CHAPTER III

PROPERTY STUDTY OF $La_{2-x}Sr_xNiO_4$ ($x \leq 0.8$) FOR IT–SOFCs CATHODE

3.1 Abstract

Materials with Ruddlesden-Popper structure (A_2BO_4) such as La_2NiO_4 system have been identified as the new cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) as their coefficient of thermal expansion values match those of the currently used electrolytes. Moreover, such materials have shown mixed ionic and electronic conductivity desirable for cathodes. The low electronic conductivity of La_2NiO_4 remains a challenge. To improve this property, investigations on $La_{2-x}Sr_xNiO_{4+\delta}$ ($x = 0$, 0.4, and 0.8) prepared via sol-gel and solid state reaction processes were carried out in this study. Effects of Sr substitution on A sites on physical and electrical properties of the compound were investigated and compared. A simple preparation sol-gel process, carried out at room temperature and using water as solvent for the synthesis of $La_{2-x}Sr_xNiO_{4+\delta}$, was successfully developed. The sol-gel synthesis method yielded more homogenous samples with higher conductivity compared to those synthesized via the solid state reaction method. Conductivity as high as 160 S/cm at 500°C was observed for $La_{1.2}Sr_{0.8}NiO_{4+\delta}$ synthesized via the sol-gel process.

(**Keywords**: Ruddlesden-Popper; Sol-gel process; SOFCs; Cathode)

3.2 Introduction

A major worldwide research thrust in solid oxide fuel cell (SOFC) technology has been the lowering of the system operating temperature from 800-1000°C to 400-600°C [1]. This reduced operating temperature reduces cost, prolongs life, increases safety of the system, and accordingly is recognized as a critical step for successful commercial implementation of SOFCs. A large focus has been on electrolyte material development; however, to maintain high efficiency at lower temperatures, new electrode material explorations are also necessary. Materials with Ruddlesden-Popper structure (A_2BO_4), such that of La_2NiO_4, system have been identified as the new cathode materials which could potentially replace the high temperature electrode materials in the lanthanum manganite perovskite family [2]. La_2NiO_4 not only has a coefficient of thermal expansion (CTE) close to the materials used as electrolytes, but is also a mixed ionic and electronic conductor [3]. However, low electronic conductivity of La_2NiO_4 is yet still a major concern [4].

Ishikawa et $al.$ studied the effects of Sr substitution for La in La_2NiO_4 and found that the electron density in $LaSrNiO_4$ is almost an order of magnitude larger than that of La_2NiO_4 [5]. Since then, several works on the Sr substitution on the A site in $La_2NiO_{4+\delta}$ based system have followed [6-8]. It has been reported that processing route and conditions can strongly affect the properties of the material [2, 9-10]. The La_2NiO_4 powder is generally synthesized via simple standard ceramic methods using oxides, carbonate or nitrate, or more recently via polymeric methods [7-9] which have been claimed to provide more homogenous single phase materials. While the latter methods can provide homogeneous single phase materials, they are usually quite complex, involving high temperature chemical processing and organic solvents [7-9]. In this work, synthesis of $La_2NiO_{4-\delta}$ via a simple sol-gel process, using water as solvent, was studied. The effects of the Sr substitution on A site on the physical and electrical properties of the $La_{2-x}Sr_xNiO_{4+\delta}$ ($x = 0$, 0.4 and 0.8) samples prepared via the sol-gel and the more common solid state reaction processes were investigated and compared.

3.3 Experimental

3.3.1 Powder Synthesis

For the sol-gel process, $La_{2-x}Sr_xNiO_4$ powders were prepared by dissolving $(CH_3COO)_3La \cdot xH_2O$ (99.9%, Sigma–Aldrich Co.), $(CH_3COO)_2Sr$ (99.995%, Sigma-Aldrich Co.), and $(CH_3COO)_2Ni \cdot 4H_2O$ (98%, Sigma-Aldrich Co.) in deionized water. The mixture was homogeneously stirred to obtain a clear solution before adding a templating agent directly. Two types of templating agents were investigated: ethanolamine (Labscan Co.) and Triethylenetetramine (TETA, Facai Com,.Ltd). The mol ratio of the templating agent used per cation was fixed at 3.21:3. After the template addition, the mixture was stirred continuously for 6 hr before being left at room temperature to gel. Afterwards, the gel was calcined at 1050°C with a heating rate of 3°C/min for 2 hr, resulting in black powder. For the solid state reaction, $La_{2-x}Sr_xNiO_4$ powders were prepared by adding the stoichiometric amount of the same starting materials as those used for the sol-gel method into a polypropylene bottle filled with 5 mm diameter ZrO_2 balls. The mixture was ball milled at 1000 rpm for 10 hr. The mixed powders were then ground and calcined at the same conditions as those prepared via the sol-gel process to obtain final products.

3.3.2 Characterization

To understand the structure of the synthesized gel, samples obtained from the sol-gel process were freeze-dried at -80°C for 24 hr and dried under a pressure of -0.012 atm for 60 hr. The blue powders obtained were then mixed with KBr to form pellets before being examined by FTIR (Nicolet) operated at a resolution of 2 cm^{-1} and a scanning range of 400-4000 cm^{-1}. Phase and crystal structures of the calcined samples were characterized using a Rigaku X-ray diffractometer with the Cu Kα source using 20-80° 2θ range with a 0.02o step angle and 1 sec count time. Morphologies of the powders were investigated using JEOL 5200–2AE scanning electron microscope (SEM). For electrical measurements, the calcined powders were compressed into bars before sintering in air at 1200°C for 5 hrs with 5°C/min heating rate. Conductivities of the samples were measured as a function of temperature by the standard dc four terminal method. Four platinum electrode terminals were connected to the sample using Pt paste. The systems were

then baked at 850°C for 2 hr and the measurements were performed starting from 850°C to room temperature at a cooling rate of 5°C/min.

3.4 Results and Discussion

3.4.1 Gel Formation

Successful formation of three dimensional La–Sr–Ni network complexes using a simple room temperature water based sol-gel process was achieved in this work. Three parameters, affecting sol and gel formation, were studied: the molar ratio of water to A site, type of template, and gelation time. Table 3.1 summarizes the amount of water needed for different La–Sr–Ni compositions. It was found that as the amount of Sr substitution increases, the amount of water needed to dissolve the starting materials decreases, by almost 25% with 0.8 mol Sr substitutions compared with no substitution. This is due to the solubility of the starting La compound which is lower in water compared to the Sr and Ni compounds. Thus, the amount of water needed decreases with decreasing La content.

The second processing factor investigated was the choice of templating agents. It was found that the mixture solutions formed gel when either ethanolamine or TETA were introduced. This indicates that both templates are effective in controlling the hydrolysis reaction and could enhance the formation and stabilization of three-dimensional network structures as discovered by Xie *et al.* [11]. That group used ethanolamine to slow down the hydrolysis of Bi^{3+} for the formation of $BaBi_4Ti_4O_{15}$ (BBT). Although both templates could aid gel formation, ethanolamine in this study has resulted in a more uniform composition, and therefore was chosen as the templating agent for further experiments. Fig. 3.1 shows FTIR spectra of the dried gels produced using the ethanolamine (Fig. 3.1(a-c)) and TETA (Fig. 3.1(d-f)) templates. No significant difference was observed between the dried gels obtained from different starting compositions, but a little difference from different templates. All spectra show a broad absorption around 3360 cm^{-1}, referring to the stretching vibration of hydroxyl groups (O–H) from water solvent and by-product (ethylene diol) produced during gel formation [9]. Strong absorption peaks localized at 1550 and 1425 cm^{-1} and weak absorption peaks around 650-900 cm^{-1} are

due to COO vibrations [9]. The results obtained match the starting materials used in this experiment. Absorption peaks at 1014 and 1052 cm^{-1} correspond to those of C–O vibrations were found for the samples using ethanolamine as template, but these peaks were almost undetectable for the samples using TETA as template. In addition, the vibration from C–N bonding, resulting from interactions between the starting metal acetate and the amine template used in this work, was only observed for the samples using ethanolamine as template at 1380 cm^{-1}. This observation gives an important indication that amine template acts as linkages between the starting materials to create network structure and allows the gel formation. This indicated that ethanolamine template is more effective than TETA template to enhance the gel formation. Time required for the gel formation was also investigated. All samples started to form stable gels after being left at room temperature for 6 hr. The gel was found to be stable up to 72 hr. Gelation time longer than 72 hr resulted in further hydrolysis or reverse reaction (reesterification) and excess solvent was observed [12].

3.4.2 Phase Formation

Fig. 3.2 shows XRD patterns of the $La_{2-x}Sr_xNiO_4$ powders prepared using the different synthesis methods. La_2NiO_4 phase (JCPDS 34-0314) with the Ruddlesden–Popper structure, K_2NiF_4, was found to be the dominant phase in all cases. For the samples prepared by the sol–gel method using ethanolamine as template, the samples with Sr substitution were found to exist as a single phase (Fig. 3.2(b-c)). With no Sr substitution, however, the sample shows extra small peaks in the XRD patterns; peaks at $2\theta = 32.04°$ and $33.18°$ corresponding to $La_3Ni_2O_7$ (JCPDS 50-0244) and a peak at $2\theta = 32.28°$ corresponding to $LaNiO_3$ (JCPDS 12-0715). This is an indication that Sr substitution on A sites helps stabilize the Ruddlesden-Popper structure. This phenomenon has been described previously by Nie *et al.*, who stated that the formation of $A_{2-x}A'_xBO_4$ structure is partially related to the oxidation state of cation at B–site and that the valence of the B cation should be approximately +2 for the K_2NiF_4 structure [13]. This is not always the case as Ni can possess the valences of +2 or +3 in air [14], and therefore, $La_3Ni_2O_7$ (Ni = +2.5) and $LaNiO_3$ phase (Ni = +3) could be formed. When La^{3+} is substituted by Sr^{2+}, Ni^{3+} could then be compensated by Sr^{2+}. Therefore, it is easier to form K_2NiF_4 structure

for the samples with Sr substitution. Similar results were found for the samples synthesized via the solid state method (Fig. 3.2(g-i)) with a small difference in slightly more pronounced additional impurity phases. La_2O_3 and NiO were found in the samples produced via the solid state synthesis while the impurity phases are almost undetectable in the samples synthesized by the sol-gel method. The difference is likely due to the more homogenously mixed starting precursors for the sol-gel synthesis before calcination. In addition, the samples prepared by the sol–gel method using TETA as template show the different results (Fig. 3.2(d-f)). The extra small peaks in the XRD patterns corresponding to $La_3Ni_2O_7$ and $LaNiO_3$ found in all compositions. This is agreement with FTIR results shown in fig. 3.1 which indicated that TETA is not effective to enhance the gel formation leading to higher amounts of impurities.

3.4.3 Electrical Conductivity

Fig. 3.3 shows conductivity results of the sintered samples as a function of temperature. In the temperature range measured. a decrease in conductivity with increasing temperature was observed in all samples. The decreasing conductivity with increasing temperature indicating metallic conducting behavior of the material. is consistent with what was reported by Ishikawa and Goodenough et $al.$ [5,15]. They found that La_2NiO_4 exhibits semi-conducting behavior at temperatures below 300°C, and a metallic conducting behavior at temperatures above 300°C. The conductivity values obtained from this experiment were found to be similar to what had been reported by other researchers for the samples with no Sr substitution, having the values between 40-100 S/cm in the temperature range of 300°–850°C [6,14]. With a small amount of Sr substitution (x = 0.4), the conductivity was found to decrease and the value increases again at higher amount of Sr substitution, x = 0.8. The results of decreasing conductivity when x = 0.4 and increasing conductivity when x = 0.8 are consistent between the samples synthesized either by the solid state or the sol-gel method. Further investigation is needed to explain such behavior.

When comparing the effects of the synthesis routes on the conductivity of the samples. it was found that the sintered samples produced from the

sol-gel synthesized powder and the samples produced from the solid state synthesized powder exhibit similar conductivities at no Sr substitution, slightly higher conductivity for the sample with x = 0.4 and much higher value for when x = 0.8. The conductivity of the $La_{1.2}Sr_{0.8}NiO_4$ sample produced from the sol-gel synthesized powder is as high as 160 S/cm at 500°C.

3.4.4 Morphological Observations

Fig. 3.4 shows SEM images of the $La_{2-x}Sr_xNiO_4$ produced via both the sol-gel (left) and the solid state (right) methods. For the samples with no Sr substitution, it was found that the sample produced from the sol-gel synthesized powder is denser than that produced via the solid state method. This is expected as the powder from the sol-gel synthesized method is supposed to have higher surface area than the one produced via the solid state method, and thus should be easier to sinter [16]. The Sr substitution for La on A site is found to have a pronounce effect on morphology of the sintered samples, especially, the sol-gel synthesized samples. Lower density and smaller grain size were observed for the samples with Sr substitution indicating slower atomic movement in such samples. Reduction in mobility of oxygen atoms for $La_{2-x}Sr_xNiO_{4+\delta}$ compared to $La_2NiO_{4+\delta}$ have been reported by Skinner *et al.* [8].

3.5 Conclusions

The synthesis of $La_{2-x}Sr_xNiO_{4+\delta}$ (x = 0, 0.4, and 0.8) via a simple room temperature sol-gel process using non-organic solvent has successfully been carried out. Both ethanolamine and TETA were found to be effective as templates for the process. Suitable gelation time was found to be in the range of 6-72 hrs. The sol-gel method yielded more homogenous powders than the solid state reaction method. Substitution of Sr for La on the A sites was found to affect phase, sintering, and conducting behavior of the synthesized samples. For samples with Sr substitution, the $La_{2-x}Sr_xNiO_{4+\delta}$ phase formed was found to be more stable than the samples without Sr substitution. Less dense morphology was observed for the samples with Sr substitution compared to those with no Sr substitution. High conductivity La_2-

$_x$Sr$_x$NiO$_{4+\delta}$ cathodes, as high as 160 S/cm at 500°C, could be obtained from this study, using the sol-gel synthesized powder.

3.6 Acknowledgements

3.7 References

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**Table 3.1** Summary of water amount used for samples with different compositions

| Composition	H_2O:A (Molar ratio)
La_2NiO_4	190:1
$La_{1.6}Sr_{0.4}NiO_4$	165:1
$La_{1.2}Sr_{0.8}NiO_4$	145:1
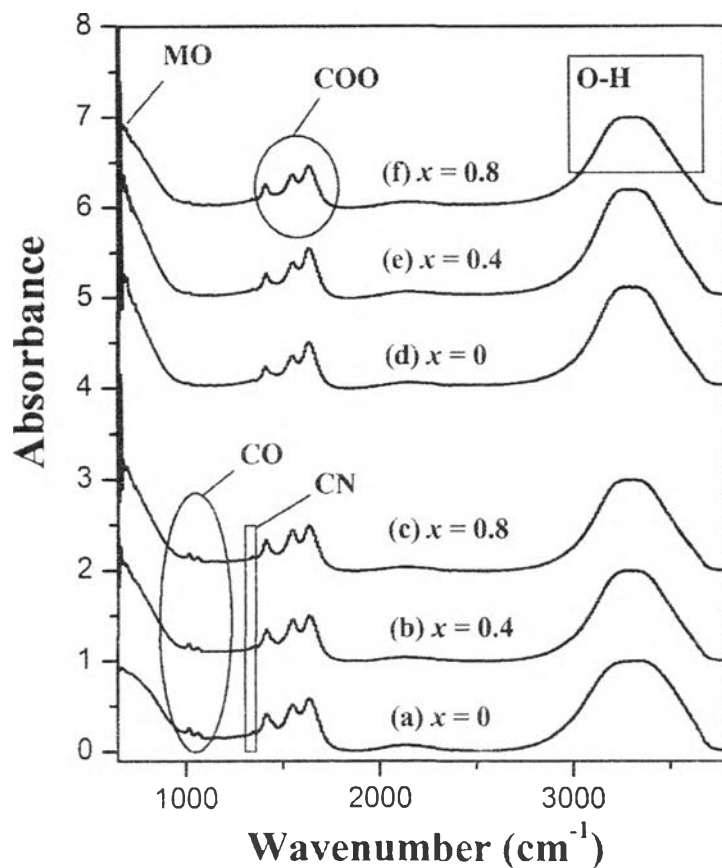
Figure 3.1 FTIR spectra of dried gel (La–Sr–Ni complex) from synthesis of La$_2$-$_x$Sr$_x$NiO$_4$ prepared using ethanolamine as template, (a) $x = 0$ (b) $x = 0.4$ and (c) $x = 0.8$ and TETA as template, (d) $x = 0$ (e) $x = 0.4$ and (f) $x = 0.8$.
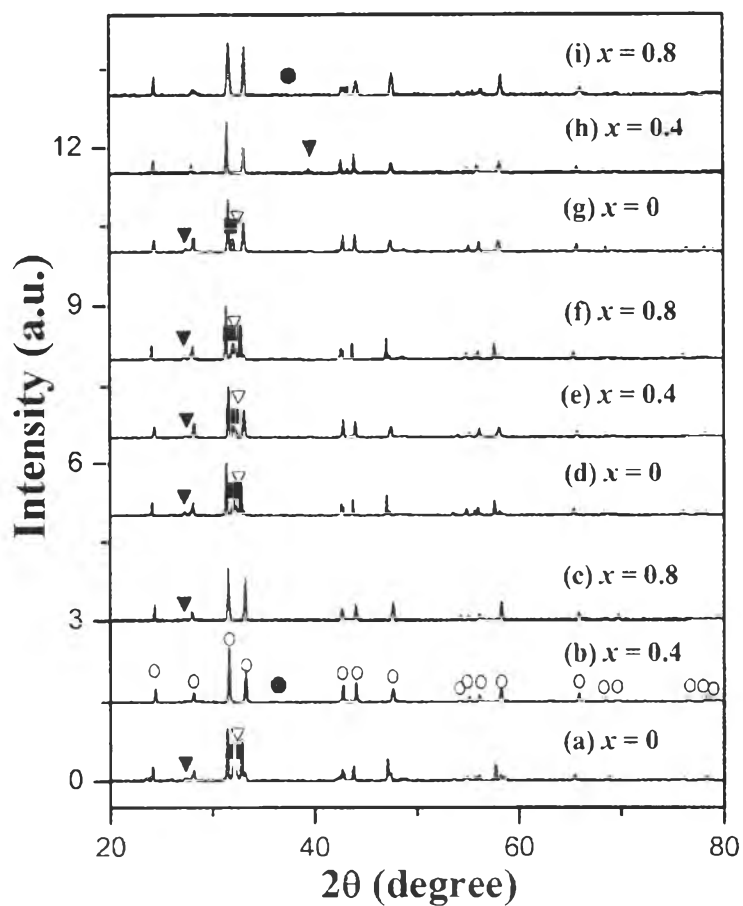
Figure 3.2 XRD patterns of the calcined $La_{2-x}Sr_xNiO_4$ powders prepared via the sol-gel process using ethanolamine as template when x is (a) 0, (b) 0.4, and (c) 0.8, the sol-gel process using TETA as template when x is (d) 0, (e) 0.4, and (f) 0.8, and $La_{2-x}Sr_xNiO_4$ prepared by the solid state reaction process when x is (g) 0, (h) 0.4, and (i) 0.8 (○ La_2NiO_4, ■ $La_3Ni_2O_7$, ▽ $LaNiO_3$, ● La_2O_3 and ▼ NiO).
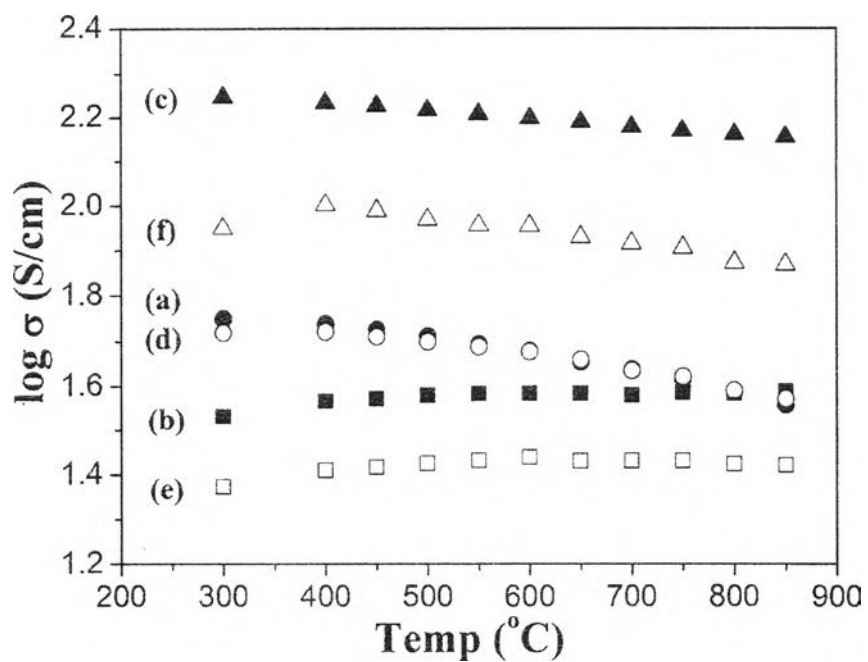
Figure 3.3 Electrical conductivity versus temperature plot of $La_{2-x}Sr_xNiO_4$ prepared via the sol-gel process (closed symbols) when x is (a) 0, (b) 0.4, and (c) 0.8; and $La_{2-x}Sr_xNiO_4$ prepared by the solid state reaction (opened symbols) when x is (d) 0, (e) 0.4, and (f) 0.8.
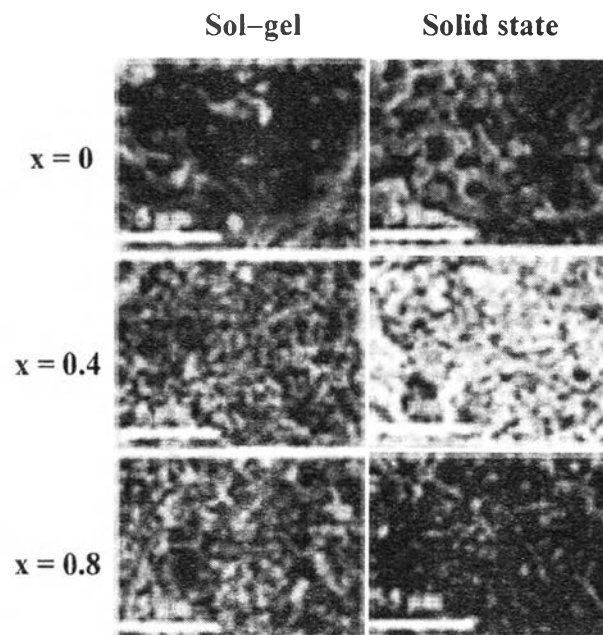
Figure 3.4 SEM images of sintered $La_{2-x}Sr_xNiO_4$ samples prepared by the sol-gel synthesized powder (left) and the solid state synthesized powder (right).