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Ceramics International 40 (2014) 4939–4944

CERAMICS INTERNATIONAL

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A novel processing method of $Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$ cathode for intermediate temperature solid oxide fuel cells

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Received 26 July 2013; received in revised form 20 October 2013; accepted 21 October 2013
Available online 29 October 2013

Abstract

The oxygen-deficient perovskite $Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$ (SYCO) is recently investigated as cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs). However, the conventional preparation methods are both energy and time consuming, which greatly hinders the commercialization of this material. In the present study, the calcination and cathode–electrolyte sintering processes are systematically investigated as a function of calcination temperature and time; and a novel cathode processing method has been established. SYCO powder calcined at 900 °C for 8 h with impurities due to incomplete phase formation, rather than the phase pure product, has been chosen for pristine cathode fabrication. The purity of this cathode can be further improved during the quick cathode–$Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) electrolyte sintering step. The XRD results confirm that the formation of undesirable secondary phase has been successfully avoided by adopting relatively low sintering temperature and short sintering time. SEM images demonstrate that the as-prepared electrode possesses good adherence between cathode and electrolyte. The polarization resistance of the cathode prepared in this method reaches 0.28 Ω cm^2 at 700 °C, significantly smaller than that of the cathode prepared by using phase pure product as the initial cathode material. This novel preparation route provides a new method of developing electrodes with high electrochemical performance for SOFCs.

Keywords: Solid oxide fuel cell; A. Sintering; D. Perovskites; E. Electrodes

1. Introduction

A solid oxide fuel cell (SOFC) is an all-solid-state energy conversion device that converts a chemical fuel directly into electricity. As a key component of a SOFC, the cathode, also known as the air electrode, is the electron receptor of the external circuit and the spot where the oxygen in air reacts with electrons [1]. A cathode material for SOFC should possess high electronic conductivity and catalytic activity, adequate porosity, thermodynamic stability and compatibility (both chemical and thermal) with other components. Some perovskite-type materials satisfying these requirements have been extensively investigated as SOFC cathodes. Lanthanum strontium manganite (LSM), for instance, is the most widely applied cathode material in high temperature SOFCs due to its good electronic conductivity and high activity for oxygen electrocatalytic reduction. However, LSM is unsuitable for IT-SOFCs (600–800 °C) because of its low ionic conductivity and poor catalytic activity [2,3] in the intermediate temperature regime. Lowering the working temperature of SOFC can result in lower systems cost and performance degradation rates [4]. To develop high performance cathodes operating at intermediate temperature is vital to accelerate the commercialization of SOFCs.

As a competitive cathode material for IT-SOFC, the oxygen-deficient perovskite $Sr_xY_{1-x}CoO_{2.65-\delta}$ has recently attracted the interest of some researchers [5–7]. Above 600 °C, SYCO is a mixed ionic–electronic conductor exhibiting good electrocatalytic activity for oxygen reduction reaction (ORR) [5]. Porras-Vazquez reported that $Sr_{0.9}Y_{0.1}CoO_{3-\delta}$ gave the area specific resistance (ASR) value of 0.40 Ω cm^2 at 700 °C [6]. Rupasov et al. fabricated $Sr_{0.75}Y_{0.25}CoO_{2.62}|Ce_{0.9}Gd_{0.1}O_{1.95}|Sr_{0.75}Y_{0.25}CoO_{2.62}$ symmetrical cells for oxygen diffusion measurement and achieved an ASR of 0.17 Ω cm^2 at 720 °C [7].

The authors have conducted a literature survey to figure out that SYCO is usually prepared by solid state reaction at 1100 °C or above for 12–96 h [5,7–16]. This conventional

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http://dx.doi.org/10.1016/j.ceramint.2013.10.088

route is both energy and time consuming, which greatly hinders the commercialization of SYCO. Therefore, in the current work, a sol–gel method has been developed to prepare $Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$ (SYCO) cathode material in an energy-saving way. In order to minimize the sintering temperature and time, the SYCO powder calcined at 900 °C for 8 h with some impurities due to incomplete phase formation has been chosen for pristine cathode fabrication. The formation of SYCO phase can be further developed during the electrode-electrolyte sintering process. An optimal polarization resistance of 0.28 Ω cm^2 at 700 °C has been achieved on the SYCO cathodes prepared in this method. This novel cathode processing technique provides an energy-saving method for SYCO preparation.

2. Experimental section

2.1. Synthesis

$Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$ (SYCO) power was synthesized by the sol–gel method. Stoichiometric amounts of strontium nitrate ($Sr(NO_3)_2$), yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ and cobalt nitrate $Co(NO_3)_3 \cdot 6H_2O$ were added into deionized water at a molar ratio of 0.7:0.3:1 with constant stirring until a clear solution formed. The cation concentration of the nitrates solution was controlled at 0.4 mol L^{-1}. Appropriate quantity of citric acid (mole ratio 2:1 of citric acid: total metal ions) was also added to the solution under constant stirring. After heated at 80 °C for 4 h, water was gradually evaporated with heating and stirring. The resulting viscous mixture was dried in vacuum oven at 160 °C to obtain the SYCO precursor. The as-formed precursor was then calcined in air at different temperatures from 900 °C to 1200 °C for various time durations.

Each SYCO sample chosen for cathode fabrication was thoroughly mixed with terpineol. The SYCO cathode paste was coated onto one side of a dense $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) electrolyte pellet (approximate thickness: 0.830 mm). After drying, the SYCO cathode was sintered at 1000–1200 °C for 0.5 h in air. Prior to the fabrication of SYCO electrode, Pt pastes were painted as counter electrode and reference electrode on the GDC electrolyte and sintered at 1000 °C for 1 h. The counter electrode was positioned symmetrically to the SYCO cathode with the active electrode area of 0.785 cm^2; the reference electrode was fixed at the rim of the GDC electrolyte. The as-formed three-electrode systems were used for electrochemical performance test.

2.2. Characterizations

The phase composition of SYCO sol–gel powder and SYCO cathodes sintered on GDC electrolyte calcined at different temperatures was characterized by X-ray diffraction (XRD) using a Japan Rigaku D/max-rb X-ray diffractometer (Cu Kα radiation, λ=1.5418 Å).

The electrochemical performance of the cathode was characterized by electrochemical impedance spectroscopy (EIS) using an electrochemical work station (Chi650D, CH Instruments Inc, China) in three-electrode mode. The frequency range from 0.01 Hz to 1 MHz was applied with signal amplitude of 5 mV under open circuit voltage. Polarization resistances were derived from the difference of the real intercepts between high frequencies and low frequencies. And the electrolyte resistances of all samples have been removed from the spectra to show the difference in the cathode polarization impedances clearly.

The microstructure and morphology of the cathodes were examined by a scanning electron microscope (SEM, FEI Quanta 200, Netherlands).

3. Results and discussion

To investigate the effect of calcination temperature and time, several batches of SYCO powder were calcined at different temperatures and time durations; see Fig. 1 for the XRD patterns. X-ray peaks of $SrCO_3$ (JCPDS card no. 52-1526), SYCO (JCPDS card no. 54-0234) and Y_2O_3 (JCPDS card no. 43-0661) are also given as guides to the eye at the bottom of Fig. 1. The XRD result indicates that the powder calcined at 900 °C for 8 h is a complex mixture containing SYCO, $SrCO_3$ and Y_2O_3. Presumably, the phase formation of SYCO is not fully completed at this stage. After calcined at 1000 or 1100 °C for 8 h, some impurities still remain. After heated at 1200 °C for 8 h or 1100 °C for 96 h, the phase formation of SYCO appears to be completed. Trace amount of Y_2O_3 impurity can

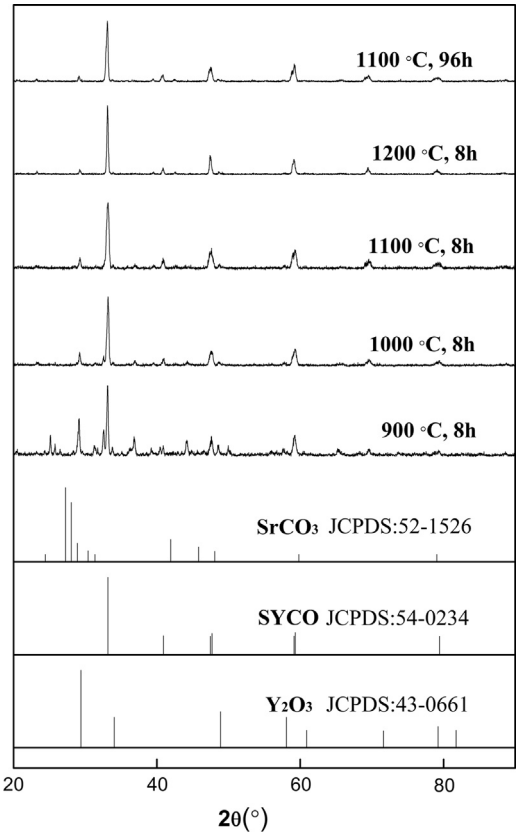

Fig. 1. X-ray diffraction patterns of SYCO sol–gel powder calcined at 900, 1000, 1100, 1200 °C for 8 h and 1100 °C for 96 h. X-ray peaks of $SrCO_3$ (JCPDS card no. 52-1526), SYCO (JCPDS card no. 54-0234) and Y_2O_3 (JCPDS card no. 43-0661) are given as guides to the eye at the bottom.

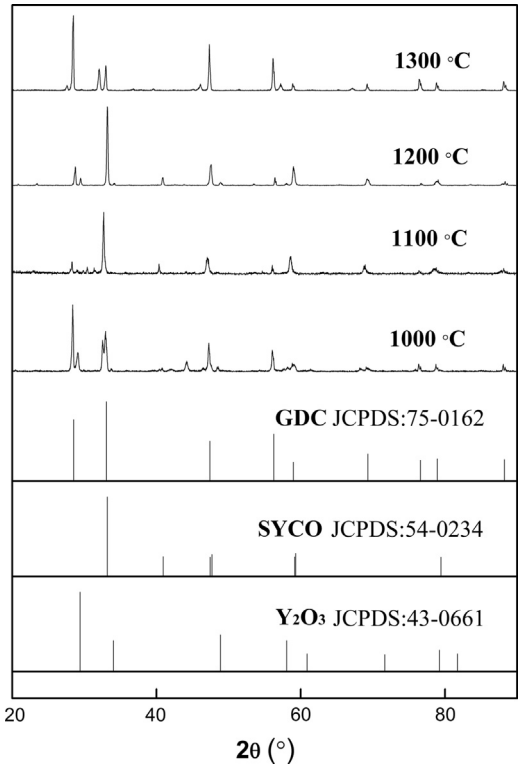

Fig. 2. X-ray diffraction patterns of SYCO cathodes sintered on GDC electrolyte at different sintering temperatures from 1000 to 1300 °C for 0.5 h. X-ray peaks of GDC (JCPDS card no. 75-0162), SYCO (JCPDS card no. 54-0234) and Y_2O_3 (JCPDS card no. 43-0661) are given as guides to the eye at the bottom.

still be identified due to evaporation of Co_3O_4 at high temperature [5,12]. The results demonstrate that the phase formation of SYCO requires high heating temperature above 1100 °C and extended heating time up to 96 h.

In order to develop an energy saving route, the conventional electrode preparation process has been modified. Instead of phase pure SYCO, the SYCO powder calcined at 900 °C for 8 h was adopted as initial cathode material. The XRD patterns of SYCO cathodes sintered onto GDC electrolytes at different temperatures from 1000 to 1300 °C for 0.5 h are presented in Fig. 2. For comparison, the standard diffraction peaks of GDC (JCPDS card no. 75-0162), SYCO (JCPDS card no. 54-0234) and Y_2O_3 (JCPDS card no. 43-0661) are displayed at the bottom of Fig. 2. Below 1100 °C, the formation of SYCO phase is incompleted. For the electrode sintered at 1200 °C, the XRD pattern can be indexed as SYCO cathode, trace amount of Y_2O_3 and GDC electrolytes. The diffraction peaks are sharp with high intensity, indicating that the perovskite SYCO phase has been essentially formed. A secondary phase can be observed when the sintering temperature is above 1300 °C, which may be caused by the diffusion of Y ions through the grain boundaries into GDC electrolyte.

The cross-sectional SEM images of the SYCO cathodes are shown in Fig. 3 with sintering temperatures of (a–b) 1000, (c–d) 1100 and (e–f) 1200 °C. It can be seen from Fig. 3(a), (c) and (e) that the porosity of the SYCO cathode sintered at 1000 °C or 1100 °C for 0.5 h is slightly lower than that of the SYCO cathode sintered at 1200 °C. High porosity can facilitate gas transfer and increase the active reaction sites of cathodes. As shown in Fig. 3(b), (d) and (f), the SYCO grain size increases with the increasing sintering temperature. Fig. 3 (f) shows that the optimal adhesion at the SYCO cathode/GDC electrolyte interface and SYCO surface/gas interface appears after sintering at 1200 °C. These results clearly indicate that both the maximum electrochemical activity reaction region of SYCO cathode and the best adhesion between cathode and electrolyte are obtained when sintered at 1200 °C.

The electrochemical performance was evaluated by EIS. Fig. 4 shows the impedance spectra of the SYCO cathodes with GDC as electrolyte sintered at 1000, 1100, 1200 °C and measured at 700 °C. When the sintering temperatures are 1000, 1100 and 1200 °C, the polarization resistances are 0.59, 0.40 and 0.28 Ω cm^2, respectively. The polarization resistance of SYCO cathode reduces with the increase of sintering temperature. 1200 °C is suggested to be the optimum sintering temperature, consistent with the XRD (Fig. 2) and SEM (Fig. 3) results discussed above. Higher sintering temperature is constructive to better adhesion between cathode and electrolyte, which decreases interfacial polarization resistance of the cathode. Fig. 5 shows the impedance spectra of the SYCO cathode using the SYCO powder calcined at 900 °C for 8 h as initial cathode material with GDC as electrolyte sintered at 1200 °C for 0.5 h and measured at various temperatures from 600 °C to 750 °C. The measured polarization resistances are 3.16, 1.06, 0.28 and 0.14 Ω cm^2 at 600, 650, 700 and 750 °C, respectively. The electrochemical performance achieved here is better than that measured by Li et al. using the same cathode ($Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$) with $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM) as electrolyte [5]. At 700 °C, our measured polarization resistance of SYCO cathode is 0.28 Ω cm^2, which is significantly lower than that of the $Sr_{0.9}Y_{0.1}CoO_{3-\delta}$ cathode (0.40 Ω cm^2) reported by Porras-Vazquez et al. [6]

For comparison, the identical cathode–electrolyte sintering process and EIS measurements have been carried out on the SYCO powder calcined at 1100 °C for 96 h. As shown in Fig. 6, the measured polarization resistances are correspondingly 5.82, 1.83, 0.76 and 0.33 Ω cm^2 at 600, 650, 700 and 750 °C, which are significantly greater than the values obtained by using the SYCO powder calcined at 900 °C for 8 h as the initial cathode material. This result confirms that the SYCO powder calcined at 900 °C for 8 h is a preferable initial material for cathode fabrication.

The Arrhenius plot of R_p for SYCO cathode sintered at 1200 °C for 0.5 h using the SYCO powder calcined at 900 °C for 8 h as the initial cathode material can be seen in Fig. 7. The Arrhenius plot roughly produces a straight line, indicating the temperature dependence of the conductivity ($1/R_p$) follows the Arrhenius-type law within the temperature range of 600–750 °C. The activation energy is 1.65 eV, which is close to the reported values in literature [5,7]. As activation energy is directly related with reaction mechanism, one can plausibly speculate that the cathode prepared in our method shares the same electrochemical reaction mechanism as other cathodes

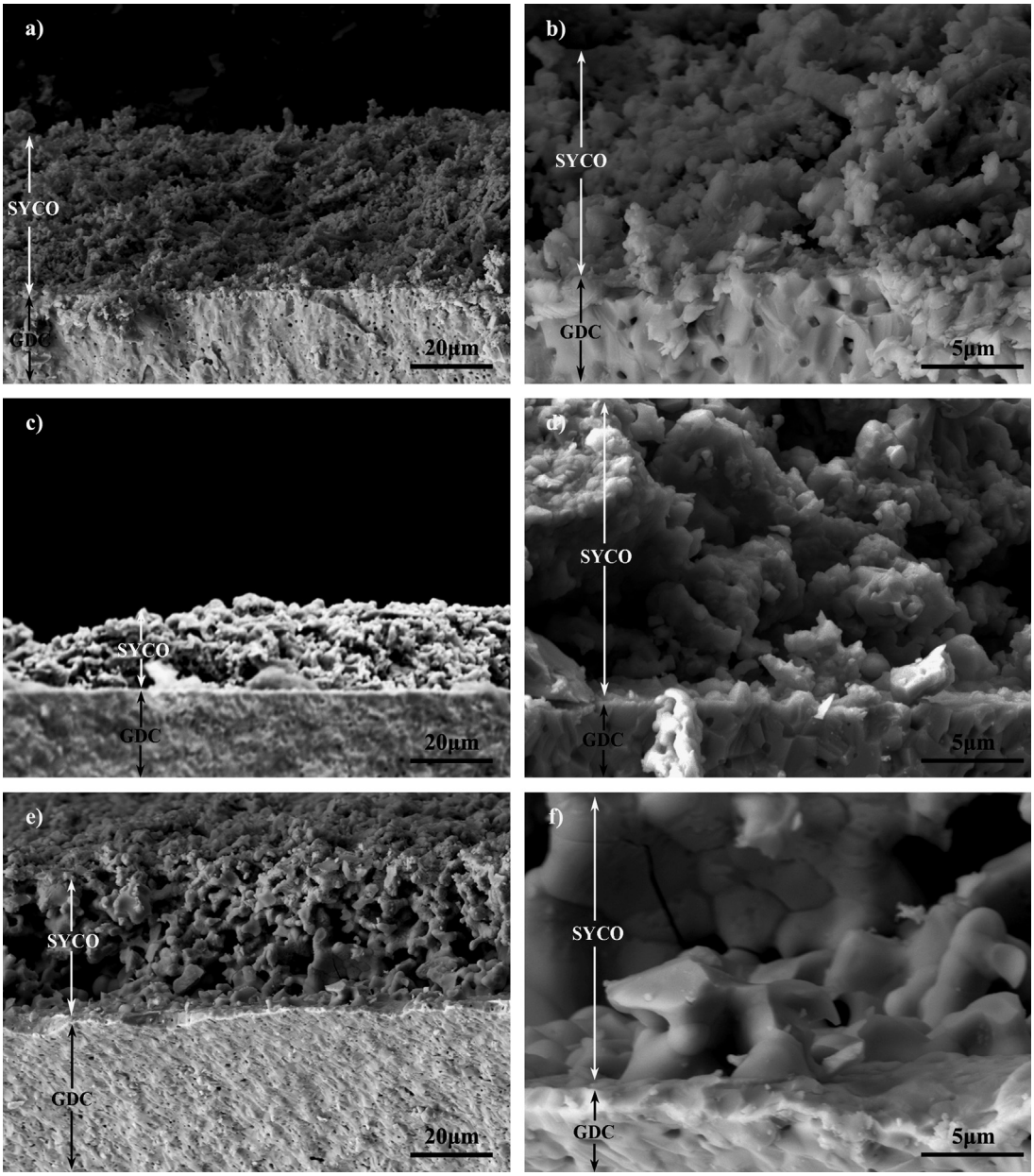

Fig. 3. SEM images of the cross section of SYCO cathodes fabricated at: (a), (b) 1000 °C; (c), (d) 1100 °C; and (e), (f) 1200 °C for 0.5 h.

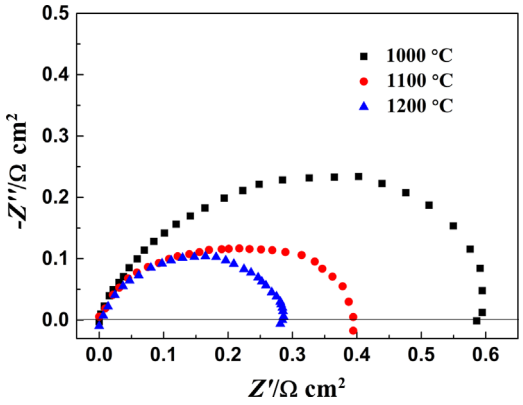

Fig. 4. Impedance spectra of the SYCO cathodes with GDC as electrolyte sintered at 1000, 1100, 1200 °C and measured at 700 °C.

prepared using relatively pure SYCO as pristine electrode material. This result further confirms that the preparation method in the paper is feasible. Slight differences among the activation energy extracted in this work and the reported values [5,7] are possibly caused by the oxygen ionic conductivity of electrolyte, which slightly varies with the electrolytes and has been theoretically related to the interfacial polarization resistance [17,18].

4. Conclusions

Perovskite $Sr_{0.7}Y_{0.3}CoO_{2.65-\delta}$ (SYCO) has been successfully synthesized by a novel sol–gel method. The SYCO powder calcined at 900 °C for only 8 h containing impurities due to incomplete phase formation was adopted as the pristine

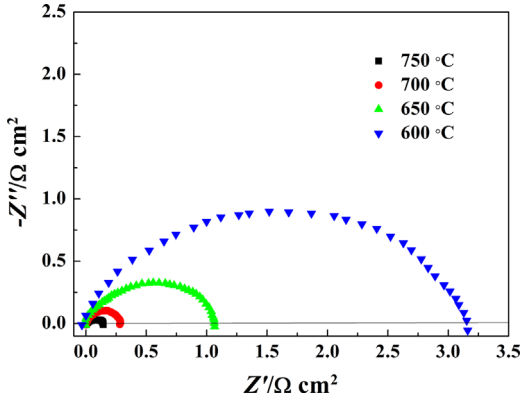

Fig. 5. Impedance spectra of the SYCO cathode using the SYCO powder calcined at 900 °C for 8 h as initial cathode material with GDC as electrolyte sintered at 1200 °C for 0.5 h and measured at various temperatures from 600 °C to 750 °C.

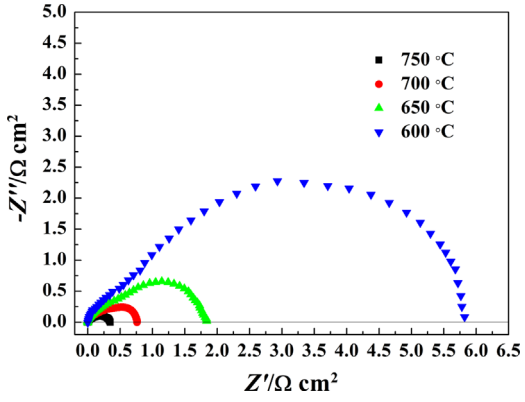

Fig. 6. Impedance spectra of the SYCO cathode using the SYCO powder calcined at 1100 °C for 96 h as initial cathode material with GDC as electrolyte sintered at 1200 °C for 0.5 h and measured at various temperatures from 600 °C to 750 °C.

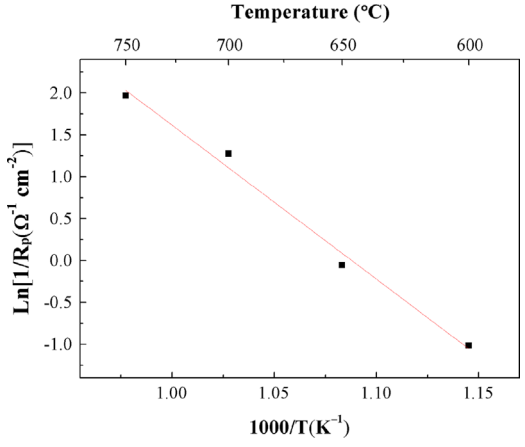

Fig. 7. The Arrhenius plot of R_p for SYCO cathode using the SYCO powder calcined at 900 °C for 8 h as the initial cathode material.

cathode material and sintered onto GDC electrolyte. The phase formation of SYCO is completed in the quick cathode-electrolyte sintering process at 1200 °C for 0.5 h. Good adherence between SYCO cathode and GDC electrolyte was obtained; and the formation of secondary phases was avoided by carefully controlling the sintering temperature and time. The polarization resistance of the as-prepared SYCO cathode can reach 0.28 Ω cm^2 at 700 °C, which stands for a better electrochemical performance than the currently reported results in literature. In contrast with the conventional solid state reaction routes, the method developed in this study is energy saving and effective for electrode preparation for SOFCs.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (51072040) and the National Program on Key Basic Research Project (973 Program 2012CB215400).

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