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Fabrication and characterization of composite electrolyte for intermediate-temperature SOFC

Ning Zuo [a], Milin Zhang [a], Zongqiang Mao [b,*], Zhan Gao [b], Fucheng Xie [b]

[a] *College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China*
[b] *Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China*

Abstract

In this study, a ceria-based composite electrolyte was investigated for intermediate-temperature solid oxide fuel cells (SOFCs) based on SDC–25 wt.% K_2CO_3. Sodium carbonate co-precipitation process by which SDC powder was adopted and sound cubic fluorite structure was formed after SDC powders were sintered at 750 °C for 3 h. The crystallite size of the particle was 21 nm in diameter as calculated from data obtained through X-ray diffraction. The conductivity of the composite electrolyte proposed in this study was much higher than that of pure SDC at the comparable temperature of 550–700 °C. The transition of the ionic conductivity occurred at 650 °C. Based on this type of composite electrolyte, single cell with the electrolyte thickness of 0.3 mm were fabricated using dry pressing, with nickel oxide adopted as anode and SSC as cathode. The single cell was then tested at 550–700 °C on home-made equipment in this study, using hydrogen/air. The maximum power density and open circuit voltage (OCV) achieved 600 mW cm^{-2} and 1.05 V at 700 °C, respectively.

Keywords: Solid oxide fuel cells (SOFCs); Intermediate-temperature; $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC); Composite electrolyte; K_2CO_3

1. Introduction

Solid oxide fuel cells (SOFCs) can directly convert the chemical energy of fuels into electricity with high efficiency, without combustion or mechanical processes. Conventional ceramic fuel cells with yttria-stabilized zirconia (YSZ) serving as the electrolyte operate at high temperatures (800–1000 °C) to achieve sufficient ionic conductivity of the electrolyte, which gives rise to various disadvantages in the long-term stability, manufacturing cost, etc. of the cell going into commercialization.[1] Therefore, it is desirable to lower the operating temperature of the SOFC system while maintaining high power outputs. During the last decade, most of the research efforts were concentrated on the reduction of the operation temperature of SOFC. So far, the temperature has been reduced from nearly 1000 °C to intermediate temperature ranging from 400 °C to 600 °C.[2,3] To achieve this purpose, a solid electrolyte with high ionic conductivity is required.[4,5] However, the ionic conductivity of all these types solid electrolytes cannot meet the requirements of real low-temperature SOFC, whose conductivity should reach $10^{(1}$ S cm^{-1}. Therefore, they must be fabricated into a very thin ((30 (m) and dense ceramic membrane, which causes high fabrication cost. In order to attain better performance of doped ceria electrolytes at low temperatures, their electrical properties are improved.[6]

To develop high-performance intermediate-temperature fuel cells (ITFCs), doped ceria, e.g., gadolinium-doped ceria (GDC), samarium-doped ceria (SDC), and yttrium-doped ceria (YDC), has been extensively studied serving as electrolytes for low-temperature ceramic fuel cells due to its high ionic conductivity. However, doped ceria will generate some electronic conduction under reducing atmosphere, which often results in power loss and substantial mechanical problems.[7] Novel ceria-based composite electrolytes consisting of two phases, ceria host phase or other phases, which are usually carbonates, sulphates, halides or hydrates, have already been successfully developed recently. These composites have a suppressed electronic conduction under reducing atmosphere and an enhanced ionic conductivity (0.01–1 S cm^{-1} within intermediate/low temperature range) compared with conventional doped ceria.[8–11] Among them, ceria–carbonate composite is the most typical composite electrolyte, and the cells in which ceria–carbonate composite is used are reported to have achieved the best performance. These

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[*] Corresponding author at: A314, Energy Science Building, Tsinghua University, Beijing 100084, China. Tel.: +86 10 62780537; fax: +86 10 62792648.
E-mail address: maozq@tsinghua.edu.cn (Z. Mao).

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materials are found to be co-ionic (O^{2-}/H^+) conductors with an ionic conductivity of 0.1 S cm^{-1} below 600 °C.

Recently, most of researches are focused on ceria–carbonate composites, e.g., doped SDC with $(Li–Na)_2CO_3$, $(Li–K)_2CO_3$ or $(Na–K)_2CO_3$.[6,12,13] However, all of these doped SDC with binary carbonate have different melting temperatures and thermal stability based on different proportions of carbonate. While the SDC doped with $(Na-K)_2CO_3$ do not exist transition point of the ionic conductivity at 400–600 °C, its performance of fuel cell is much higher than the pure SDC. But complex electrolyte system leads to a much more difficult synthesis process, and the thermal stability is inevitably lower than that of the simple system. This study aims to explore simple composite electrolyte SDC–25 wt.% K_2CO_3 by examining the influence of composite conductivities on the performance fuel cell.

2. Experiment process

$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) powder was synthesized by ammonium carbonate co-precipitation process. Precursor solution was prepared by dissolving $Ce(NO_3)_3 \cdot 6H_2O$ and Sm_2O_3 in dilute nitrate acid according to their stoichiometric proportions. 1 mol L^{-1} mixed solution of $Ce(NO_3)_3$ and $Sm(NO_3)_3$ was added dropwise into 0.5 mol L^{-1} ammonium carbonate solution according to the stoichiometric proportion ($Ce^{3+}:Sm^{3+} = 4:1$) with good stirring to form white precipitate at room temperature. The precipitate was then vacuum-filtered, washed with deionized water and ethanol for three times, and dried at 80 °C for 12 h. The calcination was performed afterwards at 750 °C for 3 h to obtain pure SDC powder, which was then mixed with 25 wt.% K_2CO_3 and sintered at 680 °C exposed to air for 30 min. The products were taken out directly from the furnace to room temperature and ground again thoroughly so that it can be applied as electrolyte. To confirm the phase structure of SDC/carbonate composites, the powder XRD (D8 Advance diffract to meter) was used for analysis at room temperature using Cu Ka-ray. The morphology and microstructure of the powder was studied using Scanning Electron Microscope (SEM, JSM-6301F, JEOL Ltd., Japan).

The composite anode was made from the mixture of 45 wt.% NiO, 45 wt.% electrolyte, and 10 wt.% starch. After heating, the starch was removed from the mixture, thus forming a porous structure of the anode. The composite cathode was made from the mixture of SSC ($Sm_{0.5}Sr_{0.5}CoO_2$) 60 wt.% and 40 wt.% electrolyte. For electrical conductivity measurement, the composite powders were cold pressed at 300 MPa into cylindrical pellets (13 mm in diameter and 1 mm in thickness) with the adoption of an uniaxial die-press. The green pellets were then sintered at 700 °C for 1 h, and both sides of the pellets were then coated with silver paste to produce silver electrode, which was later heated at 700 °C for 40 min. Electrical conductivities of the pellets were measured with its exposure to the air with AC impedance spectroscopy on No.IM6eX electrochemical workstations produced by Zahner. The impedance data were taken at the temperature ranging from 500 °C to 700 °C and with the frequency ranging from 100 mHz to 100 kHz with the adopting of an excitation voltage of 10 mV.

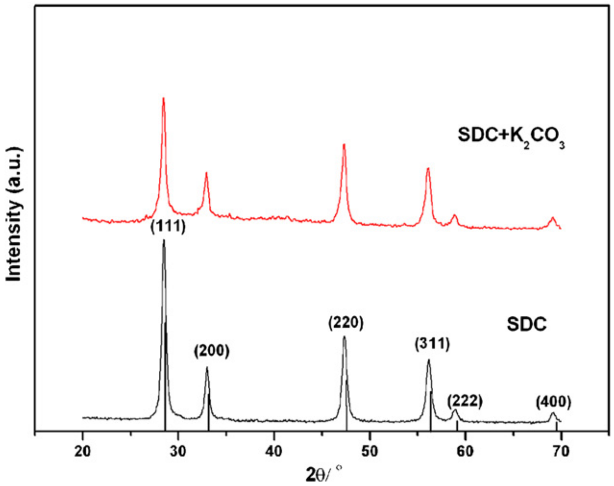

Fig. 1. XRD patterns of SDC powder and SDC–25 wt.% K_2CO_3. SDC powder had been sintered at 750 °C for 3 h, and SDC–25 wt.% K_2CO_3 was obtained from ball-milled powder with the same mass fraction as the standard of JCPDS no. 34-0394.

Anode-supported single cells were fabricated through simple dry pressing. The anode, electrolyte and cathode were uniaxially pressed into a pellet at the pressure of 300 MPa and then sintered at 600 °C for 30 min with its exposure to air. The pellet was 13 mm in diameter and 1.2 mm in thickness including 0.3-mm thick electrolyte. The effective working area of the pellet was 0.785 cm^2. Silver paste was coated afterwards on every side of electrode as current collector. During the measurement, stainless steel was employed as testing holder and silver glue was applied as the sealant. The cells were tested at the temperature ranging between 500 °C and 600 °C, with hydrogen and air used as the fuel and the oxidant, respectively. In both of the two tests, gas flow rates were controlled between 40 and 100 ml min^{-1} under 1 atm pressures. The performance of the fuel cell was tested under variable resistance loads, which regulated the cell voltage and power output. By collecting data of the cell voltage and current under each resistance load with a computer program specially designed, from which *I–V* and *I–P* curve could thus be drawn.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure SDC and SDC–25 wt.% K_2CO_3 composite electrolytes at room temperature. All the peaks well denote the structure of fluorite (JCPDS with the card file No. 34-0394) sintered at 750 °C for 3 h. The crystallite sizes of the particles were calculated from FWHM data for (1 1 1) crystal face according to Scherrer's formula:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

where D is the crystallite size in the unit of nm; λ is the radiation wavelength (0.154056 nm in this case, Cu target); the diffraction angle θ and β are the corrected line width at half-peak intensity.

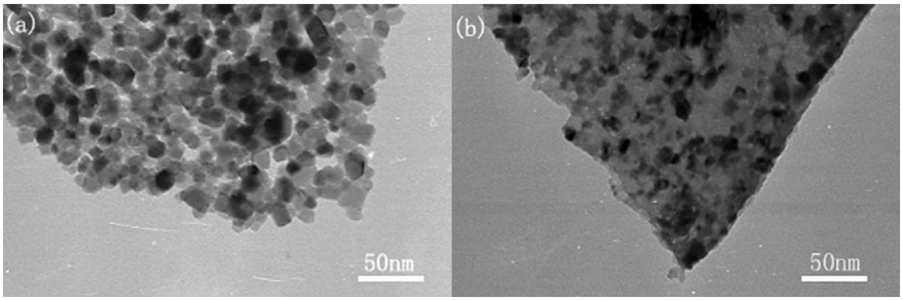

Fig. 2. TEM images of pure SDC (a) and composite electrolyte (b) powder, of which (a) shows that the diameter of SDC nano-powder averages 20 nm, and (b) shows that the mixture of SDC with K_2CO_3 makes large particle more than 300 nm in diameter.

The crystallite sizes of SDC and SDC–K_2CO_3 were calculated according to Fig. 1 to be 23 nm and 14 nm, respectively. The composite sample manifested the same properties during the diffraction, which was identified as SDC phase. It was thus indicated that the carbonates existed as an amorphous phase after thorough grinding and thermal-treatment, in which it was assumed that the carbonates could melt and be coated onto the SDC particles.

TEM images of pure SDC and composite electrolyte powder are shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), the grains are nearly spherical and uniform, with the average diameter obtained from the TEM to be about 20 nm, which is consistent with the crystallite size calculated with XRD. The particle size was similar to that of SDC prepared with sol–gel technique and glycine–nitrate process but much smaller than with oxalate co-precipitation process.[14–16] Powder grain produced in this study was on nanometer-scale, although they formed aggregate group. After mixed with 25 wt.% K_2CO_3 and heated at 750 °C with exposure to air for 3 h, they turned into large agglomerate more than 300 nm in diameter, as shown in Fig. 2(b).

The electrical conductivities of pure SDC and SDC–25 wt.% K_2CO_3 electrolytes with their exposure to air obtained according to AC impedance analysis are presented in Fig. 3. The line of the pure SDC was a almost beeline, which is in accordance with Arrhenius plots revealing the conductivity of SDC according to the Arrhenius formula:

$$\sigma T = A \exp\left(\frac{-E}{kT}\right) \tag{2}$$

where σ is a conductivity datum; E is the activation energy of electrical conduction; k is the Boltzmann's constant; T is the absolute temperature; A is the pre-exponential factor remaining a constant within a certain temperature range. Conductivity datum σ could be obtained from the following equation:

$$\sigma = \frac{L}{SR} \tag{3}$$

where L is the thickness of the sample, S is the electrode area on the surface of the sample. Activation energy of pure SDC was 0.69 eV as calculated according to formulas (2) and (3). However, sharp conductivity jumping point appeared at 650 °C on the composite electrolyte line, being about 240 °C lower than the melting point of K_2CO_3, which had been reported by Zhu et al.[10,17] It could be interpreted as super ionic phase transition in the interface between SDC and salt phase.

It is well known that oxygen ion conduction in SDC is realized by the transfer of oxygen ions via oxygen vacancies, which result from incorporation of Sm_2O_3 into CeO_2 as described by the following equation:

$$\frac{1}{2}Sm_2O_3 \Leftrightarrow Sm'_{Ce} + \frac{1}{2}V_O^{\bullet\bullet} + \frac{3}{2}O_O^{\times} \tag{4}$$

When the operating temperature at the lower region of bc part, that dominates conductivity. But activation energy of composite electrolyte was 1.30 eV, much higher than that of pure SDC. Because within the range of 400–500 °C, ions of potassium carbonate lacked enough energy to conduct masses of oxygen ions or protons. Therefore, K_2CO_3 in composite electrolyte served as the impurity for SDC to impede conduction of oxygen ions in SDC. However, thermal effect was enhanced with the increase in operating temperature. In a hydrogen fuel atmosphere, protons can be first formed on the surface of the oxygen site in the SDC lattice, and then they become interstitial ions in the interfacial

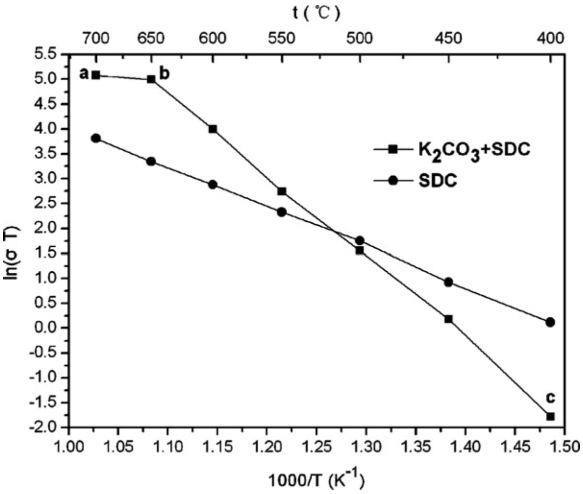

Fig. 3. Arrhenius plots of SDC/25 wt.% potassium carbonate composite electrolytes and pure SDC electrolyte. Their activation energies could be obtained using lines with different slopes: that of pure SDC was 0.69 eV, while the ab region the composite electrolyte was 0.12 eV and bc part 1.3 eV.

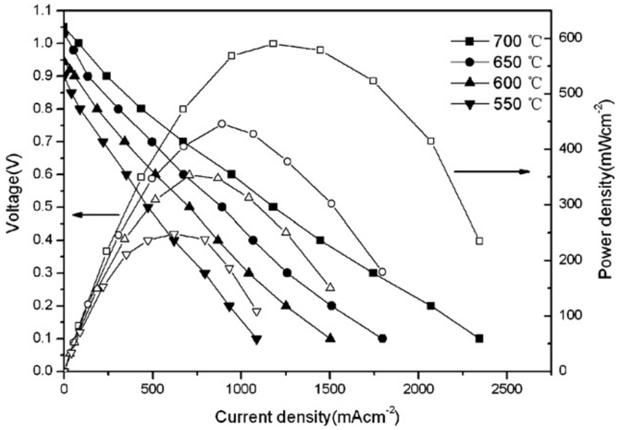

Fig. 4. *I–V* and *I–P* characteristics of H_2/air fuel cell based on SDC/25 wt.% K_2CO_3 composite electrolyte at 550–700 °C.

region of SDC and K_2CO_3. This phenomenon was described by the following equations:

$$H_2 + O_O^{\times} + 2Ce_{Ce}^{\times} \Leftrightarrow 2HO_O^{\bullet} + 2Ce'_{Ce} \quad (5)$$

$$HO_O^{\bullet} \Leftrightarrow H_i^{\bullet} + O_O^{\times} \quad (6)$$

Since there existed enough conduction units at 550 °C, conductance of composite electrolyte exceeded that of pure SDC for the first time. As the temperature continued to increase, super ionic phase transition occurred when operation temperature went over 650 °C and the activation energy fell to 0.12 eV at ab part. The detailed conduction process had already been reported previously.[6]

The performance of single cell based on SDC/25 wt.% K_2CO_3 composite electrolytes was investigated at 550–700 °C, with hydrogen adopted as fuel and air as oxidant. The voltages and the corresponding power densities as a function of current density are shown in Fig. 4. It can be seen that the open circuit voltages (OCVs) of single cells based on composite electrolytes were lower than theoretical values within the operating temperature range, with the OCV ranging from 1.05 V to 1.0 V when temperature reduced from 700 °C to 650 °C. The deviation of the measured OCVs from the theoretical OCVs might be caused by gas crossover in the composite electrolyte of less density and electronic conduction of SDC phase in the reducing environment. If the temperature fell to 600 °C, OCV dropped sharply to 0.98 V, which was due to the fact that the composite electrolyte could not maintain good density during the entire fabrication process, and a certain amount of residual pores were produced in the composite electrolyte resulting in gas crossover. Furthermore, when the operating temperature fallen below the transition phase temperature of the composite electrolyte, more pores in the electrolyte layer were thus formed, accompanied by the volume change of carbonate as it transited from molten phase to solid phase, leading to lower OCV. The maximum power densities of the cell were 602, 446, 353 and 248 mW cm^{-2} at 700, 650, 600 and 550 °C, respectively.

Until now, the long-team test performance of fuel cell based on this kind of electrolyte has not gotten the ideal effect. It has close relationship with sealing materials, using suitable one could improve this performance obviously. And that needs to be further studied.

4. Conclusions

When SDC–25 wt.% K_2CO_3 was adopted as the composite electrolyte, a ionic phase transition occurred within low temperature range, while above the transition temperature, the composite exhibited high ionic conductivities. As the operating temperature increased from 550 °C to 700 °C, performance of fuel cell significantly increased depending on the transition temperature of the composite electrolyte. Fuel cell based on composite electrolyte showed excellent performance at 550–700 °C, with the best performance reaching 602 mW cm^{-2} at 700 °C.

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