



Short communication

Effects of pore formers on microstructure and performance of cathode membranes for solid oxide fuel cells

Lifang Nie^a, Juncheng Liu^{a,*}, Yujun Zhang^b, Meilin Liu^c^a School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300160, China^b School of Materials Science and Engineering, Shandong University, Jinan 250061, China^c School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

ARTICLE INFO

Article history:

Received 31 May 2011

Received in revised form 4 August 2011

Accepted 5 August 2011

Available online 12 August 2011

Keywords:

LSCF

Pore formers

Microstructure

Tape casting

Solid oxide fuel cell

ABSTRACT

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) is the most widely used cathode material for intermediate temperature solid oxide fuel cells. In the present communication, porous LSCF cathodes are fabricated by tape casting, a low-cost and reproducible fabrication process. The effects of four different pore formers, namely, graphite, carbon black, rice starch, and corn starch, on the microstructure and electrochemical performance of the LSCF cathode are investigated. Examination of the microstructures reveals that the shape of the pores, the pore size, and the pore distribution in the final ceramic are related to the type of pore formers. Impedance analysis and cell testing show that the best performance is obtained from the cathode using graphite as the pore former. The microstructure indicates that graphite results in a porous LSCF cathode with a large surface area and high porosity, which can offer a considerably long triple phase boundary for catalytic reactions as well as channels for gas phase transport.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention in recent years due to their high energy efficiency, modularity, and excellent fuel capability [1]. For SOFCs, a critical point, however, is maintaining suitable electrochemical properties while decreasing the operating temperature to intermediate temperatures (600–800 °C). At a lower temperature, the polarization resistance of the cathode has been recognized as one of the principal factors that affect the performance of SOFCs because the overall losses due to the polarization at the electrodes are governed mainly by oxygen reduction reaction [2,3].

Recently, the materials in the $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_{3-\delta}$ family have been investigated extensively as cathodes for SOFCs due to their high ionic and electronic conductivity as well as their good catalytic activity for oxygen reduction reaction at lower operating temperatures [4,5]. For a given electrode material, however, the performance of the electrode can be altered drastically by a change in its microstructure, including pore and grain size, size distribution, and porosity [6,7]. Therefore, controlling the microstructure is also crucial for the optimization of the electrochemical performance of the cathode.

Toward this end, many methods have been proposed to provide an electrode membrane with suitable porosity for gas diffusion or electrical conductivity [8–10]. However, the most effective and popular method for the formation of a porous microstructure is the addition of pore formers to the initial powders. Starch, carbon black, graphite, and spherical polymers are some of the widely used pore formers [7,11–13]. Sanson et al. [11] studied the effect of pore formers on the slurry composition and microstructure of Ni/YSZ supporting anode. They found that rice starch and carbon black are the most promising pore formers for the production of anode by tape casting. Later, the Ni/YSZ anode with the addition of a new composite pore-former (mixture of flour and activated carbon) was found to provide appropriate porosity and suitable shrinkage matching with YSZ electrolyte film [14]. The effect of the amount of pore former (rice starch) in the anode support for SOFC was also examined. The best performance was obtained from an anode fabricated using 20 wt% rice starch [12]. To date, studies on the microstructure effect reported in the literature have focused mostly on anode substrates. In the present communication, we report our recent work on the fabrication and characterization of a porous LSCF cathode using a tape casting method. Graphite, carbon black, rice starch, and corn starch were used as pore formers. The effect of these four pore formers on the microstructure and electrochemical performance of the LSCF cathode was examined. The performance of a button cell with different pore formers was also reported.

* Corresponding author. Tel.: +86 22 24528004; fax: +86 22 24528004.

E-mail address: jchliu@tjpu.edu.cn (J. Liu).

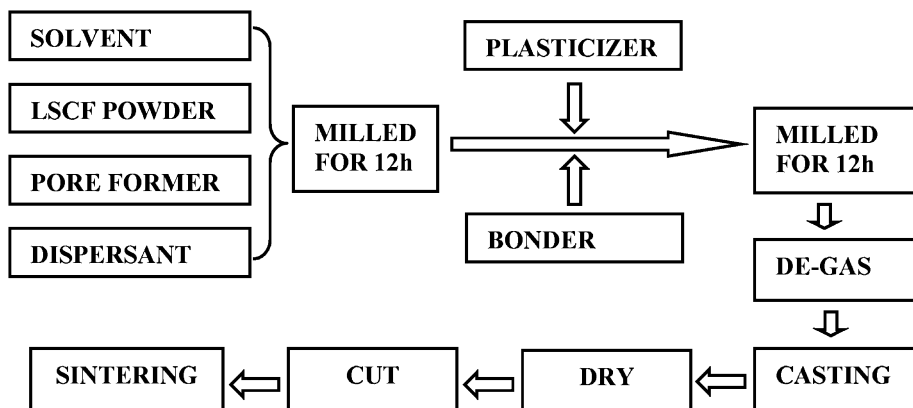


Fig. 1. Sketch of fabricating process for LSCF cathode.

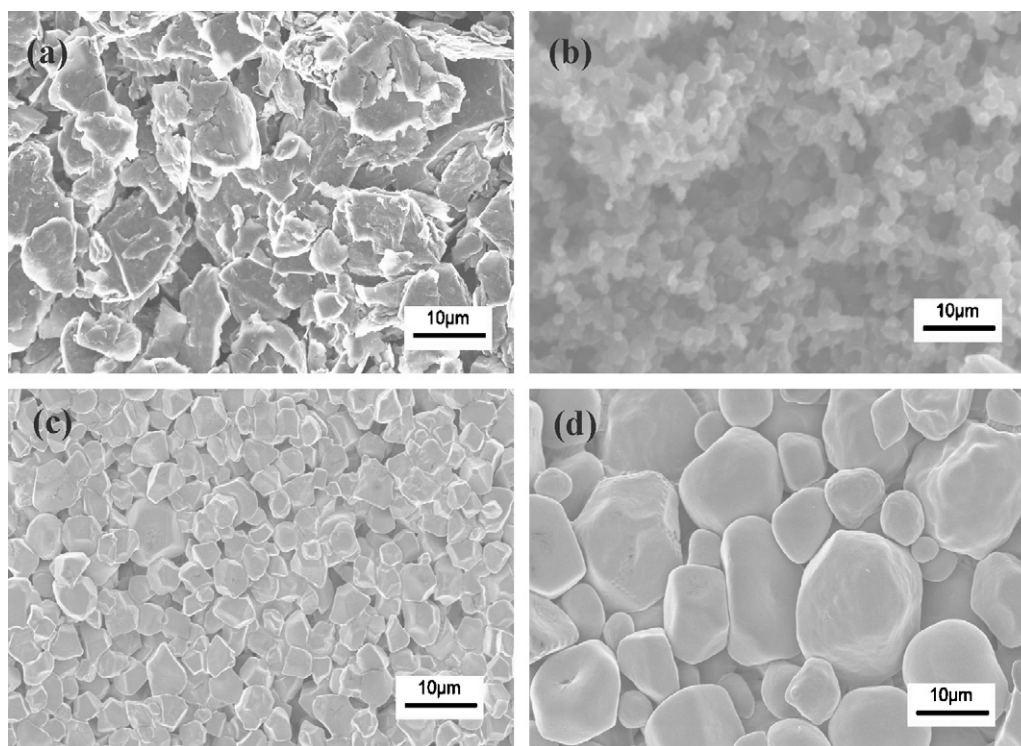


Fig. 2. SEM micrographs of the different pore formers used: (a) graphite; (b) carbon black; (c) rice starch and (d) corn starch.

2. Experimental

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ powders were purchased from Fuel-cell Material Co. Four compounds were selected: (i) rice starch (Sigma–Aldrich), (ii) corn starch (Sigma–Aldrich), (iii) graphite (Alfa Aesar), (iv) carbon black (Alfa Aesar). LSCF cathodes were fabricated by tape casting. The fabricating process for LSCF cathode is outlined in Fig. 1. To prepare the slurry for tape casting, proper LSCF powders and pore formers were ball milled for 12 h with dispersant in a mixture of xylene and ethanol. Then, two plasticizers (polyalkylene glycol and butyl-benzyl phthalate, Richard E. Mistler, Inc.) and a commercial bonder (polyvinyl butyral, Richard E. Mistler, Inc.) were added to confer adequate flexibility and strength to the tapes. The mixture was further milled for another 12 h. The resultant slurry was casted on a doctor-blade tape casting machine (Richard E. Mistler, Inc.). The thickness of cathode film is $\sim 50\ \mu\text{m}$. After drying overnight at room temperature, the green tape was cut into disks with a diameter of 5 mm.

In order to characterize the electrochemical behavior of these cathodes with different microstructures, electrolyte-supported symmetric cells with a configuration of LSCF|SDC|YSZ|SDC|LSCF were used. Dense YSZ pellets of 13 mm diameter and 1 mm thickness were prepared by dry pressing and sintering at $1450\ ^\circ\text{C}$ for 5 h. A $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.95}$ (SDC) buffer layer was drop coated on both sides of the YSZ electrolyte, which were a mixture of the SDC powder and additives dispersed in an organic solvent. Then the LSCF green tapes were bonded to the buffer layer. After dried at $80\ ^\circ\text{C}$ for 1 h, the symmetric cells were heated in a furnace at a rate of $1\ ^\circ\text{C}\ \text{min}^{-1}$ up to $400\ ^\circ\text{C}$, and $2\ ^\circ\text{C}\ \text{min}^{-1}$ up to $800\ ^\circ\text{C}$ for removal of the organic additives and pore formers, and then at a rate of $5\ ^\circ\text{C}\ \text{min}^{-1}$ up to $1050\ ^\circ\text{C}$. A holding time of 2 h was given at $1050\ ^\circ\text{C}$.

Pt mesh was attached to the LSCF cathode as the current collector for electrical measurements. Impedance spectra of the symmetrical cells were acquired under open circuit conditions using a frequency response analyzer (Solartron 1255) in stationary air at temperatures ranging from 700 to $800\ ^\circ\text{C}$. The frequency

of the applied ac voltage varied was from 10 MHz to 0.01 Hz. All data were collected in 30 min after the desired temperature was reached. The data was corrected for electrode area (0.20 cm^2), and divided by two (symmetric cell) to obtain the actual interfacial polarization resistance of each electrolyte/electrode interface. The NiO/YSZ anode supported cell performance was measured at 700°C with humidified hydrogen (3 vol% H_2O) as fuel and stationary air as oxidant. Microstructures and morphologies of the samples were examined using a scanning electron microscope (SEM, LEO1530). TGA (SDTQ600, TA Instruments, USA) of the pore formers was carried out in air atmosphere at a heating rate of 3°C min^{-1} .

3. Results and discussion

Fig. 2 shows the morphologies of the different pore formers considered in the current communication. Organic pore formers, such as rice and corn starch, differ with respect to shape and dimension and are characterized by dense particles of well-defined shape (Fig. 2c and d). Compared with corn starch, rice starch has a smaller size distribution with a particle size of about $4\text{--}5 \mu\text{m}$. On the other hand, inorganic additives are formed by aggregates of micronic or nanometric dense lamellae or sphere, as shown in Fig. 2a and b for graphite and carbon black, respectively. As can be seen, carbon black is observed to be composed of uniformly sized round particles, the average particle size of which is between 1 and $2 \mu\text{m}$.

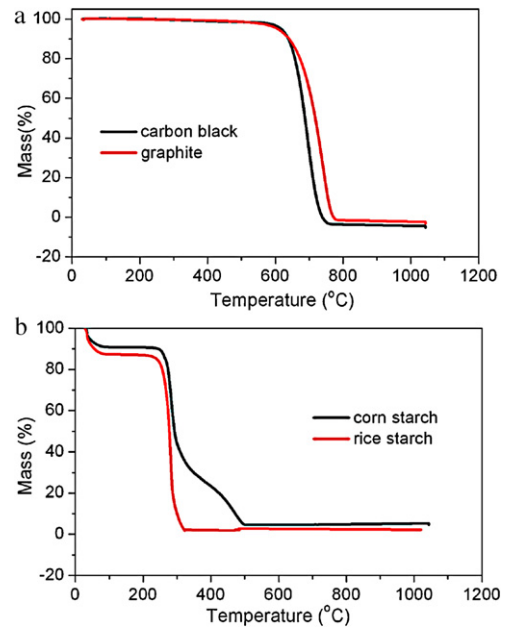


Fig. 3. Thermal decomposition in air of different pore formers.

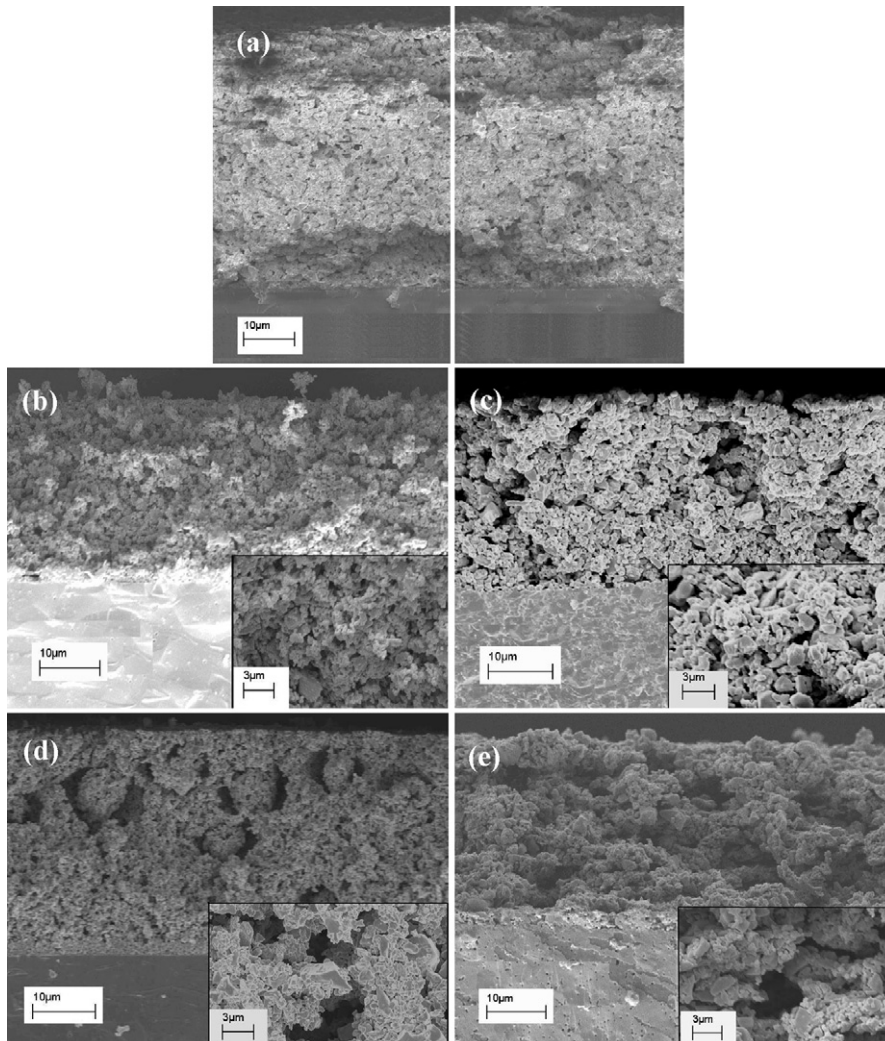


Fig. 4. SEM micrographs of the sintered LSCF tapes: (a) without pore former; (b) with graphite; (c) with carbon black; (d) with rice starch and (e) with corn starch.

Meanwhile, graphite particles consist of agglomerated platelet-like grains with a mean length ranging from 5 to 10 μm , and their edges are unclearly distinguishable.

The thermal decompositions in air of these four pore formers are depicted in Fig. 3. As can be seen from Fig. 3a, only at a relatively higher temperature ($\sim 600^\circ\text{C}$) does the amount of graphite or carbon black start to decrease. The carbon black undergoes thermal decomposition between 600°C and 750°C , and the graphite decomposes in the temperature range $575\text{--}775^\circ\text{C}$. No residue is obtained for all the four pore formers after heating. During heating, both corn and rice starch start losing water around 100°C (Fig. 3b). Decomposition of corn starch takes place in three stages: slow decomposition up to 245°C with a weight loss of 10%, fast decomposition with a weight loss 60% in the temperature range $245\text{--}345^\circ\text{C}$, and slow decomposition with a weight loss of 20% in the temperature range $345\text{--}500^\circ\text{C}$. Rice starch undergoes a faster decomposition with two stages, which is fully completed at 350°C .

The SEM images of the LSCF cathodes with and without pore formers are shown in Fig. 4. The amount of pore formers used for the four samples is $\sim 30\text{ vol}\%$ (relative to ceramic powder), whereas those of the other organic additives are kept the same. The porosity induced by an additional amount of binder is not affected by binder morphology as it is dissolved by the solvent. Clearly, the type of pore formers has a significant effect on the porous microstructure and much higher porosity can be observed in Fig. 4b–f compared with the plain cathode in Fig. 4a. When graphite is used as the pore former, the pores are relatively small, with an average pore size of about $1\text{--}2\ \mu\text{m}$, and are uniformly distributed, as seen in Fig. 4b. When carbon black is used, the pores are larger and non-uniformly distributed, as seen in Fig. 4c. Meanwhile, the ceramic structure between macropores looks a little dense, which may not be beneficial to gas phase transport. The rice starch gives a porous LSCF membrane with irregular isolated pores, the pore size of which is about $3\text{--}8\ \mu\text{m}$ (Fig. 4d). In the case of corn starch (Fig. 4e), the pores are relatively well-distributed with a size of $\sim 5\ \mu\text{m}$ in diameter, producing a more open porous microstructure. Notably, the pore former particles, especially graphite, are dissimilar in shape and size to the pores they form. This result can be attributed to the ball milling process which makes the particles or aggregates break down, leaving finer primary particles.

Fig. 5 shows the impedance spectra of the LSCF cathodes with different pore formers fabricated by tape casting technique. To demonstrate clearly the difference in electrode polarization behavior, all bulk resistances are removed from the impedance data. The catalytic activity of each electrode, as characterized by the interfacial polarization resistance R_p , is determined from the size of the impedance loop for each electrode. In general, the LSCF cathode, which uses graphite or carbon black as pore former, exhibited a lower interfacial resistance than the cathode prepared with rice or corn starch. For example, the interfacial resistance of the cathode with graphite as pore former was the lowest, reaching about 0.11 and $0.43\ \Omega\text{cm}^2$ at 800 and 700°C , respectively, compared with 0.24 and $0.81\ \Omega\text{cm}^2$ at the same temperatures for the rice starch cathode. The area-specific resistance of the cathode obtained with corn starch is 0.22 , 0.40 , and $0.78\ \Omega\text{cm}^2$ at 800 , 750 , and 700°C , respectively, similar to rice starch cathode. Based on the microstructure examination (shown in Fig. 4b), the graphite cathode might have been expected to have the best electrochemical performance because it has the largest surface area and highest porosity. These properties can offer a considerably long triple phase boundary for catalytic reactions as well as channels for gas phase transport. The R_p of the cathode with carbon black was a little higher than that of the graphite cathode (i.e., $0.13\ \Omega\text{cm}^2$ at 800°C and $0.47\ \Omega\text{cm}^2$ at 700°C). This effect can be explained by considering the relatively dense structure between macropores, as shown in Fig. 4c. Therefore, this drop in performance can be attributed to

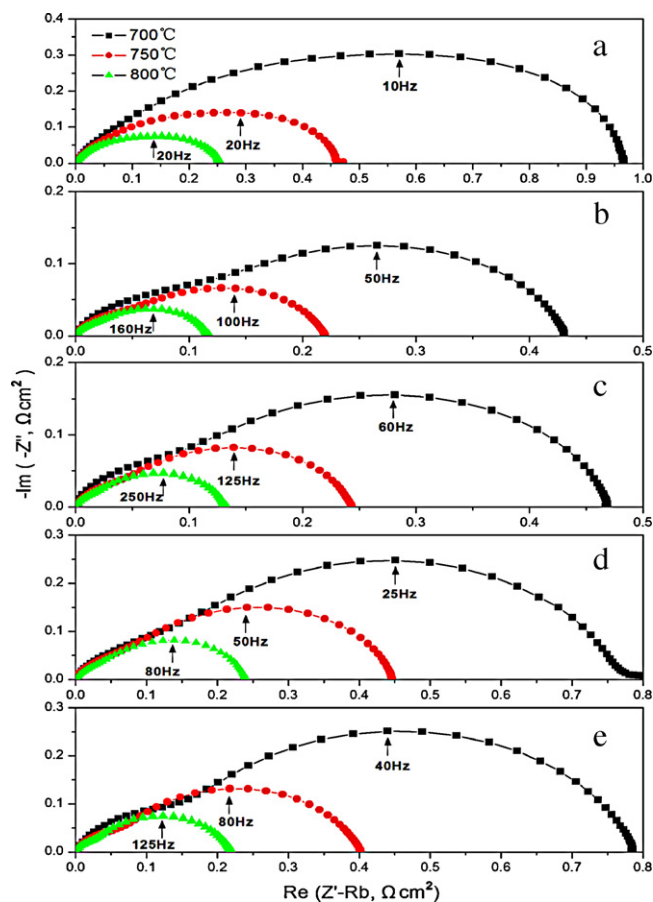


Fig. 5. Impedance spectra of LSCF cathodes with and without pore formers at various temperatures: (a) without pore former; (b) with graphite; (c) with carbon black; (d) with rice starch and (e) with corn starch.

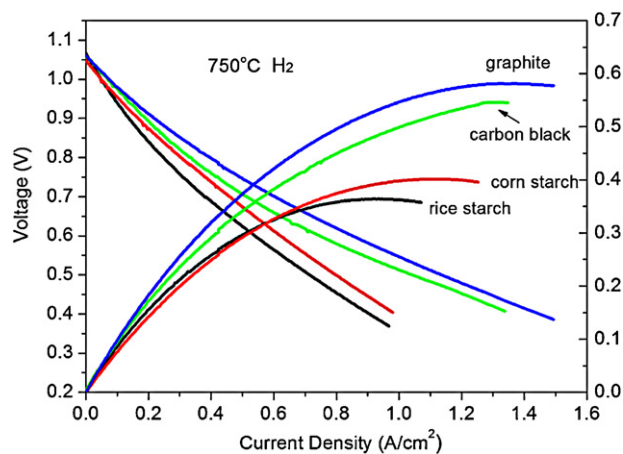


Fig. 6. $I\text{--}V$ and $I\text{--}P$ characteristics of single cell with different pore formers.

the limitations on the transport of gases through the cathode. The increase in interfacial resistance of the cathodes with rice and corn starch can also be explained by the observed microstructure, as shown in Fig. 4d and e, respectively. On one hand, the large channel pores allow the rapid transport of oxygen molecules. On the other hand, large pores may exist in the effective thickness of the triple phase boundary reaction area adjacent to the electrolyte, consequently removing some of the available surface area for chemical reaction. Further, large pores can also disrupt the electron diffusion pathways in the cathode, thereby resulting in “electronic” isolation

or diminished electronic conductivity in the regions of the cathode [15].

Fig. 6 shows the I - V and I - P characteristics of the anode supported cells measured at 750 °C. Comparing the power output of the other two cells, a much higher peak power density is observed for graphite and carbon black cell, which reaches 581 and 546 mW cm⁻² at 750 °C, respectively. The corn starch and rice starch cell merely produced 401 and 364 mW cm⁻² under the same conditions. The YSZ film and Ni/YSZ anode support were fabricated using the same process, so the obvious difference in cell performance can be ascribed to the different cathodic microstructure.

4. Conclusions

LSCF porous cathodes are fabricated by a low-cost tape casting process using graphite, carbon black, corn starch, and rice starch as pore formers. The microstructures and performance of the LSCF cathodes are found to depend sensitively on the morphology (particle size and shape) and nature (organic and inorganic) of the pore formers. Based on microstructure examination and performance

characterization, graphite is the most suitable pore former for the fabrication of cathodes for SOFCs by tape casting.

References

- [1] L. Yang, C. Zuo, W. Wang, *Adv. Mater.* 20 (2008) 3280–3283.
- [2] C. Xia, M. Liu, *Adv. Mater.* 14 (2002) 521–523.
- [3] L. Nie, M. Liu, Y. Zhang, *J. Power Sources* 195 (2010) 4704–4708.
- [4] S. Jiang, S. Zhang, Y. Zhen, *J. Electrochem. Soc.* 153 (2006) A127–A134.
- [5] A. Esquirol, N.P. Brandon, J.A. Kilner, *J. Electrochem. Soc.* 151 (11) (2004) A1847–A1855.
- [6] T.V. Reshetenko, H.T. Kim, H.J. Kweon, *J. Power Sources* 171 (2007) 433–440.
- [7] M. Prestat, A. Morandi, A. Heel, L. Holzer, et al., *Electrochem. Commun.* 12 (2010) 292–295.
- [8] F.Y. wang, G.B. Jung, A. Su, et al., *J. Power Sources* 185 (2008) 862–866.
- [9] T.L. Cable, S.W. Sofie, *J. Power Sources* 174 (2007) 221–227.
- [10] W.P. Pan, Z. Lv, K.F. Chen, et al., *Electrochim. Acta* 55 (2010) 5538–5544.
- [11] A. Sanson, P. Pinasco, E. Roncari, *J. Eur. Ceram. Soc.* 28 (2008) 1221–1226.
- [12] J.J. Haslam, A.Q. Pham, B.W. Chung, J.F. Dicarilo, R.S. Glass, *J. Am. Ceram. Soc.* 88 (2005) 513–518.
- [13] H.L. Lein, T. Tezuka, T. Grande, M.A. Einarsrud, *Solid State Ionics* 179 (2008) 1146–1150.
- [14] J.Y. Hu, Z. Lv, K.F. Chen, et al., *J. Membr. Sci.* 318 (2008) 445–451.
- [15] C.S. Tedman, H.S. Spacil, S.P. Mitoff, *J. Electrochem. Soc.* 116 (1969) 1170–1175.