PRELIMINARY INVESTIGATION OF THE HIGHER-ORDER RUDDLESDEN-POPPER PHASES FOR IT-SOFC CATHODES, \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) (\( n = 2 \) and 3)

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ABSTRACT

The Ruddlesden-Popper phase, \( \text{La}_2\text{NiO}_{4+\delta} \), has generated much interest as an alternative cathode material to the conventionally used perovskite-based materials, \( \text{La}_{1-x}\text{Sr}_x\text{BO}_3 \) (\( B = \text{Mn, Co} \)), particularly in the intermediate temperature range (873-1073 K). This is largely due to a combination of good electrical conductivity with high oxide-ion diffusion coefficients in this temperature range.

In a previous study, however, the degradation of \( \text{La}_2\text{NiO}_{4+\delta} \) into a mixed \( \text{Ni}^{2+}/\text{Ni}^{3+} \) impurity phase was reported when subjected to prolonged heating at 1173 K for two weeks. This has been attributed to the favourable stability of the \( \text{Ni}^{3+} \) ion at lower temperatures (\( T < 1273 \) K) compared to the predominant \( \text{Ni}^{2+} \) present in this phase. We report here the results of an investigative study of the higher-order, mixed \( \text{Ni}^{2+}/\text{Ni}^{3+} \) Ruddlesden-Popper phases \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) (\( n = 2 \) and 3) for possible use as cathodes in intermediate temperature solid oxide fuel cells. Details regarding the preparation and subsequent characterization of the \( \text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1} \) phases by x-ray diffraction, oxygen content determination, electrical conductivity, thermal stability and area specific resistance measurements on symmetrical LSGM cells are presented.

INTRODUCTION

The Ruddlesden-Popper phase, \( \text{La}_2\text{NiO}_{4+\delta} \), has been the source of much attention as a potential cathode material for intermediate temperature (873 – 1073 K) solid-oxide fuel cells (IT-SOFCs) (1-6). This material exhibits good electrical conductivity \( \sim \) 100 S/cm at 600-650 K (7-9). However, the aspect which makes these materials most attractive for the intended application is the fast oxide-ion conductivity observed below 1273 K. Isotopic exchange depth profiling measurements have shown that the oxide-ion diffusion coefficients are at least an order of magnitude larger than the three-dimensional conventional perovskites such as \( \text{LSCF} \) (3,4). The origin of the enhanced oxide-ion conductivity is a consequence of the layered structure, which is composed of alternating perovskite and rock-salt layers, as shown in Fig. 1. Studies have shown that excess oxygen can be accommodated in the interstitial sites of the rock-salt layers as defects (10,11); it is these excess oxide-ions, which are highly mobile that are responsible for the enhanced oxide-ion conductivities observed in this class of materials. In a previous study,
however, it was shown that prolonged thermal treatment of the La$_2$NiO$_{4+8}$ phase at 1173 K resulted in a mixed Ni$^{2+}$/Ni$^{3+}$ impurity phase (12). This is due to the preferential stability of the Ni$^{3+}$ ion relative to the Ni$^{2+}$ ion at temperatures below 1273 K.

The higher-order phases, La$_3$Ni$_2$O$_{7+5}$ ($n=2$) and La$_4$Ni$_3$O$_{10+5}$ ($n=3$) (where $n =$ number of perovskite blocks as shown in Fig. 1) are mixed Ni$^{2+}$/Ni$^{3+}$ phases with nickel oxidation states of +2.5 and +2.67 respectively for $\delta = 0$. The relative stability of the Ni$^{3+}$ ion is reflected by the decreasing temperature conditions required to synthesize these materials (13,14). Consequently, these materials are expected to be more thermally stable over time in the intermediate temperature range of operation of the fuel cell than the parent phase, La$_2$NiO$_{4+8}$. As in the La$_2$NiO$_{4+8}$ phase, the electrical conductivity for these phases originates from the Ni-O-Ni interactions in the perovskite layer. With the increase of the number of perovskite layers from $n = 1$ to 3, the electrical conductivity is expected to increase in the intermediate temperature range; indeed, a previous study has shown La$_4$Ni$_3$O$_{10+5}$ to be metallic over the range 293 – 1240 K (15).

The aim of this study was to synthesize and characterize the La$_3$Ni$_2$O$_{7+5}$ ($n=2$) and La$_4$Ni$_3$O$_{10+5}$ ($n=3$) phases for IT-SOFC cathode-use through structural and oxygen content analysis, thermal stability, electrical conductivity, and electrode performance in symmetrical cells with La$_{0.9}$Sr$_{0.1}$Ga$_{0.3}$Mg$_{0.7}$O$_{3-\delta}$ (LSGM) as the electrolyte.

**EXPERIMENTAL**

**Synthesis**

The La$_{n+1}$Ni$_n$O$_{3n+1}$ ($n = 0, 1, 2$) phases were prepared by the Pechini method. Stoichiometric amounts lanthanum- and nickel-nitrate were weighed out and dissolved in water, to which calculated amounts of excess citric acid and ethylene glycol were added. The solution was then evaporated to form a gel, which was then placed to dry overnight under vacuum at 453 K. The dried gel, obtained in this manner, was subsequently ground and pre-fired at 1023 K for 4 hrs in air to remove unwanted organic residues. Pellets were
then made for each composition and single-phase materials were obtained by firing under the following conditions in Table 1.

Table 1: Summary of synthesis conditions for the $n = 1$, 2, and 3 Ruddlesden-Popper phases.

| Sample               | T (K) | Total Time |
|----------------------|-------|------------|
| La$_2$NiO$_{4+\delta}$ | 1423  | 6 hrs      |
| La$_3$Ni$_2$O$_{7.5\delta}$ | 1373  | 2 days     |
| La$_4$Ni$_3$O$_{10.5\delta}$ | 1323  | 6 days*    |

*With one intermediate grinding.

**Structural Analysis and Phase Purity Determination**

Routine structural analysis and phase-purity identification was performed with a CuKα equipped Bruker D8 x-ray diffractometer.

**Oxygen Content Determination**

A Setaram SETSYS Evolution thermogravimetric analyzer was used for oxygen content determination by reduction under flowing 5%H$_2$-Ar gas. The samples (~50 mg) were heated to 1273 K and the weight losses observed were used to calculate the oxygen content based on nominal metal contents.

**Electrical Conductivity**

Measurements were performed in static air from 1173 K to RT by the van der Pauw method. Typical samples sizes were ~12 mm x ~12 mm x ~1.5-2 mm thick. The theoretical density for the measured La$_2$NiO$_{4+\delta}$ samples was >85%. Due to the low temperature preparation conditions, pellets of the La$_3$Ni$_2$O$_{7.5\delta}$ and La$_4$Ni$_3$O$_{10.5\delta}$ phases were cold isostatic pressed at 250 MPa to yield ~54% theoretical density after sintering.

**Impedance Spectroscopy**

Inks of all three phases were prepared by mixing ball-milled powders with ethylene glycol. These were then coated onto both sides of LSGM electrolyte pellets, which were obtained by sintering pressed pellets at 1773 K for six hours in air to yield a theoretical density of >97%. The coated pellets were then fired at 1173 K for six hours in air to promote adhesion of the ink onto the electrolyte pellet. The electrode performances were subsequently determined by a two-probe a.c. impedance method with a Solartron 1260 impedance analyzer. An a.c. signal of 50 mV was applied and data were collected between 15 MHz to 0.01 Hz in static air from 1173 K to RT.
RESULTS AND DISCUSSION

The samples prepared with the conditions described in Table 1 resulted in single-phase materials as shown by the x-ray diffraction patterns in Fig. 2. The oxygen content trends for the prepared materials show hyperstoichiometry for the La$_2$NiO$_{4+\delta}$ phase with $\delta = 0.15$, whereas oxygen deficiency for the La$_3$Ni$_2$O$_{7-\delta}$ and La$_4$Ni$_3$O$_{10-\delta}$ phases was found with $\delta = -0.05$ and $-0.22$ respectively by thermogravimetric analysis under reducing conditions.

![X-ray diffraction patterns of phase pure La$_2$NiO$_{4+\delta}$, La$_3$Ni$_2$O$_{6.95}$ and La$_4$Ni$_3$O$_{9.78}$](image)

Figure 2. X-ray diffraction patterns of phase pure La$_2$NiO$_{4+\delta}$, La$_3$Ni$_2$O$_{6.95}$ and La$_4$Ni$_3$O$_{9.78}$.

The electrical conductivity for all three phases is shown in Fig. 3. Taking into consideration the relatively low theoretical densities of ~54% for the $n=2$ and 3 samples used for the measurement, the electrical conductivities for these phases are likely to be significantly higher than La$_2$NiO$_{4+\delta}$ as shown. On this basis together with the progressive increase of perovskite layers, the electrical conductivity is expected to systematically increase from $n = 1$ to 3 due to the increasing Ni-O-Ni interactions responsible for the electrical conduction pathways. Such a systematic trend with $n$ has been found in the low temperature regime < 300 K (13).

The normalized area-specific resistance for symmetrical cells with LSGM as the electrolyte is shown in Fig. 4. From this data, the La$_4$Ni$_3$O$_{9.78}$ coated pellet has lowest area-specific resistance with an activation energy of $E_a = 1.36$ eV followed by La$_3$Ni$_2$O$_{6.95}$ and La$_2$NiO$_{4.15}$ with $E_a = 1.24$ eV and 1.27 eV respectively. The observed trend appears to be related to the systematic increase of the electrical conductivity more so than the oxygen stoichiometry trends in these materials.

The thermal stability of La$_3$Ni$_2$O$_{6.95}$ and La$_4$Ni$_3$O$_{9.78}$ was studied by annealing small pellets ~ 8 mm in diameter in air at 1173 K for two weeks. Unlike the La$_2$NiO$_{4+\delta}$ phase, no impurity formation was observed under these conditions.
In this study, the higher-order Ruddlesden-Popper phases La$_3$Ni$_2$O$_{6.95}$, La$_4$Ni$_3$O$_{9.78}$ were investigated for possible use as cathodes in IT-SOFCs. These two phases have significantly improved electrical conductivity behaviour as the number of perovskite blocks is progressively increased from $n = 1$ to 3. Furthermore, their improved longer-term thermal stability and electrode performance when LSGM is used as an electrolyte makes them more viable than La$_2$NiO$_{4.15}$ as cathode materials for IT-SOFCs.

**SUMMARY AND CONCLUSIONS**

In this study, the higher-order Ruddlesden-Popper phases La$_3$Ni$_2$O$_{6.95}$, La$_4$Ni$_3$O$_{9.78}$ were investigated for possible use as cathodes in IT-SOFCs. These two phases have significantly improved electrical conductivity behaviour as the number of perovskite blocks is progressively increased from $n = 1$ to 3. Furthermore, their improved longer-term thermal stability and electrode performance when LSGM is used as an electrolyte makes them more viable than La$_2$NiO$_{4.15}$ as cathode materials for IT-SOFCs.
REFERENCES

1. J. M. Bassat, E. Boehm, J. C. Grenier, F. Mauvy, P. Dordor and M. Pouchard, in *Fifth European Solid Oxide Fuel Cell Forum Proceedings*, J. Huijsmans, Editor, p. 586, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2002).

2. S. J. Skinner, C. N. Munnings, G. Amow, P. Whitfield, and I. Davidson, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, **PV2003-07**, p. 552, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

3. C. K. M. Shaw, J. A. Kilner, in *Fourth European Solid Oxide Fuel Cell Forum Proceedings*, A. J. McEvoy, Editor, p. 611, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2000).

4. E. Boehm, J. M. Bassat, F. Mauvy, P. Dordor, J. C. Grenier and M. Pouchard, in *Fourth European Solid Oxide Fuel Cell Forum Proceedings*, A. J. McEvoy, Editor, p. 717, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2000).

5. G. Amow, P. Whitfield, I. Davidson, R. P. Hammond, C. Munnings, and S. J. Skinner, in *Solid State Chemistry of Inorganic Materials IV*, M. Greenblatt and M. S. Whittingham, Editors, Volume 755, p. 347, The Materials Research Society, Boston, Massachusetts, USA, (2003).

6. S. J. Skinner and J. A. Kilner, *Solid State Ionics*, **135**, 709-712 (2000).

7. P. Ganguly and C. N. R. Rao, *Materials Research Bulletin*, **8**, 405 (1973).

8. J. M. Bassat, P. Odier and J. P. Loup, *Journal of Solid State Chemistry*, **110**, 124-135 (1994).

9. S. Nishiyama, D. Sakaguchi and T. Hattori, *Solid State Communications*, **94**(4), 279-282 (1995).

10. D. E. Rice and D. J. Buttrey, *Journal of Solid State Chemistry*, **105**, 197-210 (1993).

11. J. D. Jorgensen, B. Dabrowski, S. Pei, D. R. Richards and D. G. Hinks, *Physical Review B*, **40**(4), 2187-2199 (1989).

12. G. Amow, P. S. Whitfield, I. J. Davidson, C. N. Munnings and S.J. Skinner. *Journal of Ceramics International*, **30**(7), 1635-1639 (2004).

13. Z. Zhang and M. Greenblatt, *Journal of Solid State Chemistry*, **117**, 236-246 (1995).

14. Z. Zhang, M. Greenblatt and J. B. Goodenough, *Journal of Solid State Chemistry*, **108**, 402-409 (1994).

15. V. V. Vashuk, O. P. Ol’shevskaya, V. F. Savchenko and E. Ya. Puchkaeva, *Inorganic Materials*, **30**(11), 1357-1359 (1994).