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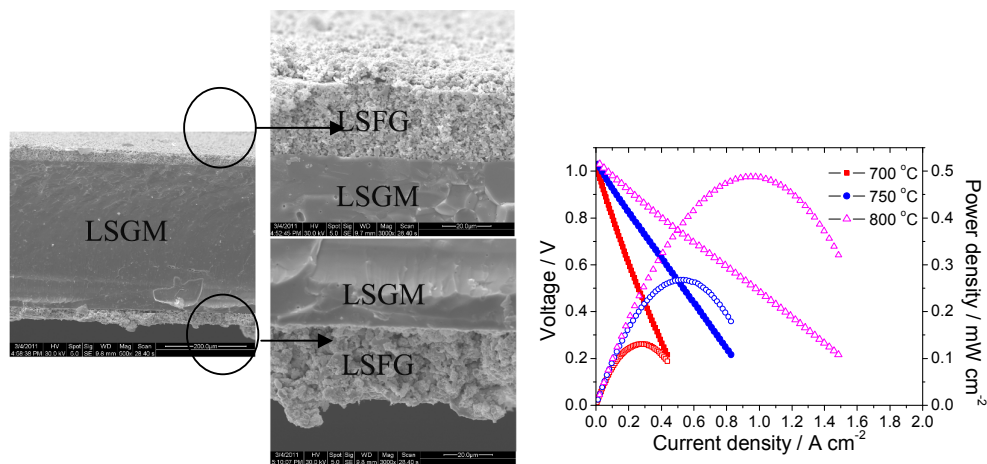
ARTICLE TYPE

La$_{0.7}$Sr$_{0.3}$Fe$_{0.7}$Ga$_{0.3}$O$_{3-\delta}$ as electrode material for symmetrical solid oxide fuel cell

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In this paper, **La$_{0.7}$Sr$_{0.3}$Fe$_{0.7}$Ga$_{0.3}$O$_{3-\delta}$ (LSFG) perovskite oxide has been successfully prepared by a microwave-assisted combustion method, and employed as both anode and cathode in symmetrical solid oxide fuel cells (SSOFCs).**
10 **Maximum power density of 489 mW cm^{-2} has been achieved at 800 ^{o}C with wet H$_2$ as fuel and ambient air as oxidant in a single cell with the configuration of LSFG|La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{3-\delta}$(LSGM) |LSFG. Furthermore, the cell have demonstrated good stability test in H$_2$ and**
15 **acceptable sulfur tolerance.**

Symmetrical solid oxide fuel cells (SSOFCs), using the same materials as both anode and cathode, have attracted much attention since they can be easily assembled, minimize problems with the diffusion between cell components and suppress possible
20 sulfur poisoning and carbon deposition.[1,2] For SSOFCs, however, the requirements of electrode materials are rather limited 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 ideal
25 electro-catalytic 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 report a novel design for enhancing the coking resistance of SOFC anode while maintain good
30 performance.[4] Ding et al found surface modification through infiltration has drastically enhanced the electro-catalytic activity and stability of the cathode.[5,6] However, those modifications will increase the system complexity.

Recently, different types of perovskite materials such as
35 Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_{6-\delta}$ (SFM),[1] La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ (LSCM),[2,7] La$_{0.8}$Sr$_{0.2}$Sc$_{0.8}$Mn$_{0.2}$O$_{3-\delta}$ (LSSM),[8] La$_4$Sr$_8$Ti$_{12-x}$Fe$_x$O$_{38}$,[9] Pr$_{0.7}$Ca$_{0.3}$Cr$_{1-y}$Mn$_y$O$_{3-\delta}$[10] and La$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.7}$Nb$_{0.1}$O$_{3-\delta}$ (LSCFN) [11] have been investigated as electrode for SSOFCs. However, the cell performance of SSOFCs is normally lower than
40 that from traditional SOFCs which can be attributed to the narrow selectivity of electrode materials. For example, the cell with configuration of La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ (LSCM) | yttria-stabilized zirconia (YSZ) |LSCM showed a peak power density of 300 mW cm^{-2} when using H$_2$ as fuel at 900 ^{o}C.[7] Shao et al
45 obtained a highest power density of 310 mW cm^{-2} when operating on wet H$_2$ at 900 ^{o}C by applying La$_{0.8}$Sr$_{0.2}$Sc$_{0.8}$Mn$_{0.2}$O$_{3-\delta}$ (LSSM) as cathode and anode.[8] Most of the materials afore mentioned

show a moderate performance. Therefore, it is highly urgent to develop new symmetrical electrodes for application in SSFCs.
50 La$_{0.7}$Sr$_{0.3}$Fe$_{1-y}$Ga$_y$O$_{3-\delta}$ perovskite-type oxides have been investigated as oxygen permeating materials due to 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 pressure (P_{O2}).[12] Further, La$_{0.7}$Sr$_{0.3}$Fe$_{1-y}$Ga$_y$O$_{3-\delta}$
55 have been proven to be active catalyst with thermal stability for catalytic combustion of methane attribute to the active surface oxygen species with high reducibility and oxygen mobility,[14] which means LSFG could be a potential anode for SOFC. On the other hand, according to the studies from Ishihara's group[15] and
60 Vivet's group,[16] La$_{0.7}$Sr$_{0.3}$Fe$_{0.7}$Ga$_{0.3}$O$_{3-\delta}$ (LSFG) shows a higher oxygen permeation rate than that of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF), a conventional cathode for SOFC.

In this study, La$_{0.7}$Sr$_{0.3}$Fe$_{0.7}$Ga$_{0.3}$O$_{3-\delta}$ (LSFG) as electrodes for SSOFCs has been evaluated on La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{3-\delta}$
65 (LSGM) electrolyte. The phase behaviour, thermal expansion behaviours and electrical conductivity of LSFG in both oxidizing and reducing atmospheres have been studied, and the output performance of the single cell has been investigated.

LSFG powder was prepared by a citric nitrate process with
70 microwave-assisted combustion method in air, as reported in our previous publication.[17] Microwave-assisted method of oxide synthesis is gaining popularity because of its high rate of reaction, efficient heat transfer, and environmental friendly nature. Solution of La(NO$_3$)$_3$, Fe(NO$_3$)$_3$, and Ga(NO$_3$)$_3$ and
75 Sr(NO$_3$)$_2$ were used as metal precursors. Polyvinyl alcohol (PVA) and citric acid were used as fuel; citric acid also had an additional function to adjust the pH value. The mole ratio of citric acid and total metal ions is controlled to be 2:1. Four metal precursors in stoichiometric ratio were dissolved in hot deionized water
80 together with PVA, resulting in a dark reddish suspension. Citric acid was then added gradually to the above 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
85 collected and sintered at 600 ^{o}C for 2 h to remove the organic residue. Subsequently, the powder was pressed into pellets before calcination at 1100 ^{o}C for 2 h. The powder was then reduced in a flowing wet (3 vol% H$_2$O) H$_2$ at 800 ^{o}C and 900 ^{o}C for 12 h for X-ray diffraction (XRD) analysis. The 1100 ^{o}C-sintered powder
90 was pressed into several rectangular bars (48 mm×6 mm×2 mm) at 200 MPa and the bars were then sintered at 1350 ^{o}C for 5 h in

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air for electrical conductivity and thermal expansion measurements.

La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{3-\delta}$ (LSGM) powder was synthesized by solid state reaction method. LSGM powders were uniaxially pressed into pellets of 15 mm in diameter at 600 MPa and then sintered at 1450 ^{o}C for 10 h to obtain dense LSGM electrolyte. The ink of LSFG was then screen-printed on the two sides of LSGM. The anode and cathode was co-sintered with electrolyte in air at 1100 ^{o}C for 2 h. The thickness of the electrode and electrolyte is about 30 μm and 320 μm. The cathode area is about 0.33 cm^2. To avoid potential catalytic influence on fuel oxidation, the Au paste was printed on the anode surface while Pt paste was printed on the cathode surface.

The powder X-ray diffraction (XRD) patterns were recorded on a D/MAX-3C X-ray diffractometer with graphite-mononchromatized Cu-Kα radiation (λ=1.5418 Å) at a scanning rate of 2 ^{o} min^{-1} in the 2θ range of 20-80°. The total electrical conductivity of LSFG in a rectangular bar shape was measured in air and wet 5% H$_2$ using the standard four probe DC method. The bar was reduced at 800 ^{o}C for 12 h before conductivity test in 5 % H$_2$ / 95 % N$_2$. Thermal expansion coefficients of samples were measured using a dilatometer (Netzsch DIL 402C) with an Al$_2$O$_3$ reference over the range of 200-1200 ^{o}C. A heating rate of 5 ^{o}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-552). The fuel flow rate was controlled at 40 sccm. Ambient air was used as oxidant. The electrochemical impedance spectra (EIS) were typically measured in the frequency range from 0.01 Hz to 1 MHz with IM6 & Zennium Electrochemical Workstations.

The synthesis of LSFG is quite challenging. It is reported that some secondary phase such as SrLaGa$_3$O$_7$ or SrLaGaO$_4$ is typically formed in La$_{1-x}$Sr$_x$Fe$_{1-y}$Ga$_y$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 micro-wave combustion method (Fig. 1 (a$_1$)), while SrLaGa$_3$O$_7$ phase is very easy to form in the powder prepared by GNP (Glycine-Nitrate Process) method (Fig. 1 (b$_1$)).
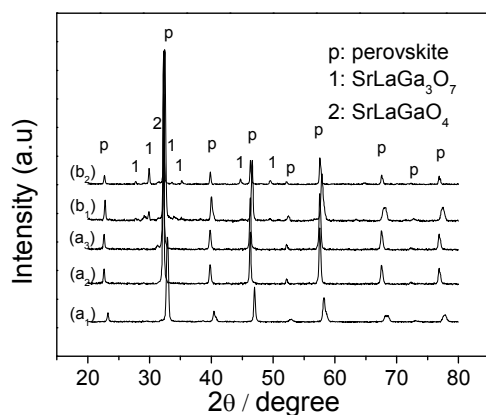

Fig. 1 XRD patterns of a1) LSFG powder obtained after 1100 ^{o}C calcination for 2 h in air (prepared by citric acid assisted micro-oven combustion method); a2) as-prepared LSFG after treatment at 800 ^{o}C in wet H$_2$ for 12 h; a3) as-prepared LSFG after treatment at 900 ^{o}C for 12 h; b1) LSFG powder obtained by GNP method; b2) as-prepared LSFG powder after treatment at 800 ^{o}C in wet H$_2$.

Therefore, it might be considered that citric acid micro-wave combustion method can lead to better crystallized LSGF and lower heat treatment temperature compared with GNP method.[19] Indeed, the nature of the combustion reagent maybe the key aspect for this method because that can strongly influence the parameters such as gelation time, porosity, 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 is corresponding to the powders obtained by a citric acid micro-wave combustion method and GNP method, respectively. After treatment in wet H$_2$ at 800 ^{o}C for 12 h, LSFG maintains the perovskite phase without any secondary phase (Fig. 1 (a$_2$)). However, SrLaGaO$_4$ can be detected in the main perovskite phase after treatment in wet H$_2$ at 900 ^{o}C for 12 h (Fig. 1 (a$_3$)).

Conductivity is another important requirement for electrode materials. Fig. 2 shows the dependence of conductivity of LSFG on temperature in reducing and oxidizing atmospheres. Obviously, the electrical conductivity values of 30-50 S cm^{-1} were exhibited at 450-900 ^{o}C in air. The sample showed a metal-like behavior of conductivity at over 800 ^{o}C, in agreement with other publications.[12,13] The conductivities at 800 ^{o}C are about 47.45 and 0.422 S cm^{-1} in air and 5 % H$_2$, respectively, which is comparable to those of La$_{0.75}$Sr$_{0.25}$Cr$_{0.5}$Mn$_{0.5}$O$_{3-\delta}$ (LSCM).[21]
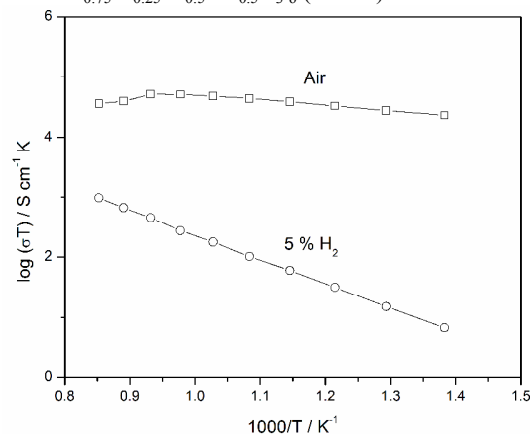

Fig. 2 Temperature (T) dependence of total conductivity (σ) of LSFG in air and 5 % H$_2$
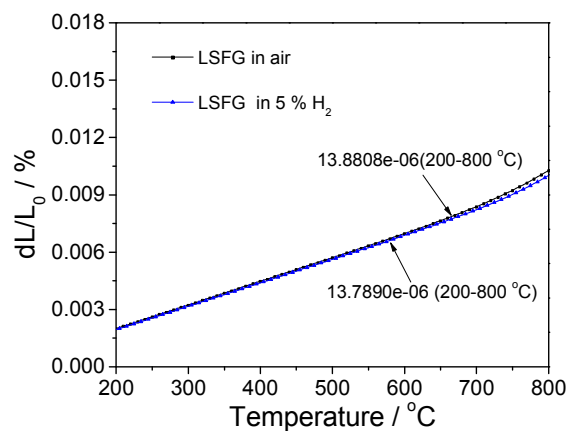

Fig. 3 Thermal expansion behaviors of LSFG in 5 % H$_2$ and air.

Fig. 3 shows the thermal expansion behavior in air and 5 % H$_2$. It can be seen that thermal expansion coefficients (TECs) for

LSFG were 13.79×10^{-6} K^{-1} in air and 13.88×10^{-6} K^{-1} in 5 % H$_2$ in the temperature range of 200-800 ^oC. The TEC closely matched with that of 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$_{3-\delta}$.[22,23] Departure of
5 oxygen from the material in reducing atmosphere causes cell expansion, due to both cationic repulsion and reduction of Fe^{4+} (0.58 Å) to Fe^{3+} (0.64 Å). The difference between the TECs of LSFG in reducing and oxidizing atmosphere is very small, indicating that the ceramic is quite stable in these two
10 atmospheres.

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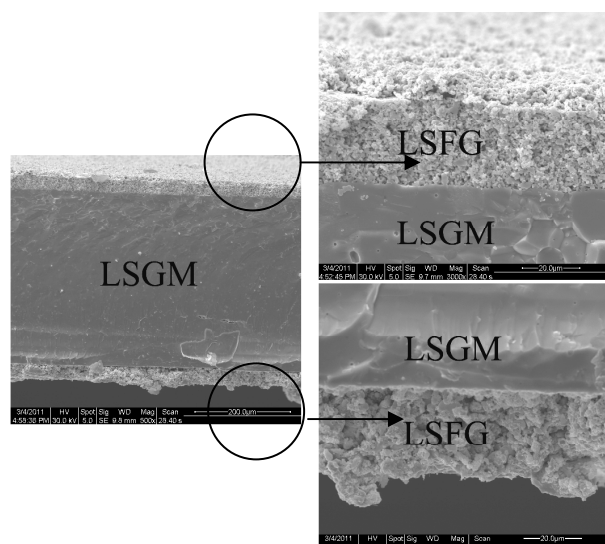15 facilitate mass transport to the TPB area, which would decrease concentration resistance.

Fig. 4 Cross-section SEM images of the single cell.

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Fig. 5 presents the I-V and I-P curves of cell with configuration of LSFG|LSGM|LSFG at different temperature when using wet H$_2$ (3 %) as fuel and air as oxidant. The cell maximum power densities (P_{max}) are as high as 133, 267 and 489 mW cm^{-2} at
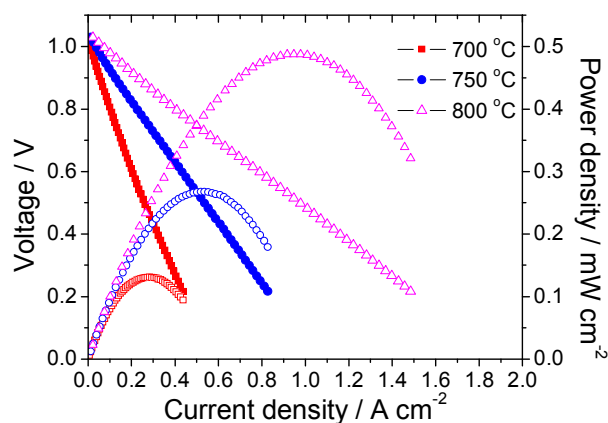25 700°C, 750 ^oC and 800 ^oC, respectively.

Fig.5 I-V and I-P curves of symmetrical cell LSFG|LSGM|LSFG at different temperatures using wet H$_2$ as the fuel and air as the oxidant.

30 Fig. 6 shows the impedance spectra of cell measured as different temperatures under open circuit conditions. The polarization of the symmetrical cell is 2.38, 1.02 and 0.43 Ω cm^2 at 700 ^oC, 750 ^oC and 800 ^oC, respectively. It can be seen that the cell performance is comparable to a conventional cell (nickel-
35 YSZ cermet as anode, YSZ film as electrolyte and Sr-doped LaMnO$_3$-YSZ as cathode)[24] and even better than those of conventional YSZ supported SSOFCs.[7,21] The increase must be attributed to the higher ionic conductivity of LSGM electrolyte and high catalytic activity and oxygen permeation rate of
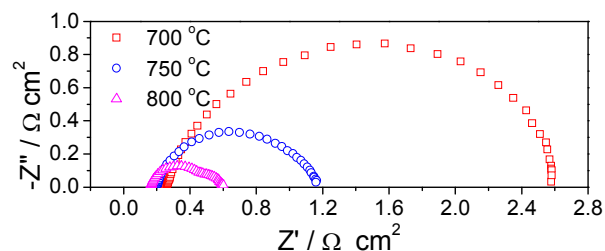40 LSFG.[14,15]

Fig.6 Impedance spectra of symmetrical cell LSFG|LSGM|LSFG measured as different temperatures under open circuit conditions.

45 Fig. 7 shows the short term stability test of the symmetrical cell in H$_2$ and H$_2$ with 100 ppm and 50 ppm H$_2$S. It can be seen that the cell voltage gradually became stable when using H$_2$ as 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
50 wet H$_2$ to H$_2$ with 100 ppm H$_2$S due to the sulfur poisoning. Fortunately, the voltage immediately recovered back to 0.75 V after the fuel gas was switched from H$_2$ with 100 ppm H$_2$S back to H$_2$. Similar behavior was also observed when the fuel gas was switched from H$_2$ to H$_2$ with 50 ppm H$_2$S. However, the voltage
55 decreased at a very low rate in 50 ppm H$_2$S. These results suggest that LSFG is a promising electrode for symmetrical solid oxide fuel cell.
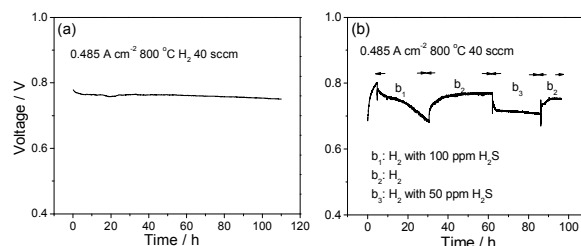

Fig. 7 Stability test in H$_2$ (a) and H$_2$ with H$_2$S (b) at 800 ^oC under
60 current density of 0.485 A cm^{-2}

Conclusions

A pure perovskite La$_{0.7}$Sr$_{0.3}$Fe$_{0.7}$Ga$_{0.3}$O$_{3-\delta}$ (LSFG) has been prepared in air by the microwave assisted combustion method and evaluated as electrode for symmetrical solid oxide fuel cell.
65 LSFG has considerable stability in both air and reducing atmosphere under cell working conditions. At 800 ^oC, conductivity values are about 0.422 and 47.45 S cm^{-1} in wet 5 % H$_2$/N$_2$ and in air, respectively. The TECs of LSFG are 13.79×10^{-6} K^{-1} in air and 13.88×10^{-6} K^{-1} in 5 % H$_2$ for 200-800 ^oC. The
70 peak power densities of a single cell using LSFG as electrode and 320 μm LSGM as electrolyte are 489 mW cm^{-2} at 800 ^oC with H$_2$

as fuel and ambient air as oxidant. The cell also shows good stability in H_2 and acceptable sulfur tolerance. All results show that LSFG is a promising electrode for symmetrical solid oxide fuel cell.

Acknowledgements

Notes and references

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