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Electrochemical Properties of $La_4Ni_3O_{10}$-GDC Composite Cathode by Facile Sol-gel Method for IT-SOFCs

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ABSTRACT

Among the Ruddlesden-Popper series, $La_4Ni_3O_{10}$ has received widespread attention as a promising cathode material by reason of its favorable properties for realizing high performance of intermediate temperature solid oxide fuel cells (IT-SOFCs). The $La_4Ni_3O_{10}$ cathode is prepared using the facile sol-gel method by employing tri-blockcopolymer (F127) to obtain a single phase in a short sintering time. There are no reactions between the $La_4Ni_3O_{10}$ cathode and the $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) electrolyte upon sintering at 1000°C, indicating that the $La_4Ni_3O_{10}$ cathode has good chemical compatibility with the GDC electrolyte. The maximum electrical conductivity of $La_4Ni_3O_{10}$ reaches approximately 240 S cm^{-1} at 100°C and gradually decreases with increasing temperaturein air atmosphere. The area specific resistance value of $La_4Ni_3O_{10}$ composite with 40 wt% GDC is 0.435 Ω cm^2 at 700°C. These data allow us to propose that the $La_4Ni_3O_{10}$-GDC composite cathode is a good candidate for IT-SOFC applications.

Key words : Solid oxide fuel cell, Cathode, Ruddlesden-Popper, Tri-blockcopolymer (F127)

1. Introduction

Solid oxide fuel cells (SOFCs) are widely viewed as a promising source of power generation with very high efficiency, high power density, low emissions, and excellent fuel flexibility at high operating temperatures (>1000°C).[1-4] Even with the many benefits of SOFC technology, the necessary high operating temperature results in a number of problems such as high cost, electrode sintering, interface reactions between cell components, and material compatibility challenges. In this regard, many studies have been devoted to the development of intermediate-temperature (600-800°C) SOFCs (IT-SOFCs) as away to reduce fabrication costs, improve long-term performance, and extend the range of applicable cell materials. However, there are major problems in the practical use of IT-SOFCs, including poor oxide-ion conductivity and the inadequate catalytic activity of conventional cathodes due to reduced operating temperature.[5-8] Therefore, the development of a new cathode material could be a key step toward the commercialization of IT-SOFCs.

In this respect, mixed oxide-ion and electronic conducting (MIEC) oxides, containing Mn, Fe, Co, and/or Ni with perovskite structures, have been studied extensively as alternative cathode materials.[9-11] Among the various MIEC oxides, cobalt containing oxides have attracted strong interest owing to their high electrocatalytic activity for the oxygen reduction reaction (ORR). In spite of their excellent properties, cobalt-containing oxides exhibit high thermal expansion coefficients (TECs) and easy evaporation of cobalt (Co).[12,13]

Alternatively, Co-free La_2NiO_4 has received significant attention as a mixed conductor material derived from K_2NiF_4-type materials for IT-SOFC cathodes by reason of its important advantages including relatively high oxygen ionic conductivity, attractive electronic conductivity, moderate TECs, and high electrocatalytic activity under oxidizing conditions.[14-16] La_2NiO_4 is the first member of the Ruddlesden-Popper homologous series; materials in this series have a general formula $La_{n+1}Ni_nO_{3n+1}$, where n represents the number of perovskite layers in a formula unit. The Ruddlesden-Popper structure can described as having alternating perovskite layers $(LaNiO_3)_n$ and rock-salt layers (LaO) along the crystallographic c direction, as shown Fig. 1. The number of perovskite layers increases with increasing n in this structure, leading to the formation of the higher order Ruddlesden-Popper phases, $La_3Ni_2O_7$ and $La_4Ni_3O_{10}$, which show faster ionic and electronic transport properties.[17-20] These effects are primarily related with the increasing concentration of Ni-O-Ni bonds, which are responsible for electronic conduction, progressive delocalization of p-type electronic charge carriers, and increasing vacancy-migration contribution to oxygen ion diffusivity.

Recently, Amow *et al.* performed impedance spectroscopy analyses of $La_{n+1}Ni_nO_{3n+1}$(n = 1, 2, and 3) symmetrical cells on $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$(LSGM) electrolyte; they found that the area specific resistance (ASR) decreases with increasing n, which was attributed to increasing electrical conductivity.[17] Furthermore, our group carried out the

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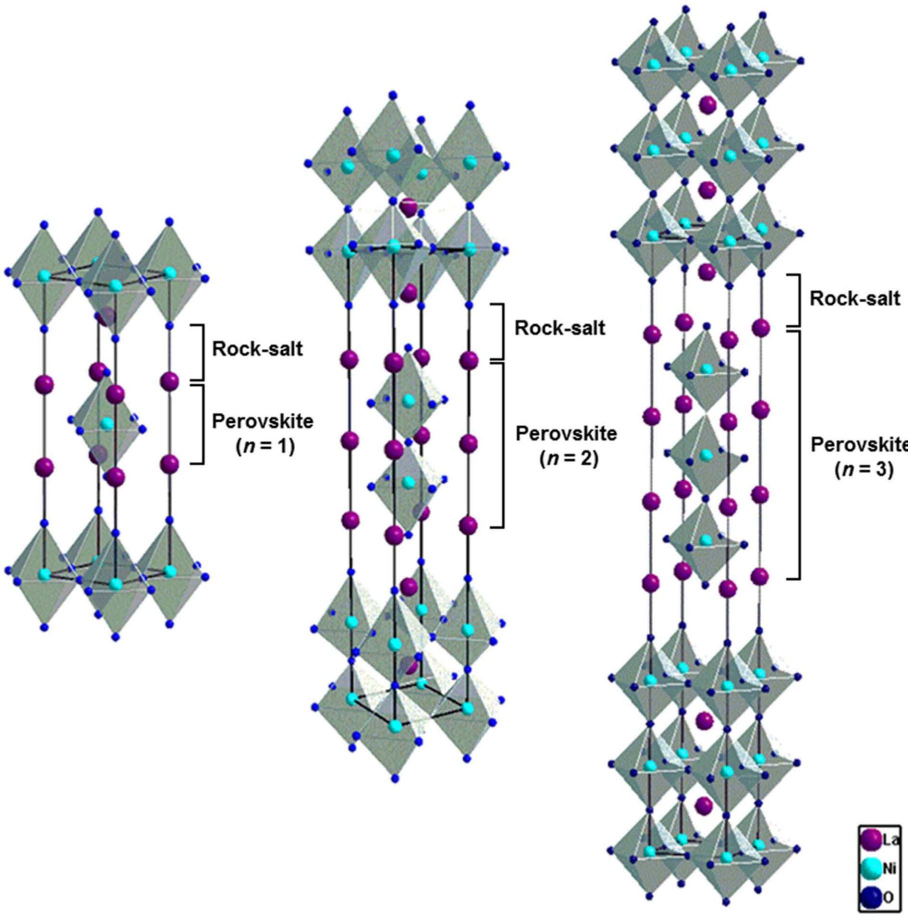

Fig. 1. The crystal structure of $La_{n+1}Ni_nO_{3n+1}$ (n = 1, 2, and 3).

preparation of $La_{n+1}Ni_nO_{3n+1}$(n = 1, 2, and 3)-YSZ composite using the infiltration method.[20] The electrical conductivity and electrochemical performance were enhanced with increasing n, which is the electronic conducting perovskite layer. As a consequence, $La_4Ni_3O_{10}$ is the most favorable cathode material for IT-SOFC applications.

To achieve a single phase of $La_4Ni_3O_{10}$, many groups have recently employed various synthesis methods such as the Pechini method, solid state reaction, and the hydrothermal method. However, using those methods, the preparation of $La_4Ni_3O_{10}$ requires multiple processes and long sintering time. For example, $La_4Ni_3O_{10}$ was synthesized by the Amow group using the Pechini method, which required sintering at 1050°C for 6 days with one intermittent regrinding step.[17] Furthermore, Zhang *et al*. prepared $La_4Ni_3O_{10}$ by calcination at 1100°C for 4 ~ 5 days in air, also with several grinding processes.[18]

With the aim of reducing the time for material synthesis, we present a facile method for the synthesis of pure phase $La_4Ni_3O_{10}$ oxide obtained by employing tri-blockcopolymer (F127) as a chelating agent. Tri-blockcopolymer (F127) is a poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide); it is used as a structure-directing agent in the synthesis of ordered mesoporous materials based on the PEO-metal complexation.[21] This paper focuses on the synthesis of pure phased $La_4Ni_3O_{10}$ using the sol-gel method; in terms of future application of this material as an IT-SOFC cathode material, we focus on the structural characteristics, electrical properties, and electrochemical performances of pure phased $La_4Ni_3O_{10}$ based on a $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) electrolyte .

2. Experimental Procedure

$La_4Ni_3O_{10}$ powder was synthesized using the sol-gel process with stoichiometric amounts of $La(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99.9%), $Ni(NO_3)_2{\cdot}6H_2O$(Aldrich), and F127 (Aldrich). F127 was dissolved in distilled water and nitrate salts were added. The homogeneous sol was dried in a dry oven at 100°C to form a gel. After drying, the gel was heated to 300°C; then, the primary powder was formed via a combustion reaction. This powder was ball-milled in acetone for 24 h and then sintered at 1100°C for 12 h in air to form a single phase. For measurement of the cell performances of $La_4Ni_3O_{10}$ powder, slurries consisting of powders, GDC, and an organic binder (Heraeus V006) were used at a weight ratio of 6 : 4 : 12.

The phase identification of $La_4Ni_3O_{10}$ was confirmed by X-ray powder diffraction (XRD) (Rigaku-diffractometer, Cu Ka radiation) with a scanning rate of 0.5° min^{-1} in the 2θ range of 20 to 80°. The microstructures of the interface between the GDC electrolyte and the $La_4Ni_3O_{10}$ cathode were examined using a field emission scanning electron microscope (FE-SEM) (Nova SEM). The electrical conductivity of the $La_4Ni_3O_{10}$ cathode was evaluated using a four-terminal DC arrangement; a potentiostat (BioLogic) was used to measure the current and voltage at intervals of 50°C at temperatures ranging from 100 to 750°C.

Electrochemical impedance spectroscopy of the $La_4Ni_3O_{10}$ cathode was performed using a symmetrical cell. The GDC electrolyte powders were pressed into pellets and then sintered at 1350°C for 4 h in air to obtain a dense electrolyte substrate. The slurry composed of $La_4Ni_3O_{10}$-GDC powder was screen-printed onto both sides of the GDC electrolytes to form symmetrical half-cells; this was followed by calcination at 1000°C for 4 h. A silver paste was used as a current collector for the electrodes. Impedance spectra were recorded under open circuit voltage (OCV) in a frequency range of 1 mHz to 500 kHz with AC perturbation of 14 mV from 600 to 750°C.

3. Results and Discussion

Figure 2 shows the XRD pattern of the $La_4Ni_3O_{10}$ cathode synthesized via the sol-gel process after heat treatment at 1100°C for 12 h in air. The pattern reveals a single-phase material exhibiting an orthorhombic structure without any impurity phase, as has been identified in other studies. It was also necessary to investigate the chemical compatibility between the $La_4Ni_3O_{10}$ cathode and the GDC electrolyte because the phase reaction between the electrode and the electrolyte can cause the formation of an undesired insulating layer at the interface, which would block oxide-ionicand electronic transport.[22] The chemical reactivity of the $La_4Ni_3O_{10}$-GDC composite was confirmed after sintering at 1000°C for 4 h by mixing the corresponding powders at a weight ratio of 6 : 4. As indicated in Fig. 3, there are no obvious reactions between $La_4Ni_3O_{10}$ and GDC upon sintering at 1000°C; the patterns indicate that the $La_4Ni_3O_{10}$ cathode has good chemical compatibility with the GDC electrolyte.

A cross-sectional SEM image of the $La_4Ni_3O_{10}$-GDC composite cathode is provided in Fig. 4. The bottom image represents the microstructure of the dense GDC electrolyte; the upper image represents the microstructure of the porous cathode $La_4Ni_3O_{10}$-GDC composite after sintered at 1000°C. The dense GDC electrolyte adheres very well to the porous composite cathode layer, without cracks, indicating the good compatibility between the electrolyte and the electrode. The thicknesses of the electrolyte and the cathode layer are approximately 800 and 20 μm, respectively.

Figure 5 shows the temperature dependence of the electrical conductivity of $La_4Ni_3O_{10}$ in air. The maximum electrical

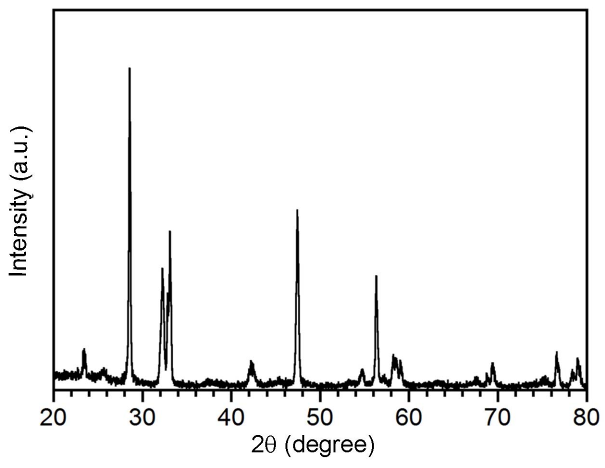

Fig. 2. X-ray diffraction pattern for $La_4Ni_3O_{10}$ powder after heat treatment at 1100°C for 12 h in air.

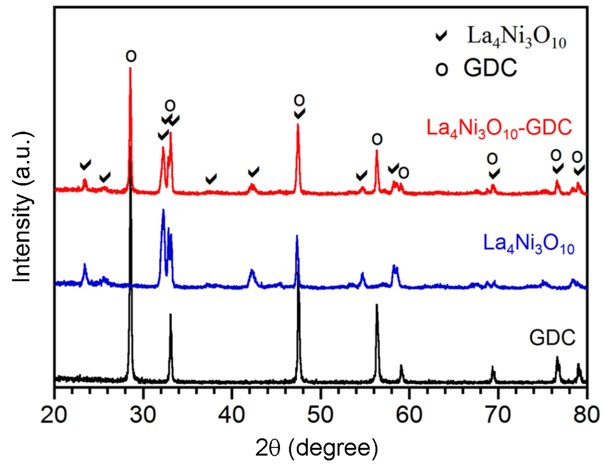

Fig. 3. X-ray diffraction pattern of $La_4Ni_3O_{10}$ and GDC mixture sintered at 1000°C for 4 h in air.

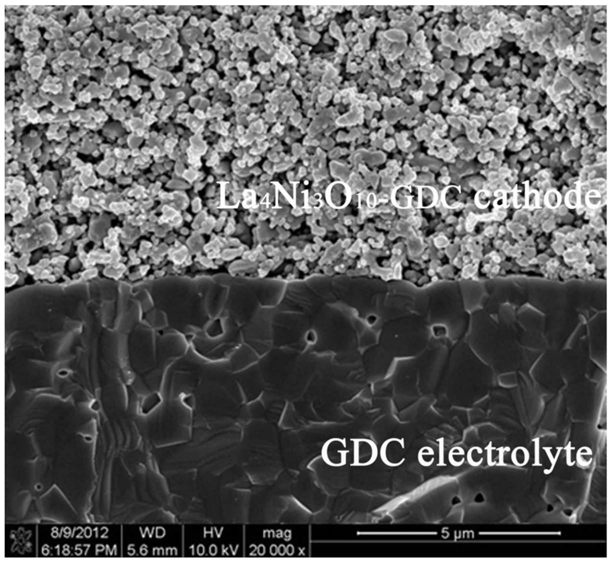

Fig. 4. Cross-sectional SEM image of $La_4Ni_3O_{10}$-GDC cathode and GDC electrolyte interface.

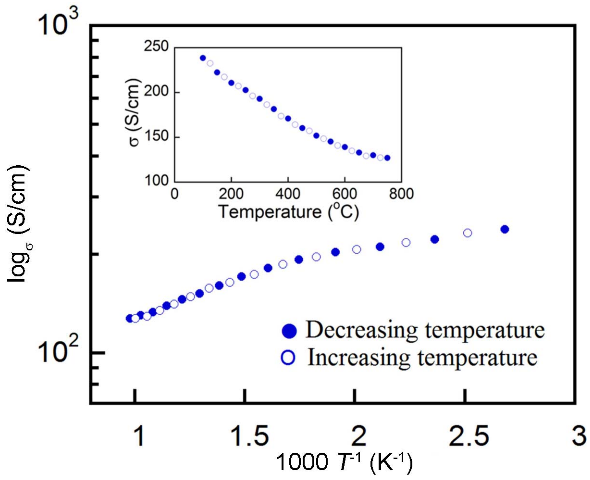

Fig. 5. The electrical conductivity of $La_4Ni_3O_{10}$ in air as a function of temperature, open and closed symbols correspond to measurements on heating and cooling.

conductivity of $La_4Ni_3O_{10}$ reaches approximately 240 S cm^{-1} at 100°C and gradually decreases with increasing temperature, exhibiting metallic conduction behavior over the whole temperature range. For an SOFC cathode material, the electrical conductivity should be higher than 100 S cm^{-1} at the operating temperature.[23)] The lowest electrical conductivity of $La_4Ni_3O_{10}$ at 750°C is about 130 S cm^{-1}, which is adequate for the sample to be employed as a cathode in IT-SOFCs.

The electrocatalytic activity for the oxygen reduction reaction of a cathode can be obtained by performing electrochemical impedance spectroscopy (EIS) measurement on $La_4Ni_3O_{10}$-GDC/GDC/$La_4Ni_3O_{10}$-GDC symmetrical cell. The cathodic polarization resistance, normalized by the geometric electrode area, that is, the area specific resistance (ASR), can be calculated from the impedance spectra acquired under open circuit conditions. When the electronic conduction in the electrolyte is negligible, the cathodic polarization resistance can be adequately approximated using the diameter of the impedance loop or the difference between the high-frequency and low-frequency intercepts at the real axis, as presented in Fig. 6(a). The ASR values of the $La_4Ni_3O_{10}$-GDC composite based on the GDC electrolyte are 0.207, 0.435, 1.066, and 2.432 Ω cm^2 at 750, 700, 650, and 600°C, respectively. These values are comparable to those reported for other conventional SOFC cathode materials, such as the value of 0.75 Ω cm^2 at 700°C for an $La_{0.8}Sr_{0.2}MnO_3$-GDC composite based on GDC electrolyte.[24)]

The impedance spectra are fitted well to the equivalent circuit, as can be seen in the inset of Fig. 6(a) and as is summarized in Table 1. In the equivalent circuit, L is the inductance induced by the cables. The real axis value at the high frequency intercepts, R_1, mainly correspond to the electrolyte and wire resistances. In the Nyquist plots, high-frequency arcs are equivalent to R_2, which is caused by charge transfer during the migration and diffusion of oxygen ions

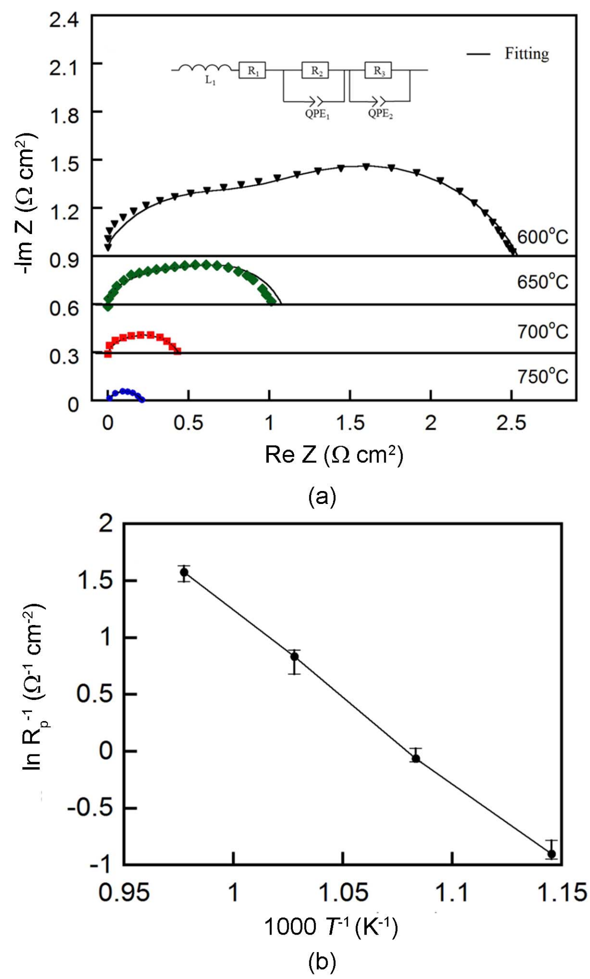

Fig. 6. (a) Impedance spectra and fitted Ny quist plots of $La_4Ni_3O_{10}$-GDC cathode on GDC electrolyte in symmetrical cell measured under OCV condition. (b) Arrhenius plot of the polarization resistance of $La_4Ni_3O_{10}$-GDC cathode.

Table 1. Fitting Result of $La_4Ni_3O_{10}$-GDC Composite with Different Temperatures

T (°C)	750	700	650	600
L (H)	2.51×10^{-7}	2.45×10^{-7}	1.98×10^{-7}	1.66×10^{-7}
R_1(Ω cm^2)	1.273	1.696	2.251	3.320
R_2 (Ω cm^2)	0.242	0.337	0.612	1.114
R_3 (Ω cm^2)	0.008	0.123	0.538	1.540

from the TPB to the electrolyte lattice. Meanwhile, low-frequency arcs correspond to R_3, which is associated with the adsorption/desorption of molecular oxygen and the diffusion of bulk or surface oxygen.[25)] From the data, R_3 can be seen to be the more prevailing factor than R_2 with decreasing temperature. Consequently, R_3 can be regarded as a rate determining step in the $La_4Ni_3O_{10}$-GDC composite system.

The temperature dependence of ASR onthe $La_4Ni_3O_{10}$-GDC composite is illustrated by the Arrhenius plot shown in Fig. 6(b). The apparent activation energy (Ea) of the

$La_4Ni_3O_{10}$-GDC was calculated and found to be 123 kJ mol^{-1}, which is close to that of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ cathode (116 kJ mol^{-1}) on samarium doped ceria electrolyte, as reported by Shao *et al.*[5] It is obvious that the $La_4Ni_3O_{10}$-GDC cathode has high activity for the oxygen reduction reaction. Therefore, the $La_4Ni_3O_{10}$-GDC composite derived using the facile sol-gel method by employing tri-blockcopolymer (F127) can be considered acceptable as an IT-SOFC.

4. Conclusions

$La_4Ni_3O_{10}$ is chosen as a base material by reason of its favorable properties for realizing high performance of intermediate temperature solid oxide fuel cells (IT-SOFCs). In order to reduce the time required to synthesize the $La_4Ni_3O_{10}$ cathode, the facile sol-gel method is employed using tri-blockcopolymer (F127). A single phase of $La_4Ni_3O_{10}$ is obtained after heat treatment at 1100°C for 12 h in air. There are no reactions between $La_4Ni_3O_{10}$ and GDC upon sintering at 1000°C, indicating that the $La_4Ni_3O_{10}$ cathode has good chemical compatibility with the GDC electrolyte. The maximum electrical conductivity of $La_4Ni_3O_{10}$ reaches approximately 240 S cm^{-1} at 100°C and gradually decreases with increasing temperature in air atmosphere. The area specific resistance value of the $La_4Ni_3O_{10}$ composite with 40 wt% GDC is 0.435 Ω cm^2 at 700°C. These data allow us to propose that the $La_4Ni_3O_{10}$-GDC composite based on GDC electrolyte, considering its electrical properties and electrochemical performance, is a preferable candidate cathode material in IT-SOFC applications.

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