



Short communication

Samarium doped ceria–(Li/Na)₂CO₃ composite electrolyte and its electrochemical properties in low temperature solid oxide fuel cell

Jing Di^a, Mingming Chen^{a,*}, Chengyang Wang^a, Jiaming Zheng^a,
Liangdong Fan^a, Bin Zhu^b

^a Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Weijjin Road 92#, Nankai District, Tianjin 300072, PR China

^b Department of Energy Technology, Royal Institute of Technology, Stockholm S-100 44, Sweden

ARTICLE INFO

Article history:

Received 6 January 2010
Received in revised form 22 February 2010
Accepted 23 February 2010
Available online 1 March 2010

Keywords:

Low temperature solid oxide fuel cell
Samarium doped ceria
Composite electrolyte

ABSTRACT

A composite of samarium doped ceria (SDC) and a binary carbonate eutectic (52 mol% Li₂CO₃/48 mol% Na₂CO₃) is investigated with respect to its morphology, conductivity and fuel cell performances. The morphology study shows the composition could prevent SDC particles from agglomeration. The conductivity is measured under air, argon and hydrogen, respectively. A sharp increase in conductivity occurs under all the atmospheres, which relates to the superionic phase transition in the interface phases between SDC and carbonates. Single cells with the composite electrolyte are fabricated by a uniaxial die-press method using NiO/electrolyte as anode and lithiated NiO/electrolyte as cathode. The cell shows a maximum power density of 590 mW cm⁻² at 600 °C, using hydrogen as the fuel and air as the oxidant. Unlike that of cells based on pure oxygen ionic conductor or pure protonic conductor, the open circuit voltage of the SDC–carbonate based fuel cell decreases with an increase in water content of either anodic or cathodic inlet gas, indicating the electrolyte is a co-ionic (H⁺/O²⁻) conductor. The results also exhibit that oxygen ionic conductivity contributes to the major part of the whole conductivity under fuel cell circumstances.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Solid oxide fuel cells (SOFCs) have received much attention in terms of environment friendliness, fuel flexibility and high energy efficiency. Conventional SOFCs use typical yttria-stabilized zirconia (YSZ) electrolytes at operational temperatures of about 1000 °C. At such high temperatures, the conductivity of YSZ is improved up to more than 0.1 S cm⁻¹, which is indispensable for high performance SOFCs [1]. However, high running temperature is accompanied by some negative effects such as thermal expansion mismatch, sealing problem and even instability of fuel cells. Extensive studies have been developed to reduce the operating temperature to relatively lower temperatures by decreasing the electrolyte thickness or introducing alternative materials with higher ionic conductivity [2,3]. Doped ceria has been studied as a potential electrolyte for low temperature solid oxide fuel cells (LTSOFCs) in view of its high ionic conductivity [4]. However, doped ceria exhibits mixed ionic and electronic conductivity in reducing atmospheres due to the partial reduction of Ce⁴⁺ to Ce³⁺. The electronic conduction leads to a loss of open circuit voltage (OCV) and a drop of power output of the cell. Furthermore, it may also cause lattice

expansion of the electrolyte, resulting in mechanical instability of cells.

Recently, novel ceria–salt composite materials are regarded as a kind of promising electrolytes for LTSOFCs [5–10]. The composition materials, composed of doped ceria and salts (carbonate, chloride, hydrate or sulphate), demonstrate conductivity of 0.01–1 S cm⁻¹ in 400–600 °C region and suppress the electronic conductivity effectively [6]. The composite electrolyte was considered to be conductors for both oxygen ion and proton under air/H₂ atmosphere, evidenced by the facts that water was generated at both sides of the electrodes [9,10]. However, little information about transfer process has been involved in the former studies during fuel cell operation. At the present time, there is still a lack of detailed mechanism uncovered for the oxygen ionic and protonic conduction in these materials.

Among the composite materials, samarium doped ceria (SDC)–carbonate composites were widely used as electrolytes for LTSOFCs with excellent power densities between 400 and 600 °C [11–13]. In this study, the conduction behavior of the SDC–carbonate composite was studied under air, argon and hydrogen, respectively. The single cells based on the composite electrolyte were fabricated and studied by evaluating the power output. The dependence of OCV on the water content of either anode or cathode gas was also investigated to demonstrate the O²⁻/H⁺ transfer process under fuel cell environment.

* Corresponding author. Tel.: +86 22 27890481; fax: +86 22 27890481.
E-mail address: chmm@tju.edu.cn (M. Chen).

2. Experimental

2.1. Preparation of $Ce_{0.8}Sm_{0.2}O_{1.9}$ -carbonate composite

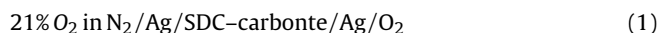
SDC powder was prepared by a nitrate–citric method. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ were dissolved in distilled water where solid citric acid was added. The molar ratio of metal to acid was selected as 1:1.2. The mixture was heated on a hot plate at $70^\circ C$ with continuous stirring and homogeneous sol was formed. After the drying process at $70^\circ C$ for several hours, the precursor was then fired in an oven at $220^\circ C$, leaving a porous and yellow ash. Finally, the resultant ash was then calcined in air at $800^\circ C$ for 2 h to remove the residual organics and pure SDC powder was obtained. The SDC powder was subsequently ground for 5 h using a ball milling process.

Li_2CO_3 and Na_2CO_3 were mixed thoroughly with a molar ratio of 52:48. Then the eutectic carbonates were mixed with SDC powder at a weight ratio of 1:4 and ball milled in alcohol for 5 h. After drying in an oven at $60^\circ C$ for 24 h, the mixture was heated at $600^\circ C$ for 0.5 h in air and taken out from oven directly for cooling. The resultant was pressed uniaxially under 30 MPa to form a pellet (13 mm in diameter and 1 mm in thickness) and sintered at $700^\circ C$ for 0.5 h.

2.2. Characterization of composite electrolyte

The morphologies of SDC and SDC–carbonate powder were observed by scanning electron microscope (SEM, JSM-6700F, JEOL Ltd., Japan). The impedance spectra under different atmospheres were conducted by PARSTAT 2273 Potentiostat/Galvanostat (Princeton Applied Research, USA) in the frequency range of 100 kHz to 0.1 Hz with an applied signal of 10 mV. Silver paste was painted on each side of the sintered pellet and used as electrodes. The measurements were made in air, Ar and H_2 between 450 and $600^\circ C$, respectively. The ionic transport behavior was studied by the oxygen and hydrogen concentration cells, which were constructed as:

Oxygen concentration cell (OCC) :



Hydrogen concentration cell (HCC) :



Their electromotive forces (EMFs) were measured using a TH1951 digital multimeter (Tonghui Ltd., China).

2.3. Fuel cell arrangement

The single cell consisted of NiO–electrolyte/composite electrolyte/lithiated NiO–electrolyte was fabricated using a uniaxial die-press. The composite anode was made by mixing NiO with composite electrolyte and the composite cathode was composed of lithiated NiO and composite electrolyte. The composite anode, electrolyte and composite cathode were cold compressed under 30 MPa in one step to form a single cell with a diameter of 13 mm and a thickness of 1 mm. The cell was thereafter sintered at $700^\circ C$ for 0.5 h in air. The performances of the fabricated single cell were evaluated between 450 and $600^\circ C$, using H_2 and air as fuel and oxidant, respectively. At the start of the test, NiO in the anode was reduced to Ni in situ. In some cases, hydrogen and air were humidified by bubbling the gases through water where the temperature was controlled.

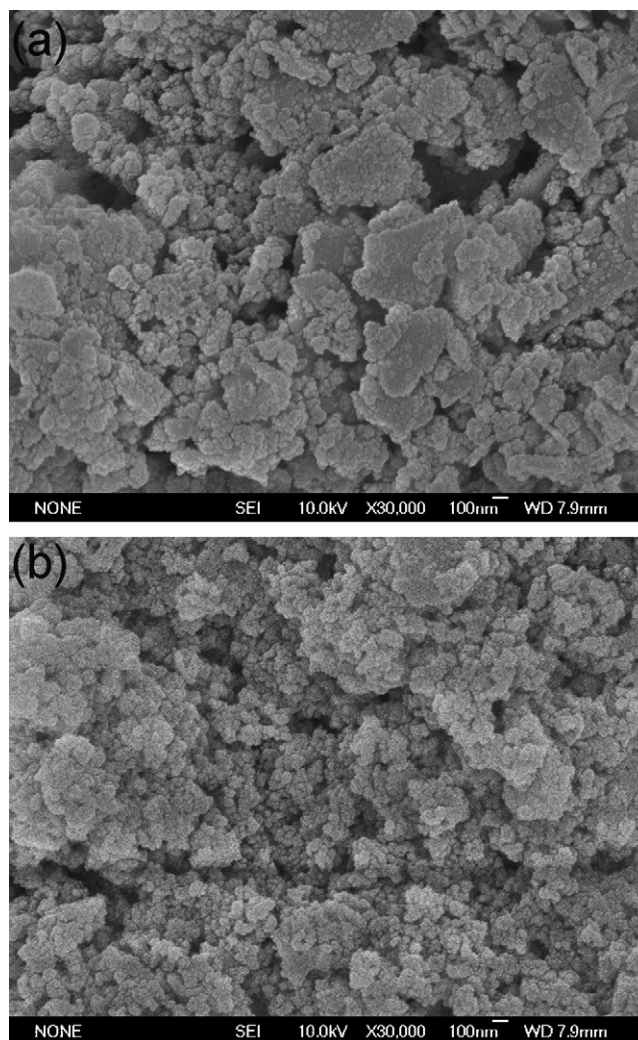


Fig. 1. SEM graphs of (a) SDC and (b) SDC– $(Li/Na)_2CO_3$.

3. Results and discussion

3.1. Characterization

3.1.1. SEM

Fig. 1 shows the SEM graphs of SDC and SDC–20 wt% (52 mol% Li_2CO_3 –48 mol% Na_2CO_3) composite powders. It can be seen that the SDC powder consisted of agglomerated nanocrystallites. For the composite sample, the morphology was similar to SDC powder but more looser structures were seen. It is deduced that the composition process, which might cause the molten carbonates to cover on the surface of the SDC particles evenly, could prevent the agglomeration of the SDC particles effectively. In addition, when the composite sample was taken from oven directly, the carbonates froze quickly to form a nano-composite based on a nano-SDC core [9]. Therefore, good dispersed composite powder was obtained.

3.1.2. Electrical performance

Impedance spectroscopy measurements were carried out in air, argon and hydrogen between 450 and $600^\circ C$, respectively. Fig. 2 shows the typical impedance results obtained at $500^\circ C$. The spectra in air and argon exhibited the features of a depressed arc related to electrochemical electrode response and a tail associated with mass transfer process. Response corresponding to electrolyte was not shown because the time constant of the bulk and grain response

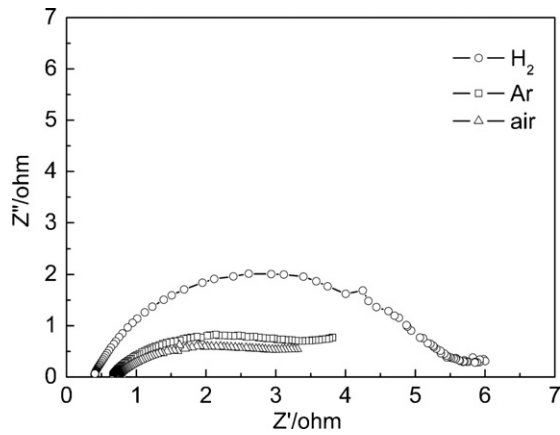


Fig. 2. Impedance spectra under different atmospheres at 500 °C.

is too short. The arc related to electrode response is usually large because of the barrier between the ionic conduction in the electrolyte and the electronic conduction in the electrode [6]. Spectrum in hydrogen took the shape of a depressed and symmetric arc, which is similar to that obtained in oxidizing atmosphere, with smaller intercept of the real axis at high frequency.

The high frequency intercept of the real axis was used to calculate the electrical conductivity (σ). Fig. 3 shows the plots of $\ln(\sigma T)$ versus T^{-1} measured in various atmospheres. The conductivity of the composite electrolyte measured in air varied from 0.007 to 0.5 S cm⁻¹ between 450 and 600 °C, 1–2 orders of magnitude higher than that of SDC. For all the plots obtained in different atmospheres, a sudden increase of the conductivity at some temperature was seen. This temperature is called transition temperature, 490 °C for air or argon and 470 °C for hydrogen. Both of such transition temperatures were lower than the melting point of (Li/Na)₂CO₃ (498 °C). This was also observed by other researchers and explained by a superionic phase transition at the interface between the oxide and the carbonates [14]. It is supposed that a fast path for ionic transport forms at the interfaces where the defects are more than that in the bulks. Above the transition temperature, the ionic defect concentrations in the constituent phases and interfaces increase greatly due to the melting transition from sublattice to bulk [10]. In addition, the molten carbonates immerse into the pores of the ceria substrate, leading to more interfaces between the SDC phase and the carbonate phase. All these factors contributed to the superionic conduction.

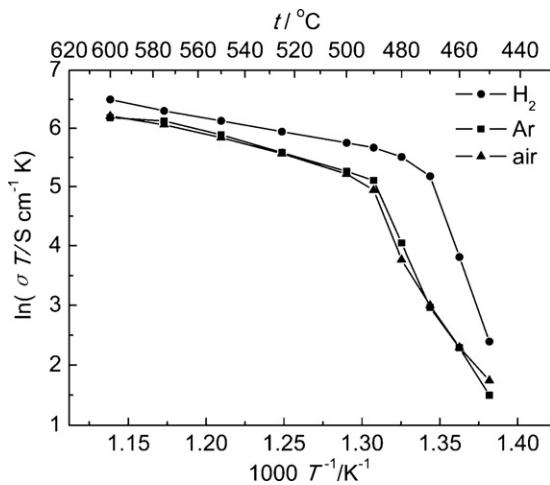


Fig. 3. Arrhenius plots of the conductivity of SDC-(Li/Na)₂CO₃ under various atmospheres.

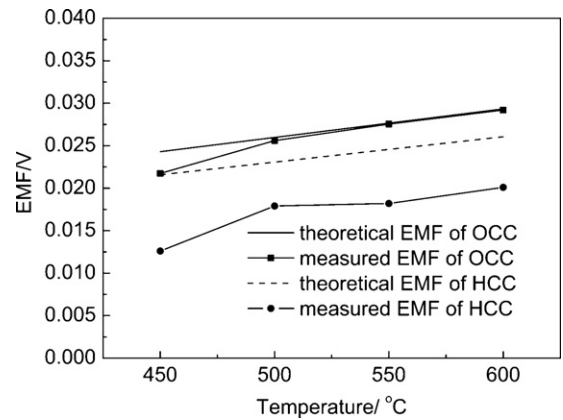


Fig. 4. EMF values for hydrogen and oxygen concentration cells.

In the temperature range of 450–600 °C, the composite electrolyte showed comparable conductivities in air and Ar, indicating that SDC-(Li/Na)₂CO₃ is stable under mild reducing condition, the same case as pure SDC. In contrast, improved conductivity in hydrogen than in air was observed. It is hard to deduce that the enhanced conductivity is contributed by proton or electron since SDC give large electronic conduction in reducing atmosphere.

In order to investigate the ionic contribution to conduction, oxygen and hydrogen gas concentration cells were fabricated. The measured and theoretical EMFs are shown in Fig. 4. The measured voltages in oxygen gas concentration cell fit well with the theoretical EMF values except at low temperatures, indicating the composite is a pure oxygen ionic conductor in oxidizing atmosphere. The deviation at low temperature was presumably due to the porous electrolyte below the melting point. On the other hand, the observed voltages in hydrogen gas concentration cell indicate the electrolyte is protonic conductor in hydrogen since proton is the only ion would contribute to the cell voltage.

3.2. Single cell characterization and performance

Fig. 5 exhibits the cross-sectional images of the single cell and the composite electrolyte sintered at 700 °C. Fig. 5(a) shows the porosity of the electrodes and the good adhesion between the electrodes and the electrolyte layers. Fig. 5(b) shows both the carbonate and SDC phases are continuous. When the temperature overcomes 500 °C, the solid oxide serves as a matrix with liquid carbonate phase surrounded. Continuous phase interface is consequently formed. Both the SDC and interface phase provide percolated networks for ions to pass through. Some pores existing in the electrolyte are observed in the cross-sectional images. Due to the low sintering temperature of only 700 °C which is restrained by the carbonate in the electrolyte, it is hard for the electrolyte to be fully dense. However, the composite electrolyte can still be used as an electrolyte of SOFC because the carbonates melt at working temperature and serve as seals to avoid gas crossover. When the temperature lowers down, the carbonates become solid and shrank, leading to residual pores in the composite electrolyte. This can be confirmed by the OCVs and *I*-*V* characteristics of the single cell with SDC-carbonate composite electrolyte, which is shown in Fig. 6. OCVs of 1.05, 1.03 and 1.03 V were achieved at 500, 550, and 600 °C, respectively, indicating that the electrolyte was gas tightening at these temperatures, whereas it reduced to 0.96 V at 450 °C as a result of the low density of the composite electrolyte at the temperature below the melting point of the carbonates. Furthermore, the OCVs are higher than that of pure SDC-based fuel cells which often give the OCV values of 0.8–0.91 V at 450–600 °C due to the electronic conduction of SDC at reducing atmosphere [15]. The

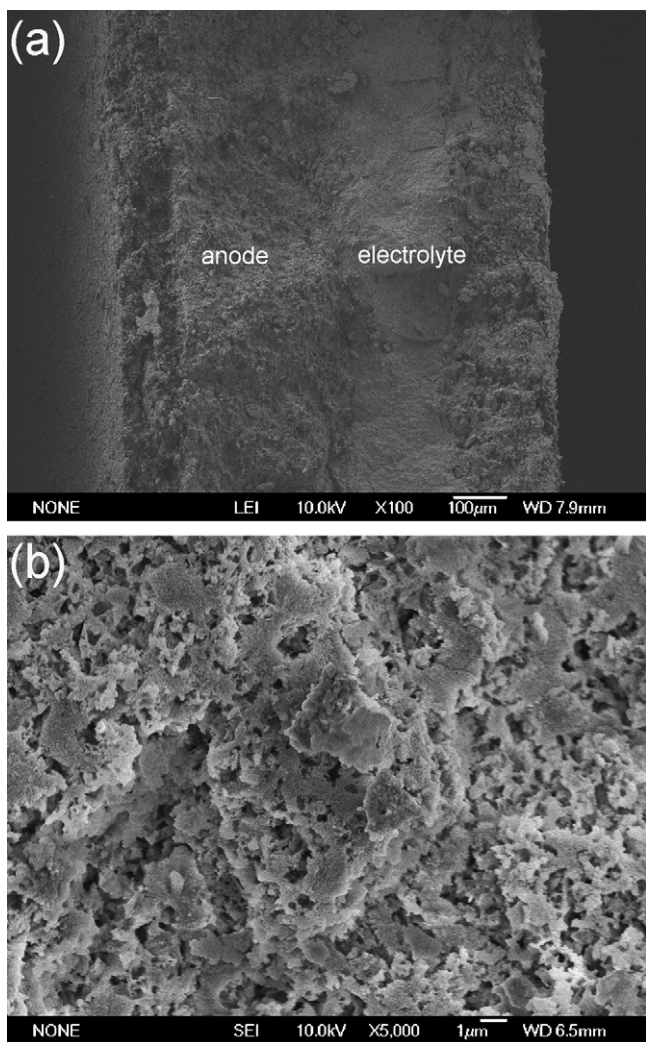


Fig. 5. Cross-sectional images of anode-supported cell: (a) entire cell and (b) electrolyte.

high OCVs indicate that SDC–(Li/Na)₂CO₃ composite electrolyte can suppress the reduction of Ce⁴⁺ to Ce³⁺.

The maximum power densities were 46, 434, 562 and 590 mW cm⁻² at 450, 500, 550 and 600 °C, respectively. Although the electrolyte thickness in this study is as thick as 180 μm, the power density is still comparable with the value of 545 mW cm⁻² for the thin-film fuel cell with a 10-μm-thick SDC electrolyte at

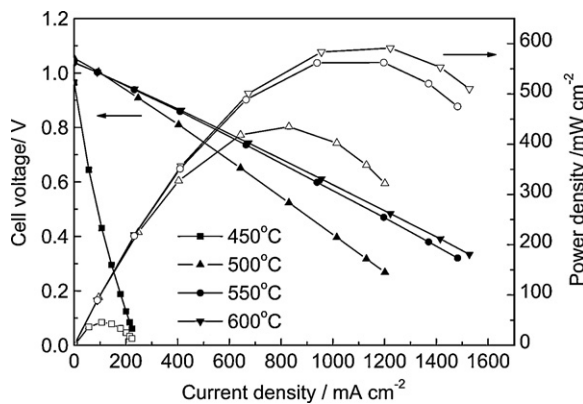


Fig. 6. Performances of the fuel cell based on SDC–(Li/Na)₂CO₃ at various temperatures.

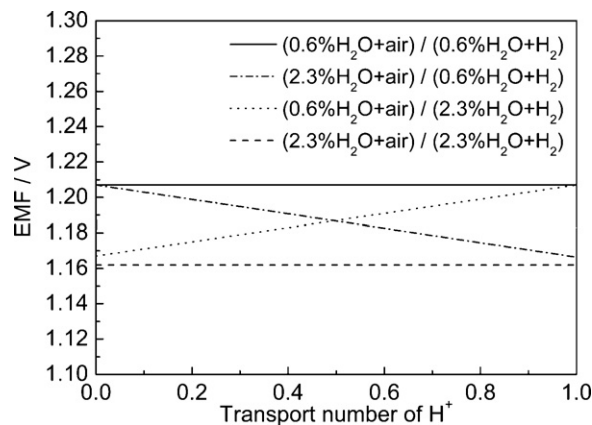


Fig. 7. Dependence of the theoretical EMF on t_H with different humidification of cathode and anode gases.

600 °C [16]. The high performance should be attributed to the high ionic conductivity of the composite electrolyte.

Besides oxygen ion, proton is believed to serve as a charge carrier in the composite electrolyte due to the fact that water was observed to be formed at cathode side. By far, the conducting mechanisms especially the ionic transport numbers are not clear. The transport number for oxygen ion or proton could be determined by oxygen or hydrogen concentration cell. However, the apparent contribution of oxygen ion and proton under fuel cell circumstance is different from the transport number in oxygen and hydrogen. This could be obtained by measuring generated water in the gas at each electrode outlet during discharge of the cell. But the problems in sealing electrode and gathering the generated water make difficulties in the accurate measurement of water amount on both sides. Therefore, more precise experiments should be designed to evaluate the transport process under fuel cell circumstance.

3.3. Effect of water vapor on EMF

The protonic conduction could be verified by the EMF behavior of a hydrogen/air cell. If the electrolyte is a protonic conductor, the EMF decreases as the water vapor pressure (p_{H_2O}) of the cathode gas increases, but remains stable when the anode gas contains more water, because p_{H_2O} at cathode side influences the EMF by Eq. (3):

$$E = E_0 - \frac{RT}{2F} \ln \frac{p_{H_2O}}{p_{H_2} p_{O_2}^{1/2}} \quad (3)$$

where E is the EMF of fuel cell, E_0 the EMF at standard pressure, R the gas constant, F the Faraday constant, p_{H_2} the partial pressure of hydrogen and p_{O_2} is the partial pressure of oxygen. On the other hand, if the electrolyte is an oxygen ionic conductor, p_{H_2O} is the partial pressure of water vapor at anode side and the EMF would be influenced by the water vapor of anode gas.

In the case of a co-ionic electrolyte, the theoretical EMF is given by Eq. (4):

$$E = t_0 \frac{RT}{4F} \ln \frac{p_{O_2}^c}{p_{O_2}^a} + t_H \frac{RT}{2F} \ln \frac{p_{H_2}^a}{p_{H_2}^c} \quad (4)$$

where t_H and t_0 are the transport numbers for proton and oxygen, a and c denote anode and cathode side, respectively. The EMF would decrease as either cathode or anode gas contains more steam.

Suppose ($t_H + t_0$) equals to 1, the dependence of the theoretical EMF under various SOFC circumstances on t_H can be calculated and is shown in Fig. 7. Four circumstances of humidified air at the cathode and humidified hydrogen at the anode were consid-

Table 1
Effects of water content on OCVs of the single cells based on SDC–(Li/Na)₂CO₃.

H ₂ O content/vol.%		OCV/V	
Anode gas	Cathode gas	500 °C	600 °C
0.6	0.6	1.053	1.036
0.6	2.3	1.045	1.022
2.3	0.6	1.017	1.012
2.3	2.3	1.009	1.002

ered. Different water contents gave different lines. The EMF was 1.207 when both air and hydrogen contained 0.6 vol.% H₂O (the solid line) and decreased to 1.162 with increasing water vapor content to 2.3 vol.% (the dash line). Both of the two lines showed slope of 0, which means the EMF is independent on t_H when anode and cathode gases contain the same water content. When p_{H_2O} at anode side was higher than that at cathode side (the dot line), the EMF increased with increasing t_H . On the contrary, the EMF decreased as t_H increased with higher p_{H_2O} at cathode side (the dash dot line). In Fig. 7, $t_H = 0$ refers to the Oxygen ionic conductor and $t_H = 1$ means the protonic conductor. When $0 < t_H < 1$, the electrolyte goes to the co-ionic conductor and the EMF decreased with a increase in water vapor content of either cathode or anode gas.

Table 1 shows the effects of water content on OCVs of the fuel cell with SDC–carbonate electrolyte. The OCVs decreased when either anode or cathode inlet gas contained a larger amount of steam. This indicates that t_H of the electrolyte is between 0 and 1, which means that SDC–(Li/Na)₂CO₃ is a conductor for both proton and oxygen ion. Higher OCVs in Table 1 were observed when the anode inlet gas contained a smaller amount of steam than what the cathode inlet gas had. Compared with Fig. 7, t_H should be in the range of 0–0.5 where the decrease of theoretical EMFs is larger when hydrogen contained more steam than air did. This suggests oxygen ion dominates the conduction process of SDC–(Li/Na)₂CO₃ in fuel cell circumstance from 500 to 600 °C. When working under fuel cell environment, oxygen ion transfers through the SDC phase and the interfaces between constituent phases via oxygen vacancy, while proton passes along the interfaces by forming HCO₃[−] with CO₃^{2−}. However, a strong evidence for the existence of interfaces is still missing and more investigations are under their ways.

4. Conclusions

The composition of SDC and 52 mol% Li₂CO₃/48 mol% Na₂CO₃ was prepared and developed as the electrolyte for ITSOFCs. The composite showed a higher ionic conductivity than that of the pure SDC at comparable temperatures in air. The gas concentration cells indicated the electrolyte is protonic conductor in hydrogen. A power density of 590 mW cm^{−2} was obtained for single cell based on the composite electrolyte at 600 °C, showing that good performance can be achieved. The high OCV up to 1.03 V at 600 °C could be attributed to the suppression of electronic conduction of SDC in hydrogen circumstance. The OCVs decreased as p_{H_2O} on either anode or cathode side increased, indicating the electrolyte is a mixed conductor (O^{2−}/H⁺), which oxygen ionic conductivity dominates.

Acknowledgement

This work was financially supported by Program of Science Foundation of Tianjin City (No. 07jcyjbc02500).

References

- [1] B. Zhu, S. Li, B.-E. Mellander, *Electrochem. Commun.* 10 (2008) 302–305.
- [2] T. Tsai, E. Perry, S. Barnett, *J. Electrochem. Soc.* 144 (1997) L130–L132.
- [3] B. Rambabu, S. Ghosh, W. Zhao, H. Jena, *J. Power Sources* 159 (2006) 21–28.
- [4] B.C.H. Steele, *Solid State Ionics* 129 (2000) 95–110.
- [5] B. Zhu, X.R. Liu, P. Zhou, X.T. Yang, Z.G. Zhu, W. Zhu, *Electrochem. Commun.* 3 (2001) 566–571.
- [6] B. Zhu, *J. Power Sources* 114 (2003) 1–9.
- [7] J.D. Hu, S. Tosto, Z.X. Guo, Y.F. Wang, *J. Power Sources* 154 (2006) 106–114.
- [8] A. Bodén, J. Di, C. Lagergren, G. Lindbergh, C.Y. Wang, *J. Power Sources* 172 (2007) 520–529.
- [9] B. Zhu, X.T. Yang, J. Xu, Z.G. Zhu, S.J. Ji, M.T. Sun, J.C. Sun, *J. Power Sources* 118 (2003) 47–53.
- [10] J.B. Huang, Z.Q. Mao, Z.X. Liu, C. Wang, *Electrochem. Commun.* 9 (2007) 2601–2605.
- [11] J.B. Huang, Z.Q. Mao, L.Z. Yang, R.R. Peng, *Electrochem. Solid State Lett.* 8 (2005) A437–A440.
- [12] X.D. Wang, Y. Ma, R. Raza, M. Muhammed, B. Zhu, *Electrochem. Commun.* 10 (2008) 1617–1620.
- [13] L. Zhang, R. Lan, X.X. Xu, S.W. Tao, Y.Z. Jiang, A. Kraft, *J. Power Sources* 194 (2009) 967–971.
- [14] T. Schober, *Electrochem. Solid State Lett.* 8 (2005) A199–A299.
- [15] D. Dong, B.B. Liu, Z.N. Zhu, S. Zhou, C.R. Xia, *Solid State Ionics* 179 (2008) 896–899.
- [16] X. Zhang, M. Robertson, C. Deêes-Petit, W. Qu, O. Kesler, R. Maric, D. Ghosh, *J. Power Sources* 164 (2007) 668–677.