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Synthesis and investigation on microstructure and electrical conductivity of Ruddlesden-Popper phase, $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC), as cathode material for intermediate temperature solid oxide fuel cells

H. Shirani-Faradonbeh[1], S. Paydar[1], I. Gholaminezad[2], S. Imanlou[1] and M.H. Paydar[1]

[1] Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran.
[2]School of Mechanical Engineering, Shiraz University, Shiraz, Iran.

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Abstract

In the present work, a Ruddlesden-Popper oxide, $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC), has been synthesized by solid state reaction for Intermediate-Temperature Solid Oxide Fuel Cells (IT-SOFCs) applications. To investigate the effect of sintering temperature on the microstructure and electrical properties, the LSNC cathode samples were fired in the temperature range of 1000–1300 °C. The crystal structure and microstructures of the synthesized and fired samples were studied by XRD and SEM, respectively. The electrical conductivity of the monolithic electrodes is investigated experimentally through the four-probe method as a function of temperature in the range of 300 – 800 °C. Our investigation revealed that the LSNC material behaves like semiconductor materials; the conductivity increases by increasing the temperature up to a specific temperature but then decreases with further temperature increases. It has also been proven that an increase in sintering temperature leads to increasing electrical conductivity. The maximum total electrical conductivity of 67.57 S cm^{-1} at 450 °C was recorded for pure LSNC material sintered at 1300 °C.

1. Introduction

Traditional cathode material, $La_xSr_{1-x}MnO_3$ (LSM), does not provide adequate performance for IT-SOFCs applications since it is a strong electronic conductor. The development of novel cathode materials with high electrochemical performance has become a crucial step towards the commercialization of IT-SOFCs [1-3]. In recent years, many perovskite-type, mixed ionic electronic conductors (MIECs) have been in-

*Corresponding author.
E-mail address: Paaydar@shirazu.ac.ir

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vestigated as possible cathodes for IT-SOFCs. Ruddlesden–Popper (R–P) oxides with a general formula of $A_2BO_{4+\delta}$ include a lanthanide or alkali-earth at the A site such as La, Nd, and Pr, and a transition metal cation (Ni, Co, Cu, Fe) at the B site. These oxides have been recently studied as a potential cathode for IT-SOFCs [4-6]. An important feature of these compounds is their oxygen over stoichiometry correlated with the mixed valence of B-site transition metal cation leading to mixed ionic-electronic conduction. Their structure is comprised of ABO_3 perovskite layers alternating with AO rock salt layers. The oxygen excess is caused by the incorporation of additional oxygen ions into the rock salt layers [4, 5, 7]. Mauvy et al. investigated the electrochemical performance of Ln_2NiO_4 (Ln = La, Nd, Pr) and found that the praseodymium nickelate exhibited the lowest cathode ASR value [8]. Furthermore, the oxygen transport and the electrode properties of this system can be easily modulated through A and/or B site substitution. Many studies have indicated that $Ln_{2-x}Sr_xMO_{4+\delta}$ (Ln = La, Nd, Pr, M = Ni, Fe, Cu, Co) oxides are mixed ionic-electronic conducting (MIEC) materials that possess both good electronic conductivity (due to the transition metal mixed valency) and ionic conductivity (due to the oxygen excess). Cheng et al. studied the effect of substitution on the Ni site in $Pr_2NiO_{4+\delta}$, on the performance of the newly synthesized cathode. They showed that $Pr_2Ni_{0.6}Cu_{0.4}O_4$ has the best cell performance in the Cu substituted $Pr_2NiO_{4+\delta}$ systems. They explained that improvement in the performance of the new cathode is related to stabilizing the high-temperature interstitial oxygen disordered tetragonal structure caused by the doping of $Pr_2NiO_{4+\delta}$ by Cu [5, 7].

In the present work, La and Sr were substituted on the A sites while Ni and Cu were substituted on the B sites in the ABO_3 perovskite structure to form a $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC) compound for application as a cathode with enhanced electrochemical performance and stability under IT-SOFCs operating conditions. In this study, the $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC) oxide was synthesized via the solid state method, and its microstructure and electrical conductivity were investigated.

2. Experimental

The original $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC) powder was synthesized using a solid state reaction route from high-purity starting chemicals, including La_2O_3, $SrCO_3$, NiO, and CuO (99.9% Inframat® Advanced Materials$^{tM)}$ with exactly stoichiometric molar ratios. These powders were mixed by an attrition mill in ethanol media for 5 hours. The resulting precursor solution was evaporated at 150 °C for 2 h. Subsequently, the powder was calcined in air at 1100 °C for 10 h to obtain the final phase of LSNC. The final powders were obtained after a 1 h milling process. Cathodes for the electrical conductivity measurements were prepared in a rectangular shape with 20 mm× 5 mm× 5 mm dimensions by dry uniaxially pressing under 200 MPa pressure. The shaped samples were sintered in the temperature range of 1100-1300 °C for 5 h in air.

The reaction products were characterized by X-ray diffraction (XRD) for the identification and purity of phase. The microstructure of the cathode powder and cross-section of the cathode samples were analyzed by Scanning Electron Microscopy (SEM). The electrical conductivity of the LSNC samples was measured by the standard four-probe DC method in an air atmosphere via a Solarton Analyatical 1287 potentiostate/galvanostate in the temperature range of 300-800 °C. The four-probe method used for measuring the electrical conductivity of the samples is schematically described in Fig. 1.

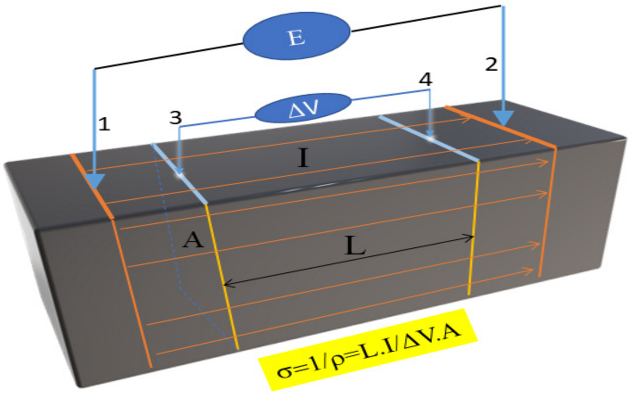

Fig. 1. Schematic of the electrical conductivity measurement by the four-probe method.

As it can be seen in Fig. 1, two probes (1 and 2) were used to apply the electrical field and measure the passed current, and two other probes (3 and 4) were used to measure the created voltage difference (ΔV). Resistance of the sample was measured by dividing ΔV by I, which was used to determine the conductivity of the samples using the following equation:

$$\sigma = 1/\rho = L.\ I\ /\ \Delta V\ .\ A \qquad (1)$$

3. Results and discussion

Fig. 2 shows XRD patterns of the synthesized $La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC) compound. It is clear that the LSNC powder shows an A_2BO_4 structure and no obvious impurity is observed. The typical XRD patterns agree well with the Ruddlesden-Popper oxide reported in the literature [9, 10].

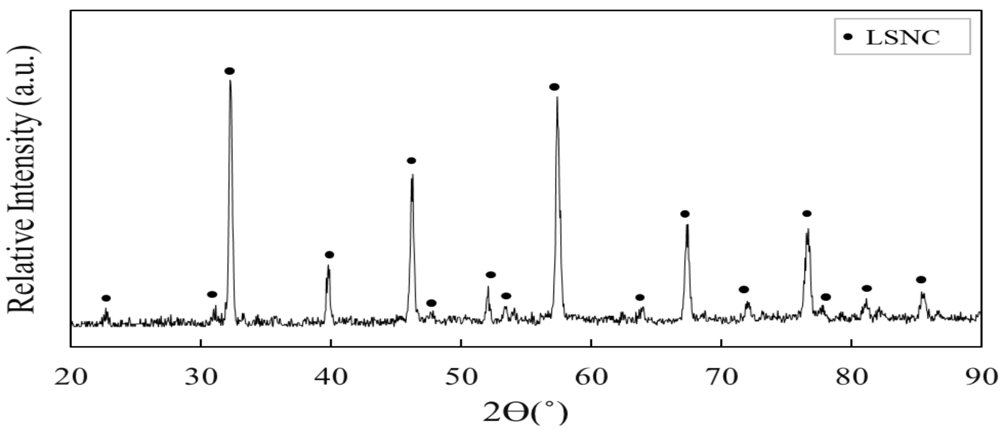

Fig. 2. X-ray diffraction pattern of LSNC calcined at 1100°C for 10h.

The particle size and shape of the LSNC synthesized powder was evaluated by SEM. Fig. 3 shows the SEM micrographs of the LSNC powder after calcination and 1-hour milling. As can be seen, LSNC powder particles appeared the most anisometric, highly polydispersed, nearly agglomerated, where the smallest particle size is around 1 μm.

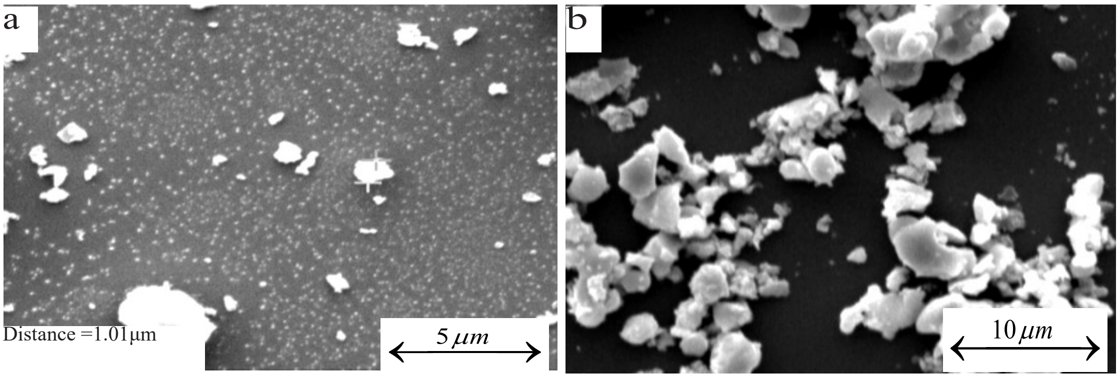

Fig. 3 SEM images of the LSNC powder.

Fig. 4 shows the electrical conductivity of LSNC cathodes sintered at different temperatures in the range of 1000 – 1300 °C as a function of testing temperature.

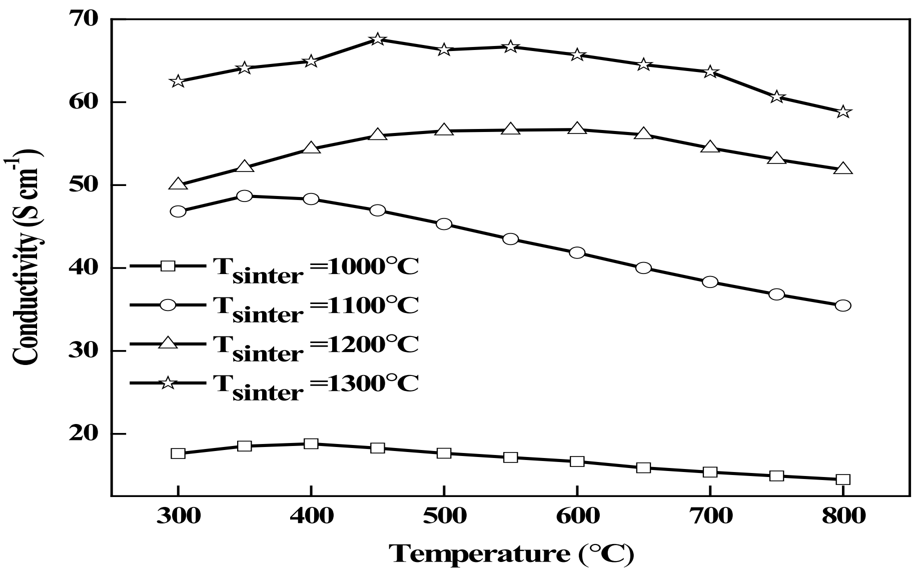

Fig. 4. Electrical conductivity of LSNC sintered at different temperatures versus temperature in air.

For each sintering temperature used, the electrical conductivity increases to a maximum distinctive temperature value in the range of 350–500 °C and then decreases decreased as the temperature increases, as it is shown in Fig. 4. In addition, the overall trend is an increase in the electrical conductivity when the sintering temperature increases in the range of 1000-1300 °C. The maximum electrical conductivity value of 67.57 S cm^{-1} at 450 °C was obtained for the sample sintered at 1300 °C. Regarding the data presented in this figure, it is clear that increasing the sintering temperature and decreasing the reminding porosities not only does the maximum conductivity increase, but the temperature at which the maximum conductivity was recorded also increases. The electrical conductivity behavior undergoes a change from semiconductor-like to metal-like. Below this characteristic temperature (the temperature at which conductivity reaches its maximum value), the electrical conduction behavior and the electrical conductivity of LSNC can be described by a thermal activate polaron hopping mechanism, following eq. (2):

$$\sigma = \left(\frac{A}{T}\right)\exp\left(\frac{-Ea}{KT}\right) \quad (2)$$

where the pre-exponential factor A is a material constant, which depends on the site fraction of carriers and the probability of neighboring ions available to participate in the hopping process, Ea is the hopping activation energy, K is the Boltzmann's constant, and T is the absolute temperature. However, in the testing temperature range (500-800 °C), a decrease in electrical conductivity for all compositions is displayed when the testing temperature increases, which implies a pseudo-metallic behavior. This can be mainly ascribed to oxygen losses on heating, implying a reduction of charge carrier (hole) concentration. Fig. 5 shows the effect of sintering temperature on the amount of reminding porosities in the microstructure of LSNC samples observed by SEM.

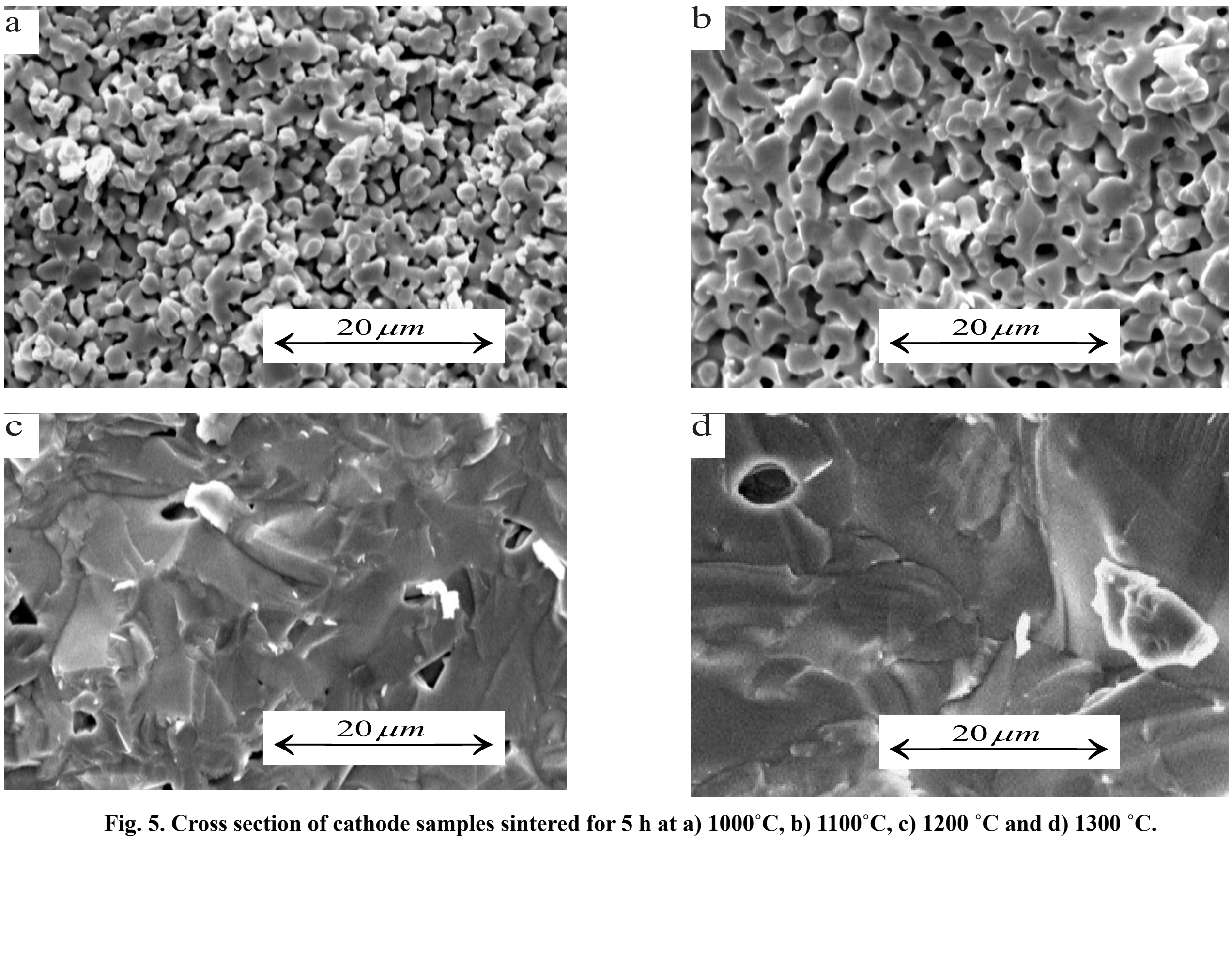

Fig. 5. Cross section of cathode samples sintered for 5 h at a) 1000˚C, b) 1100˚C, c) 1200 ˚C and d) 1300 ˚C.

As can be seen, increases in sintering temperature lead to significant decreases in the porosities of the samples. The sample sintered at 1000 and 1100 °C showed poor contact between the particles. For the cathode sintered at 1300 °C, nearly all porosities were removed, and it had full density. Sintering at a temperature lower than 1300 °C leads to some porosities remaining in the microstructure that in turn cause a decrease in electrical conductivity.

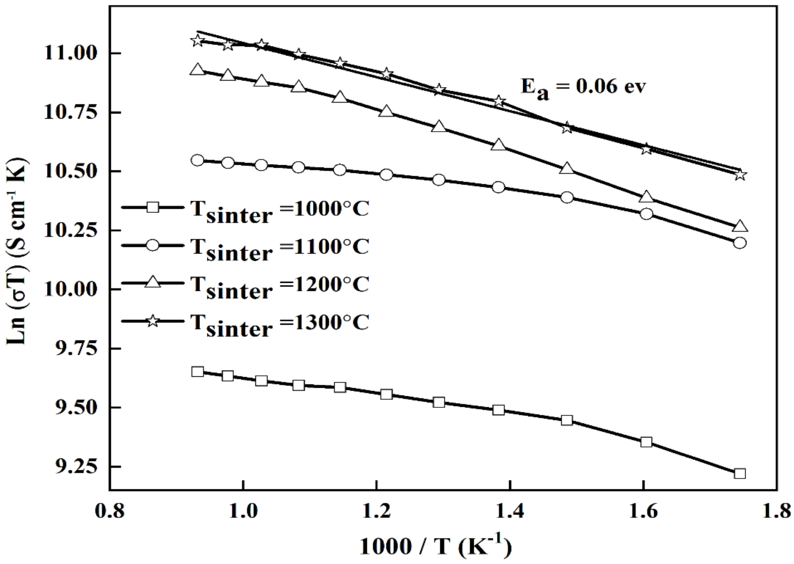

Fig. 6. Arrhenius plot of LSNCconductivity versus temperature.

The Arrhenius plots of the electrical conductivity (ln σT versus 1/T) for LSNC samples sintered at different temperatures within a range of 1000–1300 °C in the air are shown in Fig. 6. In all samples, the Arrhenius plots are linear at low temperatures, showing a semi-conducting behavior, and the electrical conductivity increases with temperature, demonstrating good conductive behavior followed by a small polaron conduction mechanism due to the hole type conduction of Cu^{2+} ions [11, 12]. The activation energy (Ea) obtained from the slope of the Arrhenius plots confirmed the small polaron mechanism of conduction. The activation energy of LSNC sintered at 1300°C is 0.06 eV in the temperature range of 300–800 °C, which is remarkably smaller than that of $La_2NiMnO_{6-\delta}$ (0.22 eV) and $La_{1.85}Ca_{0.15}(Cu_{0.7}Ni_{0.3})O_{4-\delta}$ (0.3176 eV) [9, 13]. The low value of activation energy is beneficial for enhancing electron hopping, which increases the electrical conductivity and electrochemical activity [11].

4. Conclusions

$La_{1.9}Sr_{0.1}Ni_{0.7}Cu_{0.3}O_4$ (LSNC) has been synthesized and characterized. The electrical conductivity of LSNC pure phase sintered at different temperatures was investigated in the air in the temperature range of 300–800 °C. It has been shown that the conductivity of the LSNC is related to the sintering temperature, so applying higher sintering temperature t decreases the remained porosities and also increases the conductivity. A maximum total electrical conductivity of 67.57 S

cm^{-1} was obtained for the pure LSNC sample sintered at 1300 °C in air at 450 °C. Furthermore, it was shown that the LSNC material behaved nearly the same as a semiconductor; so, the electrical conductivity increases by increasing temperature up to a specific point, after which the conductivity decreases with further temperature increases. Regarding the calculated activation energy, it has been concluded that the electrical conduction in LSNC material can be described well by a thermal activate polaron hopping mechanism.

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