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Structural and sintering characteristics of the $La_2Ni_{1-x}Co_xO_{4+\delta}$ series

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Abstract

The solid solution, $La_2Ni_{1-x}Co_xO_{4+\delta}$ ($0.00 \leq x \leq 1.00$), based on the K_2NiF_4 structure was synthesised and studied for potential use as cathodes in solid-oxide fuel cells. A structural phase transition was observed with increasing cobalt substitution, between $x = 0.50$ and 0.60 from tetragonal to orthorhombic symmetry. An apparent correlation between the area specific resistance and microstructural properties has been found for materials produced using both conventional and microwave heating. The difference in microstructure for samples prepared by these two techniques persists even after firing on CGO and LSGM pellets at 950 °C in air for 2 weeks.

Keywords: A. Microwave processing; B. X-ray methods; E. Fuel cells

1. Introduction

Recent demands for environmental protection and fuel efficiency have encouraged much work in the field of alternative energy sources. Fuel cells form a large part of this effort, and solid oxide fuel cells (SOFCs) are particularly attractive for residential, commercial and distributed power use given their very high efficiency in combined heat and power operation. SOFCs currently operate at very high temperatures (~900–1000 °C), and to reduce the production and operating costs while retaining reliability, it is desirable to reduce the operating temperature. This creates challenges for all components of the SOFC; the cathode, electrolyte, anode and interconnect.

This work is directed at developing new materials for use as SOFC cathodes. The current material of choice for this application is the perovskite $La_{1-x}Sr_xMnO_{3-\delta}$. However, cubic perovskite materials optimised to operate in the intermediate temperature range suffer from a number of problems, most notably chemical and mechanical instabilities, without a clear solution. Some previous studies have suggested that systems based on the layered K_2NiF_4 structure (Fig. 1), such as $La_2NiO_{4+\delta}$ may offer alternatives, as it exhibits relatively high electronic conductivity and oxygen diffusivity at elevated temperatures [1,2]. The parent nickelate, $La_2NiO_{4+\delta}$, is made up of alternating $LaNiO_3$ perovskite and La_2O_2 rock salt layers. Significant excess oxygen, δ, can be incorporated into the rock-salt layer as interstitial defects [3]. A series of structural changes from tetragonal to orthorhombic symmetry may be induced by varying the amount of excess oxygen in the rock-salt layer [3,4].

Previous studies have reported differences in microstructure when electroceramics have been prepared and/or sintered using microwave as opposed to conventional radiative heating [5,6]. Given the sensitivity of many material properties to microstructure, microwave heating is interesting as a possible route to novel microstructures. It has been reported that $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$, exhibited lower area-specific resistance (ASR) values for symmetrical cells based on ceria-doped gadolinia (CGO) when microwave heating was used [6]. The difference was ascribed to variations in the microstructure derived from the different firing techniques. This paper will present a summary of the structural changes in the system with increasing cobalt substitution. In addition, evidence to support the notion that the lowering of the ASR values is inherently associated with differences in microstructure with microwave heating will be presented.

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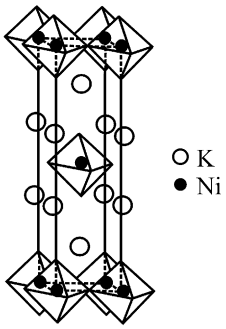


Fig. 1. Ruddlesden–Popper K_2NiF_4 structure.

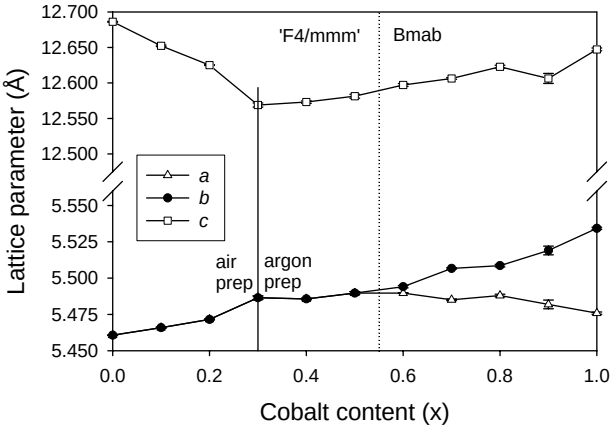


Fig. 2. Plot of lattice parameters vs. cobalt content (x).

2. Experimental

Samples of the $La_2Ni_{1-x}Co_xO_{4+\delta}$ system ($x = 0.00$–1.00, $\Delta x = 0.10$) were prepared by the Pechini method [7] and is described elsewhere [8]. For the microwave-prepared samples, a modified Milestone furnace was used. For $x = 0.00$–0.20, the samples were prepared in air, whereas the remaining compositions for $x \geq 0.30$ were prepared under argon.

Phase-purity determination was performed with a Cu Kα Bruker D8 parallel-beam X-ray diffractometer over 10–100° 2θ, a step size of 0.02° and a count time of 10 s. Unit-cell parameter determination was performed using the program TOPAS [9]. Neutron data for structural analysis were collected at room temperature on the DUALSPEC C2 high-resolution powder diffractometer located at the Chalk River Laboratories, Ontario, Canada. Approximately 2–3 g of sample were loaded into vanadium cans for data collection. The wavelength used was $\lambda = 1.3282(1)$ Å, and data collection covered a 2θ range of 10–80°, $\Delta 2\theta = 0.10°$. The patterns were refined using the GSAS package to perform Rietveld analysis [10].

Oxygen contents were determined by iodometry using potentiometric methods with a MetrOhm 751 GDP Titrino autotitrator. These results were confirmed by thermogravimetric analysis obtained under reducing conditions in 10% H_2/90% N_2 atmosphere on a STA-780 Series, Stanton Redcroft Thermal Analyzer, heated at 10 °C/min up to 850 °C. All calculations were based on nominal cation contents.

Single phase $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ produced by conventional and microwave processing were deposited onto sintered electrolyte discs of $Ce_{0.1}Gd_{0.9}O_{3-\delta}$ and $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ supplied by Praxair. The $x = 0.10$ cathode material was mixed with terpinol to form an ink, which was subsequently painted onto both sides of the electrolyte and dried, followed by sintering in a conventional furnace in air at 1000 °C for 2 h. The sintered bodies were examined using backscattering scanning electron microscopy with a Hitachi S-4700 FEG-SEM.

AC impedance spectroscopy measurements were carried out on a Solartron 1260 FRA over the frequency range

Table 1
Unit cell and atomic coordinates for $La_2Ni_{0.50}Co_{0.50}O_{4.147}$ (*F4/mmm*, $a = 5.4904(3)$ Å, $c = 12.5694(8)$ Å) and $La_2Ni_{0.4}Co_{0.6}O_{4.093}$ (*Bmab*, $a = 5.4857(3)$ Å, $b = 5.5046(3)$ Å, $c = 12.5999(6)$ Å)

Atom	Mult	x	y	z	Occupancy	U_{iso}
La	8	0	0	0.3616(2)	1	0.0065(8)
			0.0014(18)	*0.3618(2)*		*0.0064(6)*
Ni	4	0	0	0	0.499(14)	0.0026(15)
					0.391(10)	*0.0033(12)*
Co					0.501(14)	0.0026(15)
					0.609(10)	*0.0033(12)*
O(1)	8	0.25	0.25	0	1	0.0069(10)
				−0.0068(5)		*0.0053(7)*
O(2)	8	0	0	0.1713(8)	0.603(16)	0.0061(21)
			−0.0214(5)	*0.1729(5)*	*0.697(14)*	*0.0083(15)*
O(3)	8	0.25	0.25	0.25	0.083(7)	0.0061(21)
				0.2366(47)	*0.074(6)*	*0.0083(15)*
O(4)	32	−0.0689(29)	−0.0689(29)	0.1757(20)	0.097(6)	0.0061(21)
	16	*0.057(4)*	*0.0766(51)*	*0.1729(5)*	*0.138(10)*	*0.0083(15)*

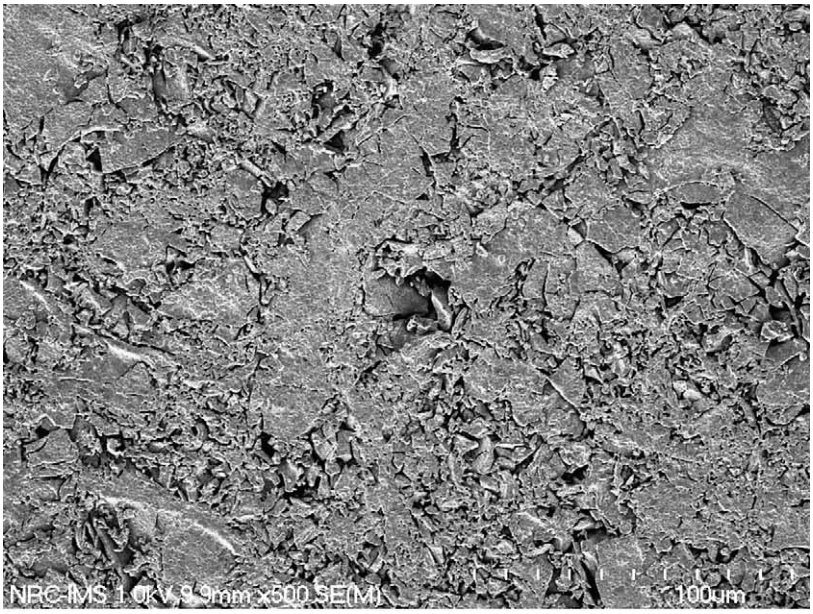
The data for the orthorhombic phase are in italics.

13 MHz to 0.01 Hz and a temperature range of 500–900 °C. This data was then normalised to give an area specific resistance for each of the symmetrical cells tested. Long-term stability was evaluated by firing the cathode-electrolyte pellets at 950 °C in air for 2 weeks.

3. Results and discussion

All of the materials prepared in this study were identified as single-phase by X-ray diffraction. As previously reported, the oxygen excess, δ, as determined by iodometric titration showed an apparent trend of increased δ with cobalt content, regardless whether the samples were prepared in air or argon [8]. A decrease in δ at $x = 0.60$ indicated a possible structural phase transition. Initial structural investigations by X-ray diffraction (XRD) revealed two general structural types, tetragonal *F*4/*mmm* (non-standard setting of *I*4/*mmm*) and orthorhombic *Bmab* with some ambiguity in the $x = 0.50$ and 0.60 compositions.

The refined unit-cell parameters (Fig. 2) indicate a deviation from the expected tetragonal *c*/*a* ratio of 3.30 and



(a)

(b)

Fig. 3. Backscattered SEM images of (a) conventional and (b) microwave prepared $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ materials after firing at 1150 °C for 6 h.

signals the presence of a structural distortion [11]. It also shows an increase in $a + b$ with cobalt content, x, whereas the c-parameter decreased sharply for the air-prepared samples, $x = 0.00$–0.20, followed by a steady increase for the argon-prepared samples, $x = 0.30$–1.00. This data, together with the dependence on δ [8], suggests the c-parameter is strongly coupled to the electronic state of the cobalt ions. Structural refinements by Rietveld analysis of the powder neutron diffraction data were carried out with the interstitial defect models proposed earlier [3,4]. Whilst the distribution of oxygen across the sites was allowed to refine, the total oxygen contents were constrained to the values obtained by iodometric titration for all the refinements. The neutron data indicated that $x = 0.50$ was still tetragonal $F4/mmm$, but $x = 0.60$ has transformed to the orthorhombic $Bmab$ cell. The refined structural parameters for these two compositions are shown in Table 1. Typical R_{wp} residuals for all compositions in the series were in the range of ~3.7–5.7%.

The sintering behaviour of the materials after firing for 6 h both conventionally and using microwaves were significantly different, as shown by the SEM images in Fig. 3. It is clear that the microwave-prepared materials were more porous than the conventionally prepared samples. It is thought that the more porous nature of the microwave-prepared sample is the cause of the improved ASR results for the microwave-prepared materials on CGO, see Fig. 4. The smaller variation in the ASR values observed with LSGM shows relative insensitivity to the type of firing method used. This can be explained by the fact that the Ruddlesden–Popper structure is structurally more closely matched to that of LSGM having a basic perovksite unit as compared to CGO, which has the antifluorite structure. Increasing the firing time in the microwave furnace to 12 h, yielded a material with similar porosity to the sample fired for 6 h in a conventional furnace.

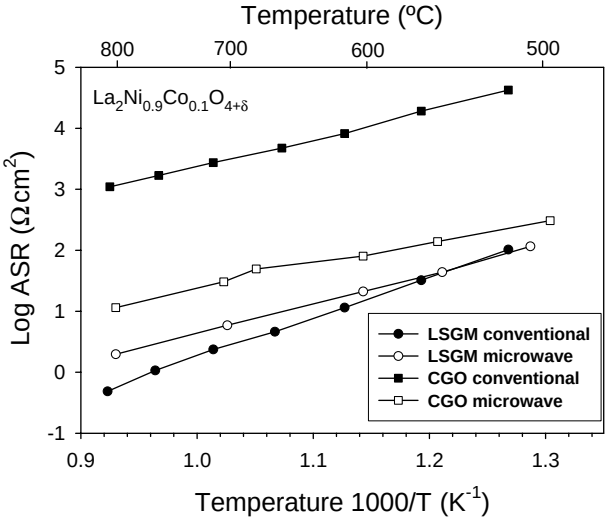


Fig. 4. Comparison of ASR data for $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ cathodes prepared by conventional and microwave methods.

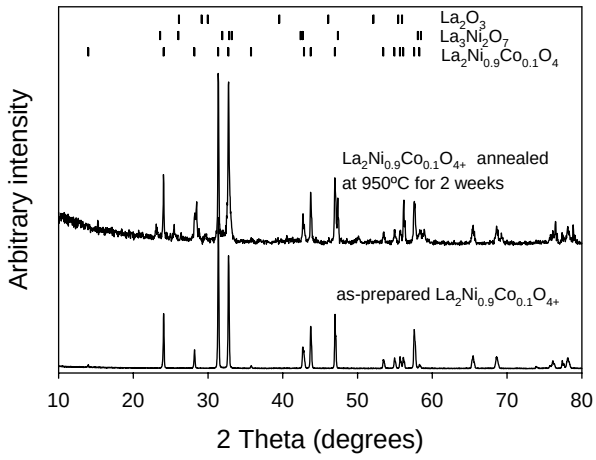


Fig. 5. X-ray diffraction pattern of as-prepared $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$, and after firing at 950 °C in air for 2 weeks on CGO. The strong (>10%) lines for $La_3Ni_2O_7$ (PDF card 82-1934), and La_2O_3 (PDF card 5-602), together with refined positions for as-prepared $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ are also indicated.

The long-term stability of $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ on both CGO and LSGM was tested by extended firing at 950 °C in air. Fig. 5 shows the X-ray diffraction pattern of $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ after firing at 950 °C for 2 weeks on CGO compared to the as-prepared powder. It can be seen that extensive decomposition has occurred. Decomposition products include oxidised lanthanum nickelates such as $La_3Ni_2O_7$. The same behaviour was observed for the electrodes deposited on LSGM. It is possible that the kinetics of the degradation reaction in the intermediate temperature SOFC range (<900 °C) may be so slow that degradation would be negligible, but further study would be necessary to confirm this.

4. Conclusions

The solid solution, $La_2Ni_{1-x}Co_xO_{4+\delta}$, has been successfully prepared by the Pechini method using both conventional and microwave heating. Successive substitution of cobalt for nickel in this series leads to a structural phase transition from tetragonal $F4/mmm$ ($x = 0$–0.50) to orthorhombic $Bmab$ ($x = 0.60$–1.00).

$La_2Ni_{1-x}Co_xO_{4+\delta}$, where $0.00 \leq x \leq 0.20$, are stable in air, and therefore are potential candidates for SOFC cathode materials. Experiments have shown that microwave preparation of $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ for 6 h leads to higher porosity than conventionally synthesised material. It is hypothesised that this is the reason for the markedly lower ASR on CGO electrolyte. The long-term stability of $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ and CGO and LSGM is questionable, given the formation of secondary phases on extended annealing at 950 °C. However, the retention of the smaller grained microstructure formed by the microwave synthesis, means that microwave processing may have benefits for long-term per-

formance, and should be investigated further with other materials.

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