Infiltrated Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$/La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ electrodes towards high performance symmetrical solid oxide fuel cells fabricated by an ultra-fast and time-saving procedure

Juan Liu$^{a,b}$, Yu Lei$^d$, Yumei Li$^e$, Jun Gao$^{a,b}$, Da Han$^{a,d,*}$, Weiting Zhan$^a$, Fuqiang Huang$^a$, Shaorong Wang$^{a,e,**}$

$^a$ CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China
$^b$ University of the Chinese Academy of Sciences, Beijing 100049, PR China
$^c$ Research and Test Center of Materials, Wuhan University of Technology, Wuhan 430070, PR China
$^d$ Engineering Laboratory for Next Generation Power and Energy Storage Batteries, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China
$^e$ University of the Chinese Academy of Sciences, Beijing 100049, PR China
$^*$ CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China
$^**$ Corresponding author.

Herein, the Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$ (SFM) precursor solution is infiltrated into a tri-layered “porous La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM)/dense LSGM/porous LSGM” skeleton to form both SFM/LSGM symmetrical fuel cells and functional fuel cells by adopting an ultra-fast and time-saving procedure. The heating/cooling rate when fabricating is fixed at 200 °C/min. Thanks to the unique cell structure with high thermal shock resistance and matched thermal expansion coefficients (TEC) between SFM and LSGM, no SFM/LSGM interfacial detachment is detected. The polarization resistances ($R_p$) of SFM/LSGM composite cathode and anode at 650 °C are 0.27 Ω·cm$^2$ and 0.235 Ω·cm$^2$, respectively. These values are even smaller than those of the cells fabricated with traditional method. From scanning electron microscope (SEM), a more homogeneous distribution of SFM infiltrated electrode when the TEC between the electrode catalyst and the LSGM skeleton are similar$^{[15]}$. For further decreasing the fabrication time and increasing efficiency, the feasibility of ultra-fast fabrication of infiltrated SFM/LSGM electrode directly used for symmetrical solid oxide fuel cell is evaluated in this study. The heating/cooling rate is 200 °C/min. The preparation time of one infiltration/calcination cycle consumed is about 10 min in this study. The optimal loading of “SFM-LSGM/LSGM-SFM” functional fuel cell at 700 °C is 880 mW cm$^{-2}$. By using CH$_4$ as fuel, the maximum power densities at 850 and 900 °C are 146 and 306 mW cm$^{-2}$, respectively.

© 2017 Published by Elsevier B.V.

1. Introduction

Solid oxide fuel cell (SOFC) is one of most efficient power generation system that can convert chemical energy directly into electricity$^{[1–4]}$. However, the high price and poor stability caused by its high operating temperature largely hinder its application. Reducing the operating temperature from 800 to 1000 °C to 500–700 °C is therefore highly motivated$^{[5,6]}$. Consequently, development of electrodes which operated at low temperature is of great importance$^{[7–9]}$.

Infiltrated electrodes are widely recognized to show excellent performance even in the low temperature range$^{[10–12]}$. A typical fabrication process (anode or cathode) is as follows: firstly, the precursor solution of catalyst is infiltrated into the porous ion-conductive skeleton; then, the crystallization of catalyst is achieved by high temperature calcination at 700–900 °C for 2–4 h. One infiltration/calcination cycle normally yields a catalyst loading of 1–5 wt%. Multiply infiltration/calcination cycles are needed to increase the optimal loading to 20–40 wt%$^{[13–15]}$. As indicated, such a fabrication process is time-consuming, which can hardly be adopted for large-scale application.

In our prior research, an integrated tri-layer structure of “porous LSGM/dense LSGM/porous LSGM” skeleton using for infiltrating was invented$^{[14–16]}$. Impressively, we found that the quick quenching (with heating/cooling rates of 10 °C/min) has no detrimental influence on the microstructure of the infiltrated electrode when the TEC between the electrode catalyst and the LSGM skeleton are similar$^{[15]}$. For further decreasing the fabrication time and increasing efficiency, the feasibility of ultra-fast fabrication of infiltrated SFM/LSGM electrode directly used for symmetrical solid oxide fuel cell is evaluated in this study. The heating/cooling rate is 200 °C/min. The preparation time of one infiltration/calcination cycle consumed is about 10 min in this study. Symmetrical solid oxide fuel cells are receiving great attention recently$^{[17–19]}$. In recent years, SFM was found to be an alternative new electrode.
material for symmetric SOFCs showing excellent performances and also has similar TEC with LSGM [20,21]. It is therefore interesting and meaningful to investigate the performances of symmetrical fuel cells using SFM as electrode material in this study.

2. Experimental

The tri-layer structured “porous LSGM/dense LSGM/porous LSGM” skeleton was fabricated by a traditional “tape-casting/laminating/co-firing” technique [14–16]. All chemical agents were purchased from Sinopharm Chemical Reagent Co., Ltd. (China), and analytical reagents were used in this study. The SFM precursor solution was prepared by dissolving \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}\) (0.28 g), \(\text{Sr(NO}_3)_2\) (1.32 g) and \(\text{Fe(NO}_3)_2\cdot 9\text{H}_2\text{O}\) (1.89 g) in a citric acid (CA: 3.65 g) solution (30 ml) with a molar ratio between Mn+ and CA of 1:2 (Mn+ is the total concentration of metal ions). Then, ammonia solution (10 ml) containing Ethylene Diamine Tetraacetic Acid (EDTA: 4.8 g) was added until a molar ratio between EDTA and metal ions of 1:1 was reached. The precursor solution was finally heating on a hot plate until a molar concentration of 0.2 mol L\(^{-1}\) was obtained.

A vertical tube furnace was used for heating. The temperature of the furnace was set at 850 °C. The “porous LSGM/dense LSGM/porous LSGM” skeleton was dipped into the above SFM precursor solution for 1 min and then was drawn out. With the aid of a stainless steel hook, the skeleton with infiltrate was quickly pulled into the furnace for calcination and then was quickly fetched out of the furnace for cooling. The heating/cooling rate adopted here is 200 °C/min, which is 20 times faster than those reported in literature [22–24]. The LSGM skeleton infiltrated with catalyst was weighed before and after each impregnation/calcination cycle to estimate the loading of the impregnated SFM. One infiltration/calcination cycle yielded an average SFM loading of 1 wt%. The infiltration/calcination process was repeated for 20 times to yield

![Fig. 1](image-url). (a–e) SEM image of the blank porous LSGM/dense LSGM/porous LSGM skeleton used for functional fuel cells and conductivities of SFM (a); SEM image of the SFM/LSGM cathode (b); SEM image of the SFM/LSGM anode (c); SEM image of SFM/LSGM cathode fabricated with traditional method (d,e).
a final loading of 21 wt%. Prior to the testing, the holding time at 850 °C for 2 h in muffle furnace is needed for achieving crystallization of SFM. As indicated, the whole process is highly automated and can be easily adopted for large-scale application.

The microstructure of SFM/LSGM composite electrode was examined by the field emission scanning electron microscope (FESEM-4800). For electrochemical characterization, silver mesh was applied on the electrode surface using silver paste as binder for current collecting and silver wires were used as the voltage and current leads. Impedance measurement of the symmetrical fuel cells was performed in static air (or hydrogen) with an IM6 Electrochemical Workstation (ZAHNER, Germany) with a frequency ranged from 0.1 Hz to 100 kHz with amplitude of 20 mV. As for symmetrical fuel cells investigated here, the effective surface area is 0.785 cm². When testing, static air and high purity H₂ (99.999%) with flowing rate of 40 sccm were used as oxidant and fuel, respectively.

3. Result and discussion

Fig. 1a shows the SEM image of the blank “porous LSGM/dense LSGM/porous LSGM” skeleton used for single cells. The thicknesses of cathode, anode and electrolyte are 300, 25 and 18 μm, respectively. From the embedded image in Fig. 1a, we can also find that the LSGM electrolyte prepared in this study is dense. SEM images in Fig. 1b,c provide insights into the morphologies of both SFM/LSGM composite cathode (Fig. 1b) and SFM/LSGM composite anode (Fig. 1c). Nanometer sized SFM particles are uniformly coated on the LSGM skeleton. Most probably, the tri-layer structured “porous/dense/porous” skeleton used for infiltrating is outstanding for high resistance to thermal shock. No SFM/LSGM interfacial detachment is detected in this study. Furthermore, the morphologies of SFM in both air and hydrogen atmosphere revealed in Fig. 1b,c are almost identical, verifying that SFM is stable in both air and hydrogen [20]. For comparison, the SEM images...
A little amount of SrMoO$_4$ can also be detected. When reduced at high temperature, SrMoO$_4$ is transferred to perovskite-type oxide which showed in Fig. 2a. Impedance measurements of the materials, the conductivities of SFM (density: 98%) are much lower, considered to be stable. Compared with the widely used Co-based electrode when operating at low temperature in reduced atmosphere, SFM is considered to be stable. The Rohm of symmetrical cathode and anode fuel cells at 600 °C are as large as 0.727 Ω·cm$^{-2}$ and 1.414 Ω·cm$^{-2}$ (electrolyte thickness: 40 μm), as revealed in Fig. 2f. We can expect that the Rohm can be reduced by decreasing the thickness of electrodes, using new electrode material with high conductivity or increasing SFM loading (21 wt% is not the optimal loading) [27]. Fig. 2f further compares the cathodic activation process or the structural instability of SFM at high temperature.

Notably, the fuel cells investigated have small diameters of 1 cm. The feasibility of fast preparation of SFM/LSGM composite anode shows a much smaller Rp with lower activation energy.

Plots of cell voltages and power densities versus current densities of the symmetrical functional fuel cell are shown in Fig. 3a. When using H$_2$ as fuel and air as oxidant, the maximum power densities recorded are 880, 359 and 236 mW cm$^{-2}$ at 700, 650 and 600 °C, respectively. The performances of single cells investigated here are higher than those of the previously reported symmetrical SOFCs. For example, when using La$_{0.9}$Sr$_{0.1}$Fe$_{0.9}$Sc$_{0.1}$O$_3$, PrBa$_{0.8}$Ca$_{0.2}$Mn$_2$O$_5$ and La$_{0.9}$Ca$_{0.1}$Fe$_{0.9}$Nb$_{0.1}$O$_3$ as electrodes, the maximum power densities are only 320, 502 and 204 mW cm$^{-2}$ at 700 °C, respectively [26,28,29]. The performance of the symmetrical functional fuel cell when operated in CH$_4$ (3%H$_2$O) is also shown in Fig. 3b. The open circuit voltages (OCV) at 850 °C and 900 °C are 0.9 V and 0.75 V, while the maximum power densities are 146 and 306 mW cm$^{-2}$ respectively. The low OCV indicates that the cathodic property of SFM for methane oxidation is still limited. Similar low OCV values can also be found in fuel cells when using SFM, La$_{0.75}$Sr$_{0.25}$MnO$_3$ and Sr$_2$FeNb$_2$O$_7$ as anodes [30–32]. The sudden change of CV curves at 0.7 V is most probably attributed to a special activation process or the structural instability of SFM at high temperature.

Notably, the fuel cells investigated have small diameters of 1 cm. The feasibility of fast preparation of large cells at such fast heating/cooling rates is under investigation now. Furthermore, the fast preparation of electrolyte and metal supported fuel cells with high mechanical strength is also under consideration.

### 4. Conclusion

The feasibility of fast preparation of SFM/LSGM composite electrode has been carefully evaluated in this study. No interfacial detachment is found between SFM and the LSGM skeleton. Both the SFM/LSGM composite cathode and composite anode fabricated with this method showed robust and extraordinary electrochemical performances. The maximum power densities of single cell when using H$_2$ as fuel are as high as 880, 359 and 236 mW cm$^{-2}$ at 700, 650 and 600 °C, respectively. When using CH$_4$ as fuel, the maximum power densities are 146 and 306 mW cm$^{-2}$ at 850 °C and 900 °C, respectively.

![Fig. 3. (a,b) Cell voltages and power densities versus current densities of “SFM-LSGM/LSGM-LSGM-SFM” single cell at different temperatures (a: H$_2$; b: CH$_4$).](image-url)
References

[14] D. Han, H. Wu, J. Li, S. Wang, Z. Zhan, Nanostructuring of SmBa0.5Sr0.5CoO3−δ cathodes for reduced-temperature solid oxide fuel cells, J. Power Sources 246 (2014) 409–416.
[15] D. Han, Y. Liu, S. Wang, Z. Zhan, Co-infiltrating Pr0.5Sr0.5Fe2O3−δ−PtO2 (x = 0.1, 0.3, 0.5, 0.7, 0.9) mixed oxides into the La0.5Sr0.5Ga0.8Mg0.2O3−δ skeleton for use as low temperature solid oxide fuel cell cathodes, Electrochim. Acta 143 (2014) 168–174.
[22] Burge Theodore E., Jason D. Nicholas, Precursor solution additives improve desiccated La0.5Sr0.5CoO3−δ infiltrated solid oxide fuel cell cathode performance, J. Power Sources 301 (2016) 287–298.
[24] Augusto Mejía Gómez, Joaquín Sacanell, Ana Gabriela Leyva, Diego C. Lamas, Performance of La0.5Sr0.5Co1−δFeO3 (δ = 0.2, 0.5 and 0.8) nanostructured cathodes for intermediate-temperature solid-oxide fuel cells: influence of microstructure and composition, Ceram. Int. 42 (2016) 3145–3155.
[26] X. Liu, D. Han, Y. Zhou, X. Meng, H. Wu, J. Li, F. Zeng, Z. Zhan, Sc-substituted La0.5Sr0.5Co1−δFeO3−δ mixed conducting oxides as promising electrodes for symmetrical solid oxide fuel cells, J. Power Sources 246 (2014) 457–463.
[31] S. Jiang, X. Chen, S. Chan, J. Kwock, K. Khor, (La0.75Sr0.25)(Cr0.5Mn0.5)O3/YSZ compositions for intermediate-temperature solid-oxide fuel cell, J. Power Sources 327 (2016) 548–554.