Synthesis and Physical Properties of La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ Ruddlesden-Popper Phase

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Abstract

A series of La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ ($x = 0, 0.1, 0.3, 0.5$ and $1$) synthesized by a gel combustion method have been investigated as a potential cathode material for IT-SOFC. La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7+\delta}$ shows a lower TEC value and higher electrical conductivity than La$_3$Ni$_2$O$_{7+\delta}$. The further addition of strontium leads to the formation of the $n = 1$ RP phase and the second phase of NiO, resulting in lower electrical conductivity than La$_3$Ni$_2$O$_{7+\delta}$ phase. The electrical conductivity at 600°C of La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ ($x = 0, 0.1, 0.3, 0.5$ and $1$) is $63, 81, 25, 20$ and $57$ S.cm$^{-1}$ respectively.

Key words : Cathode, Ruddlesden-popper

Introduction

In recent years there has been considerable interest in the An+1BnO$_{3n+1}$ oxides due to their excellent properties such as high $T_c$ superconductivity, colossal magnetoresistance, high catalytic activity and high oxide ion conductivity.$^{(6)}$ An+1BnO$_{3n+1}$ belong to Ruddlesden-Popper (RP) structure, (Greenblatt, 1997) A is usually an alkaline earth or rare earth metal ion; B is a transition metal; and $n = 1, 2, 3, \infty$. The structure of the RP phases consists of $n$ consecutive perovskite layer (ABO$_3$) alternating with a rock salt layer (AO) along the crystallographic c direction. The physical properties of the RP phases are governed primarily by the $n$ width of perovskite block, the nature of the A ion, the B-O bond distance, and the oxygen content.

La$_{n+1}$Ni$_n$O$_{3n+1}$ has been widely investigated as a possible intermediate temperature cathode material because of high mixed ionic and electronic conductivity.$^{(11, 14)}$ The crystal structure of La$_{n+1}$Ni$_n$O$_{3n+1}$ has been studied by many groups.$^{(13, 10)}$ The structure at room temperature of $n = 1$ is tetragonal while $n = 2$ and 3 are orthorhombic. The semiconductor behavior appears for $n = 1$ and 2 metal for $n = 3$. $^{(6)}$ In general, the oxidation state of nickel ions in La$_{n+1}$Ni$_n$O$_{3n+1}$ ($n = 1, 2$ and $3$) are either +2 and +3. Their electrical conductivity increases as $n$ and Ni$^{3+}$ content increase resulting from the preparation methods.$^{(3, 9)}$

Karton, et al. (1999) studied on La$_2$Ni$_{1-x}$Fe$_x$O$_{4+\delta}$ ($x = 0.02$ and $0.10$) and La$_2$Ni$_{0.88}$Fe$_{0.02}$Cu$_{0.10}$O$_{4+\delta}$. The electrical conductivity of these compositions increased with the substitution of iron, and slightly decreased with copper substitution. For La$_{2-x}$A$_x$Ni$_4$O$_4$ (A = Ca, Sr and Ba) investigated by Tang, et al. (2000), the solubility limit was reported to be $0 \leq x \leq 0.6$ for Ca, $0 \leq x \leq 1.5$ for Sr and $0 \leq x \leq 1.1$ for Ba. Both La$_{2-x}$Ca$_x$Ni$_4$O$_4$ and La$_{2-x}$Ba$_x$Ni$_4$O$_4$ compositions exhibited semiconducting behavior for all values of $x$. While the La$_{2-x}$Sr$_x$Ni$_4$O$_4$ compositions for $x < 0.6$ were semiconductor from room temperature up to 527°C. On the other hand, the composition with $x > 0.6$ showed a transition temperature from semiconductor to metal, in which it decreased as $x$ increased. However, with $x > 1.3$, this temperature determined from room temperature up to 527°C was not detected.

For $n = 2$ RP, the substitution of lanthanum by calcium on La$_{3-x}$Ca$_x$Ni$_2$O$_{7+\delta}$ was reported by Nedilko, et al. (2004). A single phase has been obtained in the compositions for $0 \leq x \leq 0.8$. In addition, Ca dopant reduced the mean oxidation state of nickel ion from 2.63 ($x = 0$) to 2.15 ($x = 0.8$). Mogni, et al. (2006) reported that the electrical
conductivity of the La$_{0.3}$Sr$_{2.7}$FeNiO$_{7-\delta}$ sample is higher than that of the La$_{0.3}$Sr$_{2.7}$Fe$_2$O$_{7-\delta}$ phase.

The electrical conductivity of cobalt doped on Ni-site of La$_{4}$Ni$_{3-x}$Co$_x$O$_{10+\delta}$(0.0 $\leq$ x $\leq$ 3.0) was observed by Amow, et al. (2006). The overall conductivity decreased as x increased up to x = 2.0. Conversely, it increased with the higher amount of Co, x > 2.0.

Many studies on La$_{3}$Ni$_2$O$_{7+\delta}$ phase have concentrated on the magnetic and electrical properties below room temperature. However, only a few works have investigated on the electrical property of La$_{3}$Ni$_2$O$_{7+\delta}$ at high temperature and the effect of the dopant on La site. The aim of this work is to investigate the effects of strontium on the phase, microstructure, thermal expansion and electrical conductivity of La$_{3-x}$Sr$_x$Ni$_{2}$O$_{7+\delta}$.

Materials and Experimental Procedures

The compositions of La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ (x = 0, 0.1, 0.3, 0.5 and 1) were prepared by gel combustion method. Stoichiometric amounts of La(NO$_3$)$_3$.6H$_2$O, Sr(NO$_3$)$_2$ and Ni(NO$_3$)$_2$.6H$_2$O (> 99%) were dissolved in minimal amount of deionized water. After mixing with a magnetic stirrer, aqueous solution of citric acid (1.5 mol of citric acid per 1 mol of total cations) was added to the mixture. The clear green mixed solution was heated on a hot plate until turned into a green gel. The gel slowly foamed, swelled and finally burnt to obtain dark residue. After grinding the residue powders were calcined in air and held at the reaction temperatures determined from STA (TA Instruments SDT2960) with a final temperature at 1100°C for 6 hrs.

The room temperature phases of calcined powder were analyzed by X-ray diffraction (XRD, Bruker D5005) before pressed into pellets and bars with a cold isostatic press (CIP, Kobelco Dr CIP) under a pressure of 200 MPa and sintered in air at 1100°C for 3 hrs.

The microstructure of the sintered pellets was characterized by scanning electron microscope (SEM, Jeol JSM-6400).

Thermal expansion coefficient of sintered bars was measured using a dilatometer (NETZSCH DIL 402EP) from 50°C to 1000°C with a heating rate of 3°C/min.

The data of electrical conductivity measured in air by a four-probe DC method were collected from 50°C to 800°C with a heating rate of 4°C/min.

Results and Discussion

X-ray diffraction patterns of the calcined La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ (x = 0, 0.1, 0.3, 0.5 and 1) powders are shown in Figure 1. The result of XRD pattern of La$_{3}$Ni$_2$O$_{7+\delta}$ powder shows a single phase in good agreement with JCPDS 50-0244 as an orthorhombic structure with a = 5.404 Å; b = 5.454 Å; c = 20.530 Å. For La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7+\delta}$, the doublet peaks of 020 and 200 tend to change to a nearly singlet peak, indicating the lattice parameters of a and b are close to each other. This implies that the structure of La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7+\delta}$ transforms to a more symmetric phase, from orthorhombic to tetragonal phase. Similarly, this phase transformation of La$_3$Ni$_2$O$_{6.95}$ reported by Amow, et al. (2006) occurs at 316°C. Therefore, strontium can shift the phase transition to a lower temperature. However, an increase of strontium content from x = 0.3-1 results in the formation of La$_{2-x}$Sr$_x$NiO$_4$ (n = 1 RP phase) and NiO as the second phase indicated by the arrows. Thus the substitution limit of Sr on a La-site in this work is x $\leq$ 0.1.

Figure 1. XRD patterns of calcined La$_{3-x}$Sr$_x$Ni$_2$O$_{7+\delta}$ powders.
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Figures 2-6. Represent SEM micrographs of all sintered compositions with the magnification of 10,000 x. All specimens show a porous structure allowing gas to transport to the all particles. The grain of La$_3$Ni$_2$O$_{7.5\delta}$ has elongate shape. With an increasing amount of strontium, the connectivity between grains improves, thus increasing the sinterability of La$_3$Ni$_2$O$_{7.5\delta}$ as shown in Figures 4-6.

Figure 2. SEM micrograph of sintered La$_3$Ni$_2$O$_{7.5\delta}$

Figure 3. SEM micrograph of sintered La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7.5\delta}$

Figure 4. SEM micrograph of sintered La$_{2.5}$Sr$_{0.5}$Ni$_2$O$_{7.5\delta}$

Figure 5. SEM micrograph of sintered La$_{2.4}$Sr$_{0.5}$Ni$_2$O$_{7.5\delta}$

Figure 6. SEM micrograph of sintered La$_{2}$SrNi$_2$O$_{7.5\delta}$

Figure 7. Shows the results of thermal expansion coefficient (TEC) for La$_3$Ni$_2$O$_{7.5\delta}$ and La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7.5\delta}$. The derivative curves also represent the peak temperature for phase transition. For La$_3$Ni$_2$O$_{7.5\delta}$ it appears at 285°C which is the transformation temperature from orthorhombic to tetragonal phase. Amow, et al. (2006) also observed a change of TEC slope of La$_3$Ni$_2$O$_{6.95}$. Their result from high temperature XRD showed the phase transformation temperature from orthorhombic to tetragonal at 316°C; however, a change in thermal expansion coefficient appeared at a lower temperature of 275°C. For this result, the peak of La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7.5\delta}$ cannot be observed easily but its derivative shows a small peak indicated by an arrow. In addition, this peak is observed at the lower temperature than that of La$_3$Ni$_2$O$_{7.5\delta}$ indicating the lower transition temperature. The TEC value of La$_{2.9}$Sr$_{0.1}$Ni$_2$O$_{7.5\delta}$ is lower than that of La$_3$Ni$_2$O$_{7.5\delta}$ as given in Table 1. For x $\geq$ 0.3, the TEC value is higher than that of La$_3$Ni$_2$O$_{7.5\delta}$
resulting from a formation of $n = 1$ RP phase as indicated by XRD result in Figure 1. The TEC value of \( \text{La}_2\text{NiO}_{4\pm\delta} \) \((n = 1)\) reported by Amow, \textit{et al.} (2006) is higher than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) \((n = 2)\). In addition, TEC value of $x \geq 0.3$ compositions increases with the amount of strontium content.

The temperature dependences of the electrical conductivity for \( \text{La}_{3-x}\text{Sr}_x\text{Ni}_2\text{O}_{7\pm\delta} \) are shown in Figure 8. The data of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) exhibit a thermally activated semiconducting behavior from room temperature to 300°C. Above this temperature, however, the conductivity tends to decrease with increasing temperature. The conduction behavior of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) shows a similar result although the maximum conductivity value occurs at lower temperature than \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \). This turning point is possibly related to the transition temperature. An observed transition temperature of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) is lower than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) which is in agreement with XRD and TEC results. The electrical conductivity of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) is higher than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) at all measuring temperatures. The electrical conductivities at 600°C of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) and \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) are 63 and 81 S.cm$^{-1}$ respectively. In contrast, the electrical conductivities at 600°C of \( \text{La}_{2.7}\text{Sr}_{0.3}\text{Ni}_2\text{O}_{7\pm\delta} \), \( \text{La}_{2.5}\text{Sr}_{0.5}\text{Ni}_2\text{O}_{7\pm\delta} \) and \( \text{La}_2\text{SrNi}_2\text{O}_{7\pm\delta} \) are 25, 20 and 57 S.cm$^{-1}$ respectively. The conductivity values of the last three compositions are lower than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) since the phase changes from $n = 2$ RP to $n = 1$. Amow, \textit{et al.} (2006) reported that the electrical conductivity of \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) reduced as $n$ decreased. The electrical conductivity above 300°C of \( \text{La}_2\text{SrNi}_2\text{O}_{7\pm\delta} \) increases and is similar to that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \).

The temperature dependences of the electrical conductivity for \( \text{La}_{3-x}\text{Sr}_x\text{Ni}_2\text{O}_{7\pm\delta} \) are shown in Figure 8. The data of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) exhibit a thermally activated semiconducting behavior from room temperature to 300°C. Above this temperature, however, the conductivity tends to decrease with increasing temperature. The conduction behavior of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) shows a similar result although the maximum conductivity value occurs at lower temperature than \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \). This turning point is possibly related to the transition temperature. An observed transition temperature of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) is lower than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) which is in agreement with XRD and TEC results. The electrical conductivity of \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) is higher than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) at all measuring temperatures. The electrical conductivities at 600°C of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) and \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7\pm\delta} \) are 63 and 81 S.cm$^{-1}$ respectively. In contrast, the electrical conductivities at 600°C of \( \text{La}_{2.7}\text{Sr}_{0.3}\text{Ni}_2\text{O}_{7\pm\delta} \), \( \text{La}_{2.5}\text{Sr}_{0.5}\text{Ni}_2\text{O}_{7\pm\delta} \) and \( \text{La}_2\text{SrNi}_2\text{O}_{7\pm\delta} \) are 25, 20 and 57 S.cm$^{-1}$ respectively. The conductivity values of the last three compositions are lower than that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \) since the phase changes from $n = 2$ RP to $n = 1$. Amow, \textit{et al.} (2006) reported that the electrical conductivity of \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) reduced as $n$ decreased. The electrical conductivity above 300°C of \( \text{La}_2\text{SrNi}_2\text{O}_{7\pm\delta} \) increases and is similar to that of \( \text{La}_3\text{Ni}_2\text{O}_{7\pm\delta} \).
Figure 9. Arrhenius plots of electrical conductivity of \( \text{La}_{3-x}\text{Sr}_x\text{Ni}_2\text{O}_{7-\delta} \) (\( x = 0, 0.1, 0.3, 0.5 \) and 1)

Conclusions

\( \text{La}_{3-x}\text{Sr}_x\text{Ni}_2\text{O}_{7-\delta} \) are synthesized by a gel combustion method. The single phase of \( \text{La}_3\text{Ni}_2\text{O}_{7-\delta} \) can be obtained after calcination at 1100°C for 6 hrs. Doped with strontium, the structure tends to change from orthorhombic to tetragonal. In this work, \( \text{La}_{2.9}\text{Sr}_{0.1}\text{Ni}_2\text{O}_{7-\delta} \) performs a lower TEC but higher conductivity than \( \text{La}_3\text{Ni}_2\text{O}_{7-\delta} \). With \( x \geq 0.3 \) the \( n = 1 \) RP phase and NiO take place, resulting in lower electrical conductivity.

Acknowledgment

This work was supported from the National Metal and Materials Technology Center.

References


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