4 Cross-sectional scanning electron microscopy images of the single cell.

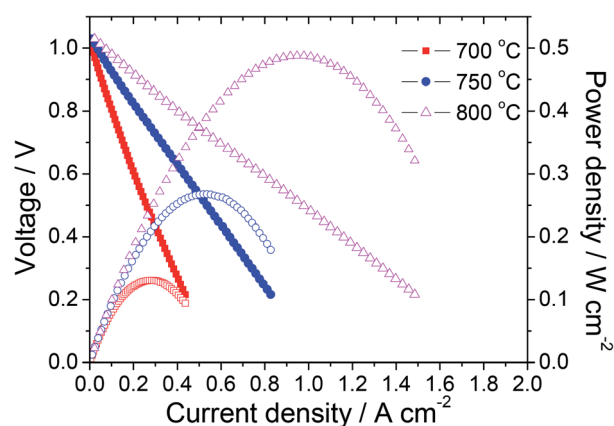


Fig. 5 *I*-*V* and *I*-*P* curves of a symmetrical LSGF|LSGM|LSFG cell at different temperatures using wet H₂ as the fuel and air as the oxidant.

the electrolyte and Sr-doped LaMnO₃-YSZ as the cathode)²⁴ and even better than those of conventional YSZ-supported SSOFCs.^{7,21} The cell performance increase must be attributed

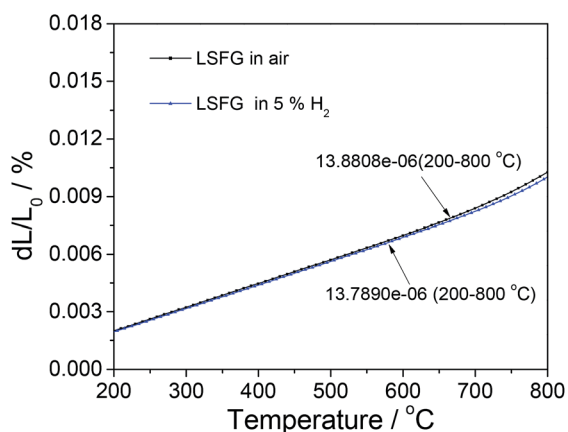


Fig. 3 Thermal expansion behavior of LSGF in 5% H₂ and air.

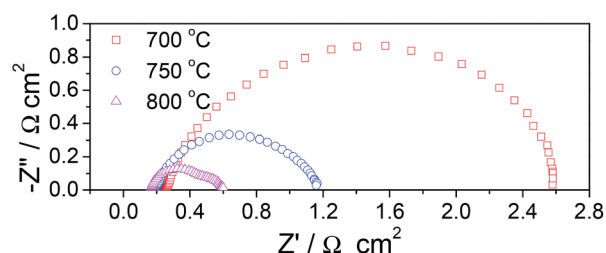


Fig. 6 Impedance spectra of the symmetrical cell LSGF|LSGM|LSFG measured at different temperatures under open-circuit conditions.

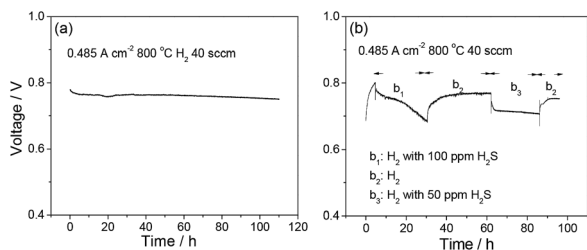


Fig. 7 Stability test in H₂ (a) and H₂ with H₂S (b) at 800 °C with a current density of 0.485 A cm⁻².

to the higher ionic conductivity of the LSGM electrolyte and the high catalytic activity and oxygen permeation rate of LSGF.^{14,15}

Fig. 7 shows the results of the short-term stability test of the symmetrical cell in H₂ and H₂ with 100 ppm and 50 ppm hydrogen sulfide (H₂S). It can be seen Fig. 7(a) that the cell voltage gradually became stable when using H₂ as the fuel. As shown in Fig. 7(b), a sharp linear decrease in voltage from 0.80 V to 0.67 V was observed after the fuel was switched from wet H₂ to H₂ with 100 ppm H₂S because of the sulfur poisoning. However, the cell voltage immediately recovered back to 0.75 V after the fuel gas was switched from H₂ with 100 ppm H₂S back to H₂. Similar behavior was also observed when the fuel gas was switched from H₂ to H₂ with 50 ppm H₂S. However, the voltage decreased at a much lower rate in 50 ppm H₂S. These results suggest that LSGF is a promising electrode for a SSOFC.

Conclusions

A pure perovskite La_{0.7}Sr_{0.3}Fe_{0.7}Ga_{0.3}O_{3-δ} (LSFG) was prepared in air by the microwave-assisted combustion method and evaluated for use as the electrode for a SSOFC. LSGF has considerable stability in both oxidizing and reducing atmosphere under the cell working conditions. At 800 °C, conductivity values are about 0.422 and 47.45 S cm⁻¹ in wet 5% H₂/N₂ and in air, respectively. The TECs of LSGF are 13.79 × 10⁻⁶ K⁻¹ in air and 13.88 × 10⁻⁶ K⁻¹ in 5% H₂ over a temperature range of 200–800 °C. The peak power densities of a single cell using LSGF as the electrode and 320 μm LSGM as the electrolyte were 489 mW cm⁻² at 800 °C with H₂ as the fuel and ambient air as the oxidant. The cell also shows good stability in H₂ and acceptable sulfur tolerance. All the results show that LSGF is a promising electrode for a SSOFC.

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