

Preparation and electrochemical properties of $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ electrolyte

JUAN LI, RUISONG GUO* and HONG JIANG[†]

Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, China

[†]Guizhou Broadcasting and Television College, Guiyang 550004, China

MS received 12 October 2011

Abstract. The perovskite Yb-doped strontium cerate–zirconate material, $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$, was prepared by solid-state reaction and the structure was characterized by X-ray diffraction. The calcination process of the powder was investigated by thermogravimetric/differential thermal analysis (TG–DTA). The high temperature conductivities were measured by d.c. four-probe technique in the temperature range from 500 to 950°C in wet hydrogen and effect of temperature on conductivity was investigated. The conductivity increased with the elevation of temperature from 500 to 950°C. The highest conductivity of $4.4 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ was observed for $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ at 950°C. The current–voltage (I – V) and current–power (I – P) characteristics of the single cell (H_2 , Pt/ $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ /Pt, O_2) at temperature range from 600 to 850°C were tested. With the temperature increasing from 600 to 850°C, the open circuit voltage (OCV) decreased from 1.164 to 1.073 V and the ionic transfer number decreased from 0.996 to 0.946. At 850°C, the maximum power density of $25.2 \text{ mW}\cdot\text{cm}^{-2}$ was observed.

Keywords. Ceramics; fuel cells; solid state reactions; electromotive force; ionic conduction.

1. Introduction

Perovskite materials such as SrZrO_3 , BaZrO_3 , SrCeO_3 and BaCeO_3 , when doped with rare-earth oxide, are known to be proton conductors in a wet atmosphere at high temperature (Reichel *et al* 1996; Schober 2001; Sammes *et al* 2004; Shi *et al* 2005; Wang *et al* 2010; Bi *et al* 2011). This kind of materials have been the subject of extensive investigation since Iwahara *et al* (1981) demonstrated the utility in hydrogen sensors and other solid state ionic devices. Of the materials in this class, acceptor-doped SrCeO_3 and BaCeO_3 ceramics show high proton conductivity in hydrogen and/or wet atmosphere. However, these two kinds of materials have rather poor stability and endurance in the CO_2 or wet atmosphere, which is not suitable for practical use (Bhide and Virkar 1999; Matsumoto *et al* 2006; Xie *et al* 2009). In contrast, acceptor-doped SrZrO_3 and BaZrO_3 ceramics show high stability but lower proton conductivity (Hibino *et al* 1992; Kreuer 1999; Zuo *et al* 2006).

In an attempt to find a composition exhibiting both high conductivity and good stability, cerate–zirconate solid solutions replacing Ce in BaCeO_3 or SrCeO_3 with Zr have been investigated because BaCeO_3 and BaZrO_3 , or SrCeO_3 and SrZrO_3 can form solid solution easily. In recent years, such cerate–zirconate solid solutions have

been widely reported, such as $\text{BaCe}_{0.85-x}\text{Zr}_x\text{Er}_{0.15}\text{O}_{3-\alpha}$ ($0.0 \leq x \leq 0.4$) (Yin *et al* 2011), $\text{BaCe}_{1-x-y}\text{Zr}_x\text{Y}_y\text{O}_{3-\delta}$ ($x = 0, 0.1, 0.2, 0.3, 0.4$; $y = 0.15, 0.20$) (Barison *et al* 2008), $\text{BaCe}_{0.45}\text{Zr}_{0.45}\text{M}_{0.1}\text{O}_{3-\delta}$ ($\text{M} = \text{In}, \text{Y}, \text{Gd}, \text{Sm}$) (Lv *et al* 2009), $\text{Sr}(\text{Ce}_{0.6}\text{Zr}_{0.4})_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ (Zhang *et al* 2009), $\text{Sr}(\text{Ce}_{0.5-x}\text{Zr}_{0.5-x})\text{Dy}_{2x}\text{O}_{3-x}$ (Li *et al* 2007), $\text{Sr}(\text{Ce}_{0.6}\text{Zr}_{0.4})_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (Zhang *et al* 2008) and so on.

In the previous study, we have investigated the electrical properties of perovskite material with the formula of $\text{Ba}(\text{Ce}_{0.5-x}\text{Zr}_{0.5-x})\text{Yb}_{2x}\text{O}_{3-x}$ ($2x = 0.1, 0.15, 0.2, 0.25$) (Li *et al* 2008). The results showed that the highest conductivity was observed when $2x = 0.2$. In this paper, a solid solution, $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$, has been prepared and its conductivity and cell performance have been investigated.

2. Experimental

$\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ was prepared by conventional solid-state reaction. High-purity oxide powders of SrCO_3 (99.9%), CeO_2 (99.9%), ZrO_2 (99%) and Yb_2O_3 (99.9%) were mixed and ball milled with stabilized zirconia balls in de-ionized water for 6 h. Solvents were evaporated and the dried powders were subsequently calcined in air at 1200°C for 2 h. The synthesized powders were then wet-milled again in a planetary mill for 6 h, dry pressed into bars and pellets and cold isostatic pressed under 200 MPa. The bars and pellets were subsequently sintered in air at 1600°C for 4 h. The calcination process was carried out by intelligent WCT-2C

*Author for correspondence (rsguo@tju.edu.cn)

thermal analysing balance based on the thermogravimetric/differential thermal analysis (TG-DTA). X-ray diffraction analysis was performed on the surfaces of the samples using nickel filtered Cu $K\alpha$ radiation ($\lambda = 0.15405$ nm) (BDX3300).

The high temperature conductivities were measured by a d.c. four-probe technique at a temperature range from 500 to 950 °C in wet hydrogen. The conductivity was recorded every 50 °C after soaking for 20 min. A constant d.c. current source was used to supply the required current and the voltage drop across the probes was measured with a digital millimeter. For cell performance and ionic transfer number measurement, sintered pellet (diameter: 11.2 mm, thickness: 1.5 mm) was used as an electrolyte. Porous platinum was applied as electrodes by painting on both sides of electrolyte and calcined in air at 850 °C for 2 h. The electrode area was 0.8 cm². Platinum wires were used as current and voltage probes. The cell performance was measured from 600 to 850 °C with humidified hydrogen (H₂ + 3% H₂O) as fuel and oxygen as oxidant. The cell current-voltage curves were recorded at a scanning rate of 10 mV·s⁻¹. To further understand the nature of conductivity mechanism in SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}, comparison of open circuit voltage (OCV) with theoretical electromotive force (EMF) by means of EMF-method (Norby 1988) were performed to estimate the ionic transport number of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} with the cell: H₂, Pt/SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}/Pt, O₂.

3. Results and discussion

3.1 Thermal analysis

The TG-DTA curves of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} are presented in figure 1. An endothermic peak at 940 °C indicated that the reaction occurred as SrCO₃ → SrO + CO₂, accompanied by carbon dioxide gas release and weight loss. At about

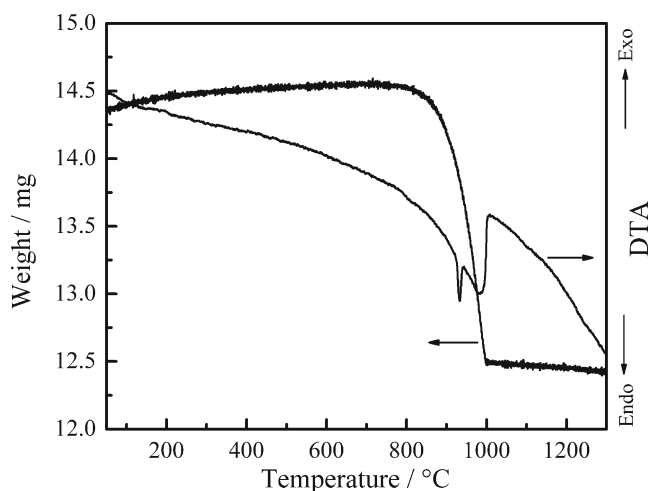
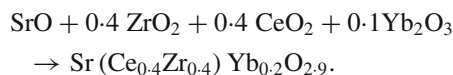


Figure 1. TG-DTA curves of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}.

1000 °C, a broad exothermic peak appeared indicating the formation of the solid solution. The reaction happened during this process can be expressed as follows



Therefore, it was determined to end at 1200 °C for 2 h for the calcination process in order to ensure high sinterability of the powders.

3.2 Phase stability in reducing atmosphere

Figure 2 shows X-ray diffraction patterns of as-sintered SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} sample (a) and the sample after treating in wet H₂ at 950 °C for 4 h (b). For comparison, standard XRD patterns of SrCeO₃ (JCPDS 47-1689, lattice parameters, $a = 0.6153$ nm, $b = 0.6012$ nm, $c = 0.8589$ nm) and SrZrO₃ (JCPDS 44-161, lattice parameters, $a = 0.5818$ nm, $b = 0.8204$ nm, $c = 0.5797$ nm) are also plotted. The result shows that only the targeted perovskite phase was formed. Compared with the standard XRD patterns of SrCeO₃ and SrZrO₃, all of the corresponding peaks of as-sintered SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} almost locate the peaks between SrCeO₃ and SrZrO₃ due to the simultaneous existence of the Ce⁴⁺ and Zr⁴⁺ in SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} (calculated lattice parameters, $a = 0.5971$ nm, $b = 0.5853$ nm, $c = 0.8386$ nm). However, there is no peak shift or new peak coming out for the sample after treating in wet H₂ compared with the as-synthesized sample, revealing no change of crystalline structure after treating in wet H₂ at 950 °C for 4 h.

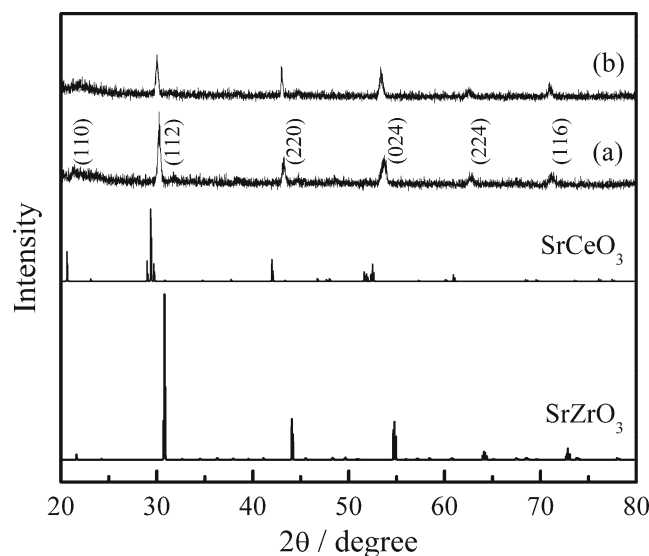
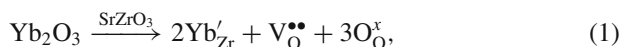


Figure 2. XRD patterns of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}. (a) as-sintered SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} and (b) SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} after treating in wet H₂ at 950 °C for 4 h. Standard XRD patterns of SrZrO₃ (JCPDS 44-161) and SrCeO₃ (JCPDS 47-1689) are also included.

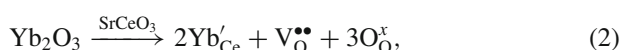
Therefore, $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ can be assumed to be stable in wet hydrogen atmosphere.

3.3 Conductivity

The perovskite material doped with a trivalent cation has been shown to be protonic conductors in H_2 or H_2O rich atmospheres. For Yb-doped strontium cerate–zirconate material, when two trivalent cations Yb^{3+} substituted for Zr^{4+} or Ce^{4+} , an oxygen ion vacancy is created in the crystal for charge compensation. These reactions can be written as:



or



where Yb'_{Zr} and Yb'_{Ce} indicate Yb^{3+} in the Zr^{4+} and Ce^{4+} sites, respectively and $\text{V}_{\text{O}}^{\bullet\bullet}$ stands for oxygen ion vacancy in Kroeger–Vink notation. By means of high-temperature treatment in water vapour containing atmosphere, the oxygen ion vacancies may be replaced by protons, which reside on oxygen ions to form substitutional OH^- ion defects. The reactions, in Kroeger–Vink notation, are written as:



The material then becomes a protonic conductor in which proton hops from one O^{2-} ion to an adjacent one (Nowick *et al* 1999).

Figure 3 shows typical Arrhenius plots of the total conductivity of $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ perovskite material in wet hydrogen atmosphere in the temperature range from 500 to 950°C. A linear behaviour is observed. It is clear that the conductivity of $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ increases with the elevation of temperature. At 950°C the highest conductivity of $4.4 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$ is observed.

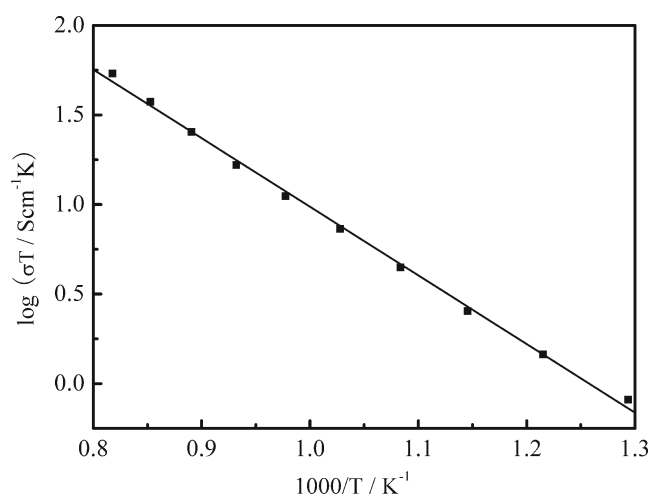


Figure 3. Arrhenius plots of conductivity of $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ in wet H_2 atmosphere.

3.4 Cell performances

The open circuit voltage (OCV) was measured in the temperature range from 600 to 850°C using $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ as electrolyte materials in order to further confirm the existence of ionic conduction. The current–voltage (I – V) and current–power (I – P) characteristics of the single cell at a temperature range from 600 to 850°C are shown in figure 4. With the temperature increasing from 600 to 850°C, OCV decreases from 1.164 to 1.073 V. At 850°C, the maximum power density of $25.2 \text{ mW}\cdot\text{cm}^{-2}$ is observed, which is much lower than the reported cell performances with similar proton conductor electrolytes, such as $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_x$ (Balachandran *et al* 2007) and $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ (Yang *et al* 2010). It has to be noted that the relative poor power density is due to the fact that the thickness of the electrolyte is 1.5 mm which gives very high Ohmic resistance.

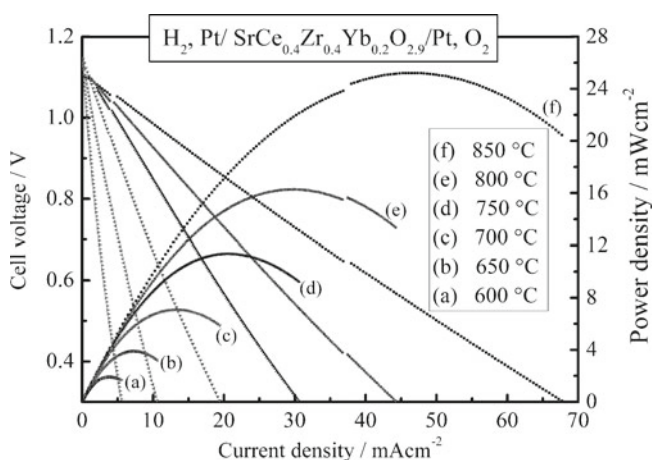


Figure 4. I – V and I – P curves of $\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}$ with H_2/O_2 as operating gases at various temperatures.

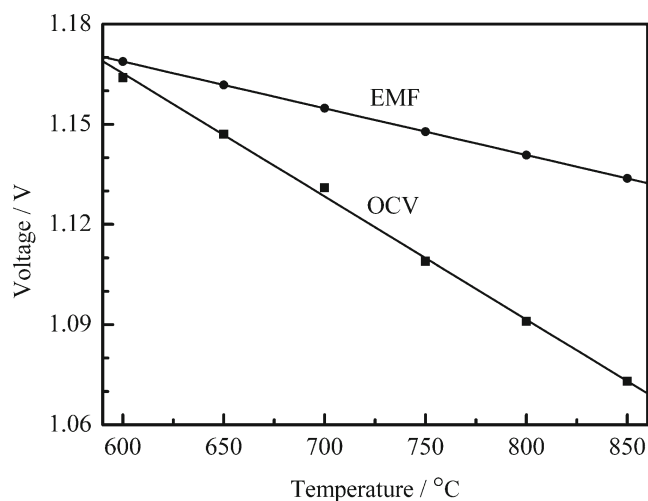


Figure 5. OCV and EMF of cell H_2 , $\text{Pt}/\text{SrCe}_{0.4}\text{Zr}_{0.4}\text{Yb}_{0.2}\text{O}_{2.9}/\text{Pt}$, O_2 at different temperatures.

Table 1. Ionic transfer number of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} at different temperatures.

Temperature (°C)	600	650	700	750	800	850
Ionic transfer number	0.996	0.987	0.979	0.966	0.956	0.946

The OCV and theoretical electromotive force (EMF) of the cell H₂, Pt/SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}/Pt, O₂ at different temperatures are shown in figure 5. The EMF is given by

$$\text{EMF} = E_0 + \frac{RT}{4F} \ln \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}, \quad (4)$$

where, E_0 is the reversible voltage, R the universal gas constant, T the temperature, F the Faraday's constant and P the partial pressure of the given species. The measured OCV is close to EMF at lower temperature. However, with increasing temperature, the deviation between OCV and EMF increases. Similar observation has been reported by Taherparvar and co-workers (2003) on Yb-doped SrCeO₃. This may be due to the development of mixed conductivity on the SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} electrolyte, since at high temperature, more oxygen vacancies will be produced at the hydrogen side and more holes will be formed at the oxygen side. Moreover, cell gas leakage at the hydrogen side may also contribute to the lower OCV compared with EMF. The calculated ionic transfer numbers based on EMF and OCV are summarized in table 1. With the temperature increasing from 600 to 850°C, the ionic transfer number decreases from 0.996 to 0.946. This result shows that the conductivity of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} shown in figure 3 is dominantly ionic.

4. Conclusions

Single phase perovskite electrolyte, SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}, was prepared by solid-state reaction at a sintering temperature of 1600°C and characterized by X-ray diffraction. The conductivity of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} was studied in wet hydrogen atmosphere at a temperature range from 500 to 950°C. The results indicated that the conductivity of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} increases with increasing temperature. The highest conductivity of 4.4×10^{-2} S·cm⁻¹ was observed at 950°C. The current–voltage (I – V) and current–power (I – P) characteristics of the single cell (H₂, Pt/SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9}/Pt, O₂) at a temperature range from 600 to 850°C were performed. The results showed that with the temperature increasing from 600 to 850°C, the open circuit voltage (OCV) decreased from 1.164 to 1.073 V and the ionic transfer number decreased from 0.996 to 0.946 which indicated that the conductivity of SrCe_{0.4}Zr_{0.4}Yb_{0.2}O_{2.9} is

dominantly ionic. At 850°C, the maximum power density of 25.2 mW·cm⁻² was observed.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos 50872090 and 51072130) and Guizhou Province–University Scientific and Technological Cooperation Program (No. [2011] 7002).

References

- Balachandran U, Lee T H and Dorris S E 2007 *ECS Trans.* **7** 987
- Barison S, Battagliarin M, Cavallin T, Doubova L, Boldrini S, Malavasi L and Gerbasi R 2008 *J. Mater. Chem.* **18** 5120
- Bhide S V and Virkar A V 1999 *J. Electrochem. Soc.* **146** 2038
- Bi L, Fabbri E, Sun Z Q and Traversa E 2011 *Energy Environ. Sci.* **4** 409
- Hibino T, Mizutani K, Yajima T and Iwahara H 1992 *Solid State Ionics* **57** 303
- Iwahara H, Esaka T, Uchida H and Maeda N 1981 *Solid State Ionics* **3–4** 359
- Kreuer K D 1999 *Solid State Ionics* **125** 285
- Li J, Cui Y Q, Guo R S, Yu F and Wang M 2007 *Chinese J. Power Sources* **31** 459
- Li J, Yu F and Guo R S 2008 *Chinese J. Power Sources* **32** 27
- Lv J D, Wang L, Lei D, Guo H X and Kumar R V 2009 *J. Alloys Compd* **467** 376
- Matsumoto H, Shimura T, Iwahara H, Higuchi T, Yashiro K, Kaimai A, Kawada T and Mizusaki J 2006 *J. Alloys Compd* **408–412** 456
- Norby T 1988 *Solid State Ionics* **28–30** 1586
- Nowick A S, Du Y and Liang K C 1999 *Solid State Ionics* **125** 303
- Reichel U, Arons R R and Schilling W 1996 *Solid State Ionics* **86–88** 639
- Sammes N, Phillips R and Smirnova A 2004 *J. Power Sources* **134** 153
- Schober T 2001 *Solid State Ionics* **145** 319
- Shi C S, Yoshino M and Morinaga M 2005 *Solid State Ionics* **176** 1091
- Taherparvar H, Kilner J A, Baker R T and Sahibzada M 2003 *Solid State Ionics* **162–163** 297
- Wang W B, Liu J W, Li D, Wang H T, Zhang F and Ma G L 2010 *Solid State Ionics* **181** 667
- Xie K, Yan R Q, Chen X R, Dong D H, Wang S L, Liu X Q and Meng G Y 2009 *J. Alloys Compd* **472** 551
- Yang L, Zuo C D and Liu M L 2010 *J. Power Sources* **195** 1845
- Yin J L, Wang X W, Xu J H, Wang H T, Zhang F and Ma G L 2011 *Solid State Ionics* **185** 6
- Zhang J C, Wen Z Y, Huang S H, Wu J G, Han J D and Xu X X 2008 *Ceram. Int.* **34** 1273
- Zhang J C, Wen Z Y, Han J D, Liu Y, Wu J G and Xu X G 2009 *J. Alloys Compd* **473** 308
- Zuo C D, Lee T H, Dorris S E, Balachandran U and Liu M L 2006 *J. Power Sources* **159** 1291