

Solid State Ionics 152-153 (2002) 531-536



www.elsevier.com/locate/ssi

# Microstructure and electrical properties of porous $Y_{1-x}Ca_xFeO_3$ cathode materials by gelcasting process

Xingqin Liu\*, Jianfeng Gao, Yafei Liu, Ranran Peng, Dingkun Peng, Guangyao Meng

Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Accepted 21 March 2002

## Abstract

Porous  $Y_{1-x}Ca_xFeO_3$  (YCF) ceramics were successfully fabricated by a gelcasting process followed by sintering the gelled mixture of  $Y_2O_3$ , CaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. A pure YCF ceramic was obtained when the gelcast with  $x \le 0.10$  was calcined at 1250 °C in air for 5 h. Results showed that the specimen with x=0.10 had the lowest porosity. This contributed to the formation of a solid solution, which might greatly facilitate the sintering process of specimens. The  $Y_{0.9}Ca_{0.1}FeO_3$  specimens calcined at 1200–1275 °C for 5 h have an open porosity of 66.2–16.4% and mean pore size of  $1.91-0.69 \mu m$ . The electrical conductivity of the porous specimens was investigated by the DC four-probe method. The results showed that Ca<sup>2+</sup> doping greatly improves the conductivity of YCF specimen and dramatically reduces the activation energy for conductivity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cathode; Perovskite; Gelcasting process; Porous Y1-xCaxFeO3 ceramics; Sintering aid additive; Electrical conductivity

# 1. Introduction

There has been a strong trend to develop intermediate temperature SOFCs (IT-SOFC) in order to avoid the technical difficulties in high-temperature SOFCs. The major efforts for this purpose are to search high-conductivity electrolytes and to develop thin film preparation techniques. However, in many cases, the electrochemical activity of the cathode becomes a main problem to achieve high performance at reduced temperatures because of the higher dissociation energy of oxygen molecule and a lower diffusion rate of oxygen species. For instance, the well-known cathode materials La<sub>0.9</sub>Sr<sub>0.1</sub>MnO<sub>3 -  $\delta$ </sub> (LSM) exhibits a polarization

E-mail address: xqliu@ustc.edu.cn (X. Liu).

resistance of less than 1  $\Omega$  cm<sup>2</sup> at 1000 °C, but it increases to above 2000  $\Omega$  cm<sup>2</sup> at 500 °C. Therefore, there is a need to search new cathode materials to meet the requirement of IT-SOFCs. These cathode materials should be characterized by sufficient oxide ion conductivity in addition to the high electronic conductivity. Considering that the oxide-ion diffusion in ferrites/ cobaltites is some orders of magnitude higher than in manganites [1–9], many investigations in recent years are focused on such perovskite-type materials.

The perovskite-type oxide, YFeO<sub>3</sub>, is considered as a candidate for cathode material. It is found this p-type conductivity can be sufficiently enhanced by incorporating CaO up to a certain amount [10]. In this work, we report the fabrication of porous  $Y_{1-x}Ca_xFeO_3$ (YCF) ceramics directly from the related oxides or carbonates by gelcasting process and present the correlation between phase compositions, microstruc-

<sup>\*</sup> Corresponding author. Tel.: +86-551-3606249; fax: +86-551-3631760.

ture, porous properties, electrical conductivity and preparation conditions.

## 2. Experimental procedure

Analytically pure  $Y_2O_3$ ,  $Fe_2O_3$  and  $CaCO_3$  with different Y/Ca molar ratios were premixed, then the powder mixture was mixed by ball-milling with an aqueous solution of organic monomers, acrylamide (AM) and *N,N'*-methylene-bis-acrylamide (MBAM) for more than 10 h. After being initiated by ammonium persulfate and catalyzed by *N,N,N',N'*-tetramethylethylene-diamine, the resulting slurry was molded on a vibrating table which gelled after a while. The gelled specimens were then demolded, dried, machined, and sintered in a program-controlled furnace at different temperatures, ranging from 1100 to 1400 °C, for 5 h in air.

The structure of calcined specimens was identified by XRD and the microstructures observed by SEM. The density and open porosity were determined by Archimedes method. The average pore size and pore size distribution of the sintered porous specimens were obtained with the bubble-point technique. For DC conductivity measurement of specimens by the four-probe method, the green gelcasts were cut into small rectangular bars ( $2.5 \times 2 \times 6$  mm), and sintered at 1250 or 1300 °C for 5 h.

#### 3. Results and discussion

# 3.1. X-ray diffraction investigations

The gelcasts with different CaO dopant were sintered at 1250 °C for 5 h, and the products were identified by XRD. As showed in Fig. 1, the specimen with a Y/Ca equal to or smaller than 9:1 shows complete orthorhombic yttrium orthoferrite YFeO<sub>3</sub> diffraction patterns. It implies the complete substitutional solid solution of Ca<sup>2+</sup> in place of Y<sup>3+</sup> in the system when the solid solubility is no more than 10 mol% (a). On the contrary, the specimens with more Ca<sup>2+</sup> doping turn out to contain some impurities, Y<sub>2</sub>O<sub>3</sub> and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (b, c). It is very interesting that no cubic CaO diffraction patterns appears though calcium oxide should have existed from the



Fig. 1. XRD patterns of the gelcasts with different raw material ratios calcined at 1250 °C/5 h. (a) Y/Ca  $\leq$  9/1, (b) Y/Ca = 8/2, (c) Y/Ca = 7/3. \*: Orthorhombic Y<sub>1-x</sub>Ca<sub>x</sub>FeO<sub>3</sub>; Y: Y<sub>2</sub>O<sub>3</sub>; F: Fe<sub>2</sub>O<sub>3</sub>.

decomposition of the raw material calcium carbonate at such high temperature (decomposition at 825 °C for aragonite, and 898.6 °C for calcite) [11]. The ionic radii of  $Ca^{2+}$  (0.099 nm) is slightly larger than  $Y^{3+}$ (0.093 nm), therefore, the former might be able to form a more stable structure at A sites of ABO<sub>3</sub> perovskite structure. As a result, some  $Y_2O_3$  instead of CaO remains in the products of high Y/Ca ratio systems, and the higher Y/Ca ratio is in the raw materials, the more amount of yttria is left.

The green specimens with Y/Ca = 9/1 were calcined at different temperatures for 5 h in air, and then identified by XRD. It is found that final phase compositions depend greatly on the calcining temperature. Yttrium orthoferrite, or its solid solution, has already become the main phase at 1100 °C, and the minor impurities are yttria, hematite and CaO. It suggests that the diffusion and solid solution of calcium ions into the perovskite structure may be a thermodynamically controlled process, and a temperature higher than 1100 °C is favorable to the solid solution reaction against the simple formation of YFeO<sub>3</sub>.

# 3.2. Pore parameters of sintered specimens

#### 3.2.1. Porosity and sintering shrinkage

The effects of calcining temperature and  $Ca^{2+}$  doping on the open porosity ( $\rho_o$ ) of the specimens

are illustrated in Fig. 2. Neither the calcining temperature nor the Y/Ca ratio plays much influence on  $\rho_o$ until the gelcasts were calcined at 1250 °C, where  $\rho_o$ drops at first and reaches a lowest value, and then rises with the Ca<sup>2+</sup>-doping amount. The higher the temperature, the smaller  $\rho_o$  is, especially for the specimen with Y/Ca = 9/1. According to Fig. 1, a pure Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> phase has been obtained at 1250 °C, thus, the decrease in porosity is independent of the phase transformation and it may reflect the sintering behavior of the specimen.

Ca<sup>2+</sup> doping greatly facilitates the sintering process of the specimens and CaO acts as the sintering aid, the optimal amount of Ca<sup>2+</sup> doping emerges at Y/ Ca=9/1, more CaO addition does not show much influence on the sintering ability of specimens. On the contrary, the Y<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> system without CaO addition, though pure YFeO<sub>3</sub> phase had formed at 1250 °C, still went through the smallest changes in open porosity with the temperature, and the  $\rho_o$  value can reach as high as 51.7% even at 1400 °C. Thus, it can be concluded that the solid solubility is very important for porous microstructure development, and forming solid solution is a precondition in favor of sintering.

## 3.2.2. Pore size distributions and mean pore sizes

Fig. 3 shows the influence of  $Ca^{2+}$  doping on the pore size distributions of the YCF ceramic calcined at 1250 °C for 5 h. As  $Ca^{2+}$  doping rises, the mean pore size ( $d_p$ ) decreases at the beginning and then increases gradually.  $d_p$  values of the specimens with 10, 20 and



Fig. 2. Open porosity of specimens with various raw material ratios calcined at different temperatures.



Fig. 3. Pore size distributions of the specimens with different preparation conditions. (a) YCF ceramics calcined at 1250 °C for 5 h. (b)  $Y_{0.9}Ca_{0.1}FeO_3$  ceramics calcined at different temperatures for 5 h.

30 mol% Ca<sup>2+</sup> doping are 0.99, 1.07 and 1.27  $\mu$ m, respectively. Compared with the pure YFeO<sub>3</sub> specimen, whose  $d_p$  value is about 2.05  $\mu$ m, all of the doped perovskite ceramics possess smaller average pores. As we see from Figs. 2–4, an observable sintering and solid solution behaviors had appeared for specimens with pure Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> phase in the temperature range of 1250–1400 °C. Consequently, it was the ceramic sintering process that caused the dramatic drop in  $d_p$ . Analogy to pure Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in the final product have almost no effect on either the average pore diameters or pore size distri-



Fig. 4. SEM photographs of the fracture surfaces of the gelcasts with Y/Ca=9/1 calcined at different temperatures. (a) Green, (b) 1200 °C/5 h, (c) 1250 °C/5 h, (d) 1400 °C/5 h.

bution (e.g. 20 mol%  $Ca^{2+}$  gelcast), while too much impurity phases may form bigger  $d_p$  value and wider pore range than Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub>.

The pore size distributions in the  $Y_{0.9}Ca_{0.1}FeO_3$  ceramics are closely related to the sintering temperatures, as shown in Fig. 3b. The average pore size drops as the sintering temperature increases. In the meantime, the range of pore size distribution becomes narrower. There are still a few impurities in the specimen annealed at 1225 °C for 5 h. These might give occasion to some big pores left in the ceramics, leading to an abnormally wide pore size distribution. For all specimens, the pore size distributions are within a very narrow range (1.5 µm), which is a favorable result for a porous ceramic.

#### 3.3. SEM of the specimens

The SEM photographs of the section of the specimens based on  $Y_{0.9}Ca_{0.1}FeO_3$  gelcasts after different heat histories are shown in Fig. 4. Fig. 4a displays the morphology of the green gelcast, grains of the raw materials with different shape and size are bound with each other via the gels formed from the polymerization of organic monomers. Fig. 4b indicates the case of the gelcast calcined at 1200 °C for 5 h, many acicular phases and big grains present themselves in the photograph in addition to the some original granular appearances.

The perovskite-type complex oxides had formed and become the main phase at temperature higher than 1100 °C, the rapid growth of their (112) faces might be responsible for the production of needle shapes. Moreover, the pore sizes in Fig. 4b are mostly around  $1-4 \mu m$ , affirming the measurement in Fig. 3. At a temperature as high as 1250 °C (Fig. 4c), no more acicular phases can be found in the specimen, instead, uniform physical phases and porous structures dominate the whole morphology of the specimen. Referring to Fig. 1, the porous ceramics here are made of pure Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> phase, and the specimen was sintered at 1250 °C. Therefore, it is the sintering process that drives the transformation of needleshaped phases into neck-connected granules, in reverse, the transformation in grain shape brings on big shrinkage and results in low porosity, as seen in Fig. 2. Most of the pores are around 1 µm though some large pores (  $\sim 5 \,\mu\text{m}$ ) can be found. It seems to suggest that Fig. 4c disagrees with Fig. 3b to some extent. This is understandable because the pore size distribution in Fig. 3 mainly depends on the smallest pores of connected pore channels, those large pores on fracture surface failed to be checked by the bubblepoint method. For the specimen sintered at 1400 °C (Fig. 4d), few pores can be found in the sample, which verifies the low porosity in Fig. 2 ( $\rho_0 = 0.9\%$ ). On the other hand, the 1400 °C specimen underwent large shrinkage and the molten glassy phases are the main phase in the system, thus, sintering and melting of the solid solution are responsible for the low porosity and large shrinkage at higher temperature (1300-1400 °C, cf. Fig. 2).

## 3.4. Electrical conductivity of the specimens

The DC conductivity of the YCF ceramics varies with temperature as illustrated in Fig. 5. The data were collected from a temperature-dropping procedure, namely the specimens were calcined at a ramping rate of 5  $^{\circ}$ C min<sup>-1</sup> to 1100  $^{\circ}$ C, then cooled to the desired temperature and kept at the temperature for at least 20 min to reach thermal equilibrium. It turns out that the data are reproducible within a few percent of discrepancies by temperature-rising or temperature-dropping way.

It is obvious from Fig. 5 that the Ca<sup>2+</sup> doping enormously enhances the conductivity of the specimens and the  $\sigma$  values reaches around 10 S cm<sup>-1</sup> for the Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> ceramics sintered at 1300 °C, which confirms the results reported by Yoo and Kim [12]. Because YFeO<sub>3</sub> is a kind of p-type semiconductive material, CaO doping can bring in more holes and, thus, raises the conductivity:

$$\operatorname{CaO} + 1/4\operatorname{O}_2 + \operatorname{Y}_Y^X \to \operatorname{Ca}_Y' + h^{\cdot} + 1/2\operatorname{Y}_2\operatorname{O}_3$$

For the specimens calcined at 1250 °C, the  $\sigma$  values is a little lower than that of 1300 °C because hole transfer is greatly confined by the considerable number of pores in the porous ceramic. According to Fig. 3b and 4c, there are numerous pores in specimens calcined at 1250 °C for 5 h, the effective transfer channel for electron holes can only be provided by the connected-necks of the partly sintered ceramics. Even then, the conductivity is still of the same magnitude



Fig. 5. The DC conductivity of YCF ceramics with various Ca content against temperature in an air atmosphere.

Table 1	
A comparison of the hole-hopping activation energy, $E_{\rm a}$	

$X/T_{\text{sinter}}$ (°C) 0/1250 0.1/1250 0.2/1250 0.3/1250 0.1/12 $E_{a}$ (eV) 0.445 0.148 0.151 0.169 0.131	I III		···· · · · · · · · · · · · · · · · · ·		· · 877 u	
$E_{0}$ (eV) 0.445 0.148 0.151 0.169 0.131	$X/T_{\text{sinter}}$ (°C)	0/1250	0.1/1250	0.2/1250	0.3/1250	0.1/1300
a ( · · /	$E_{\rm a}~({\rm eV})$	0.445	0.148	0.151	0.169	0.131

as that reported for dense ceramics. Among the specimens calcined under same conditions (1250 °C/5 h), the highest electrical conductivity appears when x=0.1-0.2 for  $Y_{1-x}Ca_xFeO_3$  ceramics, though there are a few impurities in Y<sub>0.8</sub>Ca<sub>0.2</sub>FeO<sub>3</sub> specimen (cf. Fig. 1). Based on the experimental results by others, a certain amount of impurities do not affect  $\sigma$  values even at a high CaO-doping amount (x=0.5) for this perovskite system [12]. In our study, the case of YCF ceramics with x = 0.1 - 0.2 agree with the literature, but the conductivity of the specimen with x = 0.3 drops abruptly. The conductivity difference in a porous ceramics rests with complicated factors, the reasons here might ascribe to higher porosity, bigger pores, and too much impurities emerging in the latter samples (cf. Figs. 1-4), which still need further investigation.

The activation energy of hole hopping can be derived from Fig. 5 by fitting the related curves in straight lines, and the calculated results are listed in Table 1. The energy barrier of conduction for the Ca<sup>2+</sup>-doping gelcasts is remarkably smaller than that without doping, and increases with the doping amount but drops with the sintering temperature. All of these are corresponding to the above discussion. In other words, the conductivity depends on the phase constituents, the pore structure and sintering properties. The  $E_a$  values for the doping samples are within 0.13–0.17 eV, which are lower than those in Ref. [10] (0.15–0.19 eV).

# 4. Conclusions

(1) Gelcasting process has been successfully employed to fabricate porous perovskite YCF ceramics directly from the related oxides and carbonate, and pure  $Y_{0.9}Ca_{0.1}FeO_3$  solid solution ceramics can be obtained when firing the specimen with Y/ Ca=9/1 at 1250 °C for 5 h.

(2) The properties of porous perovskite ceramics such as porosity, average pore size and pore size distribution, can be controlled by adjusting the preparation conditions (e.g. raw material ratio and sintering temperature). The open porosity and average pore size of the  $Y_{0.9}Ca_{0.1}FeO_3$  ceramics sintered at 1200-1275 °C are around 66.2-16.4% and 1.91-0.69 µm, respectively. The lowest porosity emerges at the specimens with  $Y_{0.9}Ca_{0.1}FeO_3$  composition. Thus the formation of solid solution might greatly facilitate the sintering process of the specimens and CaO acted as the sintering aid.

(3) Ca<sup>2+</sup> doping greatly influences the electrical conductivity as well as its apparent activation energy of the YFC ceramics. The DC electrical conductivity of the 10–20 mol% Ca<sup>2+</sup>-doping YFC specimens is  $\sim 4.5-7$  S cm<sup>-1</sup>, 230–1500 times larger than that of pure YFeO<sub>3</sub> ceramics ( $\sim 0.003-0.03$  S cm<sup>-1</sup>), and the conductive activation energy of the porous Y<sub>0.9</sub>Ca<sub>0.1</sub>FeO<sub>3</sub> ceramics is  $\sim 0.148$  eV, only one-third that of specimen without doping ( $\sim 0.45$  eV).

#### Acknowledgements

The authors would like to thank the Natural Science Foundation of China (no. 20071029), The

Anhui National Science Foundation and the Ministry of Science and Technology of China (no. G-2000026409) for their financial support.

## References

- [1] M. Kertesz, et al., J. Solid State Chem. 42 (1982) 125-129.
- [2] F.H. Van Heuveln, H.J.M. Bouwmeester, J. Electrochem. Soc. 144 (1997) 134–140.
- [3] J. Mizusaki, et al., J. Electrochem. Soc. 136 (1989) 2082– 2088.
- [4] S.B. Adler, Solid State Ionics 111 (1998) 125-134.
- [5] B.C.H. Steele, et al., Solid State Ionics 106 (1998) 255-261.
- [6] B.C.H. Steele, Solid State Ionics 86-88 (1996) 1223-1234.
- [7] R.A. Lane, et al., Solid State Ionics 106 (1998) 175-187.
- [8] J.A. Lane, et al., Solid State Ionics 121 (1999) 201–208.
- [9] N.E. Trofimenko, H. Ullmann, J. Eur. Ceram. Soc. 20 (2000) 1241–1250.
- [10] C.-S. Kim, H.-I. Yoo, J. Electrochem. Soc. 143 (1996) 2863– 2870.
- [11] D.R. Lide, CRC Handbook of Chemistry and Physics, 71st edn., CRC Press, USA, 1992, pp. 4–52.
- [12] H.-I. Yoo, C.-S. Kim, Solid State Ionics 53-56 (1992) 583-591.