Cation inter-diffusion and formation of intermediate phases in CoO and La$_2$NiO$_{4+\delta}$ diffusion couples

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Abstract

Cation interdiffusion between La$_2$NiO$_{4+\delta}$ (LN) and CoO diffusion couples was investigated by thermal annealing in ambient air at 1200 °C for 48 and 168 hours, and analysis of the cross sections by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Co diffusion into the LN layer was significant, while Ni diffusion into the CoO layer was minor. Formation of LaCoO$_3$, LaCo$_{0.5}$Ni$_{0.5}$O$_3$, and La$_3$(Ni$_{0.8}$Co$_{0.2}$)$_2$O$_7$ were observed in the LN layer at increasing distance from the boundary.

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## 1. Introduction

Lanthanum nickelate (LN), belongs to the Ruddlesden-Popper (RP) series, consisting of LaNiO$_3$ perovskite alternating with LaO rock salt layers [1]. In ambient atmosphere LN is orthorhombic below 150 °C and tetragonal at higher temperatures [2]. LN exhibits both electronic and ionic conductivity, and is a promising mixed conductor. Co$_3$O$_4$ (spinel) is stable below 900 °C in ambient atmosphere while CoO (rock salt) is stable above [3].

Annealing of diffusion couples followed by a combination of SEM- and EDS-analysis across the interface is a versatile method used in assessment of counter diffusion and formation of secondary phases [4-6]. Determination of cation diffusion in high temperature oxide systems is important to foresee the components' compatibility, and predict the sintering and creep properties [7].

In this project we aimed at designing an oxygen permeable membrane able to self-heal in case of microcracking during operation, based on the assumption of fast diffusion of $Co^{2+}$ in $La_2NiO_{4+\delta}$. The cation interdiffusion was studied on LN/CoO diffusion couples exposed in ambient air at 1200 ℃ followed by SEM/EDS analysis across the interface. To the best of our knowledge, no similar study has been reported in the literature.

## 2. Experimental

CoO (99.9 %) and LN (99.0 %) powder were purchased from CerPotech AS. The reaction between CoO and LN was investigated using stoichiometric powder mixtures, calcined in air at 1200 °C for 8 h, followed by XRD analysis using Bruker AXS D8 Advance diffractometer. Ø10 mm LN pellets were sintered in air for 8 hours at 1300 °C at heating and cooling rates of 200 °C/h. One pellet surface was polished using SiC paper and diamond suspension. CoO pellets were prepared by sintering in air at 1400 °C for 4 h and polished. Samples were ultrasonically cleaned using isopropanol, and oven-dried at 80 °C.

 Densities were determined using the Archimedes method and averaged to 98.1 % for LN and 92.3 % for CoO relative to the theoretical density.

The polished surfaces were aligned in contact and annealed in ambient air at 1200 °C for 48 and 168 h. To avoid detachment after annealing, the diffusion couple were carefully mounted in epoxy prior to polishing of the cross-section.

The polished cross sections were ultrasonically cleaned and examined by SEM and EDS to assess the elemental distribution across the interface. In EDS analysis, matrix effects were accounted for by application of the ZAF algorithm.

### 3. Results and Discussion

Fig. 1 shows the line scan of the cation composition and B/A-ratio ((Co + Ni)/La) versus diffusion distance. Since CoO is stable in ambient air at 1200 °C [8], it was considered to be maintained during annealing.

The black area between the CoO and LN corresponds to epoxy introduced during sample preparation. The interspace was expected due to some surface roughness and the fact that they were aligned without clamping. Wetting between epoxy and oxides during casting gave a <5 μm separation between CoO and LN.

Between the diffusion couple, there is a significant drop in atomic composition. However, its non-zero composition may be related to the introduction of components during polishing, despite the ultrasonic cleaning.

Significant diffusion of Co into the LN layer, minor diffusion of Ni and negligible diffusion of La into the CoO layer is observed.

In Fig. 1(a), the resulting phases in the LN layer following the diffusion of Co is not obvious since no plateaus in the Co content, which decreases continuously with distance, reaching almost zero at 50 μm. The B/A-ratio ((Co+Ni)/La) depicts the phases formed. The general formula for RP phases ($A_{n+1}B_nO_{3n+1}$) corresponds to $A_2BO_4$, $A_3B_2O_7$ and $A_4B_3O_{10}$, with B/A ratios of 0.5, 0.67 and 0.75 for n = 1, 2 and 3, respectively. For a perovskite phase ($ABO_3$), the B/A ratio is 1. Hence, according to the B/A ratio, a perovskite is formed between 15 and 25 μm, corresponding to $La(Co,Ni)O_3$ and the LN phase is preserved from 35 μm, with some Co on the B-site.
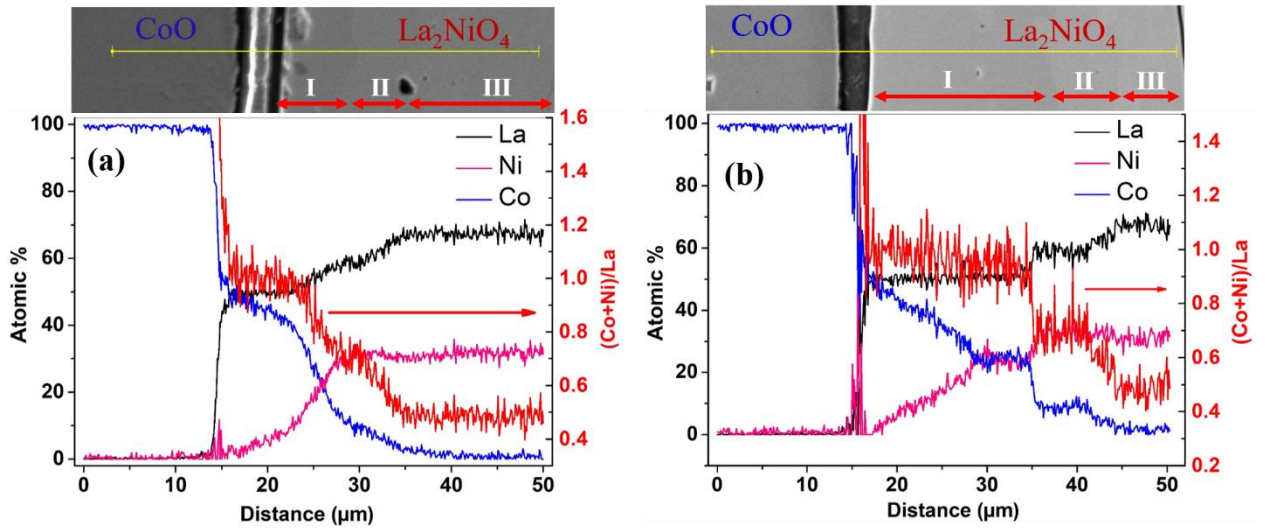
**Figure 1.** Cation compositions and B/A ratio ((Co+Ni)/La) versus distance in the diffusion couple annealed in air at 1200 °C for 48 h (a) and 168 h (b).

The diffusion couple annealed for 168 hours (Fig. 1(b)) shows distinct plateaus with respect to the B/A ratio, corresponding to intermediate phases formed. There is a small increase in the diffusion distance of Co when increasing the time from 48 to 168 hours. In region I, the average value of the B/A ratio is approximately 1, confirming the formation of a $LaNi_{1-x}Co_xO_{3-\delta}$ perovskite phase.  In this region, the La content is constant (~50%) and the remaining 50% is distributed between Ni and Co.  Co content decreases while Ni content increases with distance from the boundary layer. Between 28 and 35 μm, the content of Ni and Co is equal and constant, corresponding to the formation of a $LaNi_{0.5}Co_{0.5}O_{3-\delta}$ perovskite phase due to reaction between LN and CoO,  which is supported by the calcination of CoO/LN powder mixture with molar ratio 1:0.5, followed by XRD analysis. Pawley fit of the XRD diffractogram of the sample is shown in Fig. 2. The fitting was conducted with reference to a rhombohedral perovskite $LaNi_{0.5}Co_{0.5}O_{3-\delta}$ (*R-3c*). The lattice parameters were 5.464 Å and 13.130 Å for "a" and "c" respectively, in agreement with previously reported [9], and support the formation of a perovskite as observed by the EDS analysis. However, in further studies it is recommended to confirm

the formation of new phases by X-ray microscopy as recently reported for electrolyte/cathode interfaces [10].
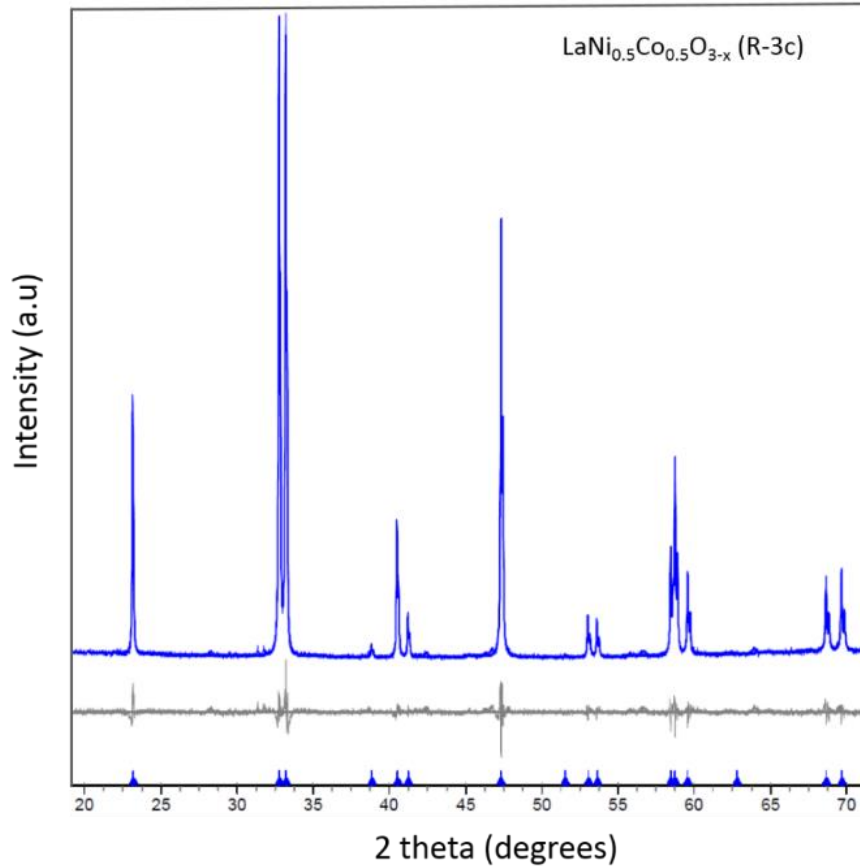


**Figure 2.** Pawley fitting of the XRD diffractogram resulting from reacting a 1:0.5 powder mixture of CoO and LN at 1200 °C in air. The formation of $LaNi_{0.5}Co_{0.5}O_{3-\delta}$ is confirmed.

A steep decrease in the Co content is observed in Fig. 1(b) at about 35 μm, accompanied with a decrease in the B/A ratio to about 0.7, corresponding to the formation of $La_3(Ni,Co)_2O_7$ RP phase. In this region the Ni and Co compositions are about 30% and 8%, respectively, corresponding to the formation of a RP phase with stoichiometry $La_3(Ni_{0.8}Co_{0.2})_2O_7$. At about 45-50 μm, the B/A ratio is equal to 0.5, equivalent to the pristine LN phase. However, since some small amounts of Co is present, the composition is more correctly described as $La_2(Ni_{1-x}Co_x)O_4$.

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Fig. 3 shows a SEM image of the diffusion couple annealed at 1200 °C for 168 hours, and the EDS point analysis is indicated by spectrum 1 to 4. There is a difference in contrast between spectrum 2 and 3 due to the formation of intermediate phases.

Spectrum 1 corresponds to $Co_{1-x}Ni_xO$ with minor content of Ni and La. The composition of spectrum 2 at the LN side reveals a significant diffusion of Co into the LN layer. According to the B/A-ratio a perovskite phase with composition $LaCo_{0.9}Ni_{0.1}O_3$ is formed. Spectrum 3 and 4 show both a stoichiometry corresponding to an RP phase ($La_2(Ni_{1-x}Co_x)O_4$, with negligible amounts of Co in Spectrum 4, in agreement with the EDS line scan discussed in Fig. 1b, where the formation of intermediate phases were documented by the (Co+Ni)/La ratio. The Ni content in spectrum 2 is low because Co diffusion into the LN layer is significantly higher than Ni diffusion into the CoO layer. The presence of a high proportion of Co reduces the relative amount of Ni in the LN. La content in the LN layer is relatively high due to neglibible La diffusion into CoO. However, although the EDS analysis was done by applying the ZAF algorithm, even higher accuracy may be achieved by using standard references, which is recommended in future work.
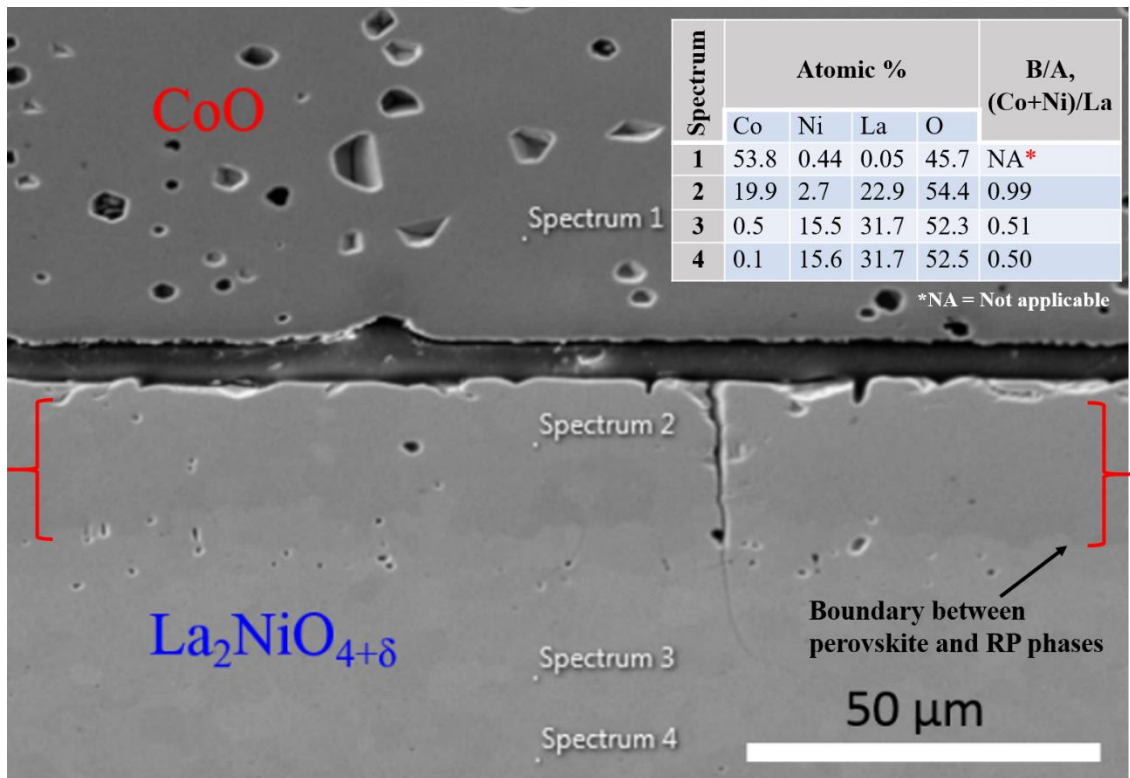
**Figure 3:** SEM image of the cross section of CoO–LN diffusion couple annealed at 1200 °C for 168 h. The inset shows the corresponding atomic compositions and the B/A-ratio.

In the context of self-healing by formation of intermediate phases, the findings may be useful in various high temperature electrochemical devices such as oxygen transport membranes, hydrogen transport membranes, solid oxide fuel cells, and proton conducting fuel cells [11].

## 4. Conclusion

Cation interdiffusion was investigated using $La_2NiO_{4+\delta}$ and CoO as diffusion couples. Significant diffusion of Co into the $La_2NiO_{4+\delta}$ was observed, with minor diffusion of Ni into the CoO layer and negligible diffusion of La into the CoO layer. The diffusion of Co was followed by a reaction forming the perovskite phase $LaNi_{1-x}Co_xO_{3-\delta}$ close to the boundary layer. The Ni-Co composition in the $LaNi_{1-x}Co_xO_{3-\delta}$ was changing with distance. Away from the boundary layer next to the perovskite phase, a RP phase with

the composition $La_3(Ni_{0.8}Co_{0.2})_2O_7$ was formed for diffusion couples annealed at 1200 °C for 168 h.

## 5. References

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