

Determination of Ni²⁺ self diffusion coefficient in La₂NiO_{4+d} by the solid state reaction method

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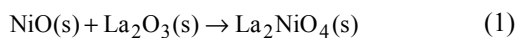
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La₂NiO_{4+d} exhibits mixed oxide ionic and electronic conductivity in combination with low thermal and chemical expansion, properties of interest for oxygen gas separation membranes [1]. The oxygen potential gradient across the membrane during operation enforces migration of cations that may lead to kinetic decomposition and demixing and morphological instability. Thus, cation diffusion, in principle, determines the membrane's life-time, and data on these processes is, as such, invaluable.

This contribution addresses cation diffusion in La₂NiO_{4+d} studied by the solid-state reaction method. The self diffusion coefficient of the faster moving cation in La₂NiO_{4+d} is thereby determined, can be compared with data for other materials, and may serve as basis for evaluating the life time of La₂NiO_{4+d} membranes.

In the solid-state reaction method, two diffusion couples, in this case dense polycrystalline samples of NiO and La₂O₃, are held in contact in a spring-load assembly and annealed in the temperature range from 950 to 1350 °C, for different durations at each temperature. Effects of the oxygen partial pressure on the growth kinetics were investigated by annealing in oxygen, air and argon (~10 ppm O₂).

XRD and EPMA confirmed that single-phase La₂NiO_{4+d} forms according to overall reaction:



The thickness of the product layer increases as a function time corresponding to parabolic kinetics, as illustrated in Fig. 1.

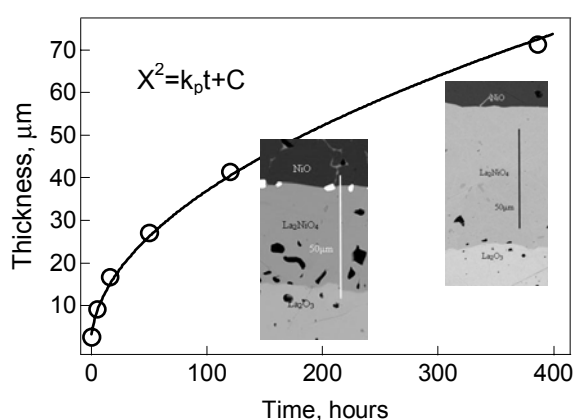


Figure 1: Product thickness as a function of annealing time in air at 1350°C, with SEM cross-sections of the product layer after 120 and 500 hours. The position of the Pt-marker at the NiO/La₂NiO₄ interface shows that Ni diffusion dominates the growth.

The inert markers, in this case Pt painted at the interface

between NiO and La₂O₃ before the annealing, end up at the NiO/La₂NiO₄ interface (cf. Fig. 1). This indicates that the growth is determined by Ni diffusion across the product layer.

From the classical works of Wagner's [2] we have

$$k_p = -\frac{V_m}{RT} \int_{\mu_{\text{Ni(Ni)}}}^{\mu_{\text{Ni(La)}}} D_{\text{Ni}^{2+}} c_{\text{Ni}^{2+}} d\mu_{\text{Ni}} \quad (2)$$

relating the parabolic rate constant, k_p , and the Ni²⁺ self-diffusion coefficient, $D_{\text{Ni}^{2+}}$. The self diffusion coefficient of Ni in La₂NiO_{4+d} can now from the temperature dependence of k_p and by integration of Eq (2) be expressed as:

$$D_{\text{Ni}^{2+}} \left(\frac{\text{cm}^2}{\text{s}} \right) = (1.1 \pm 0.5) \cdot 10^{-2} \cdot \exp\left(\frac{-271 \pm 7 \text{ kJ/mol}}{RT} \right) \left(1 - \exp\left(\frac{\Delta G_T^0}{RT} \right) \right)^{-1} a_{\text{La}_2\text{O}_3} \quad (3)$$

Here, ΔG_T^0 is the Gibbs energy of the reaction in Eq. 1. Since nickel diffusion depends also on the activity of La₂O₃, $a_{\text{La}_2\text{O}_3}$, across the La₂NiO₄ layer, the self-diffusion cannot be represented by one simple Arrhenius relation. Rather one may give values valid for the two interfaces, La₂NiO₄/La₂O₃ and La₂NiO₄/NiO. This we do in Fig. 2 where the calculated self-diffusion coefficients are plotted in an Arrhenius representation.

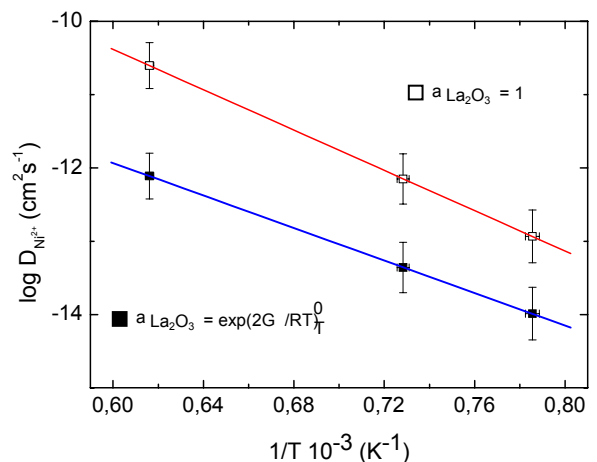


Figure 2: Log D_{Ni} vs $1/T$ at the La₂NiO₄/La₂O₃ and La₂NiO₄/NiO interfaces as measured in air

The activation energies Ni self diffusion at the La₂NiO₄/La₂O₃ and La₂NiO₄/NiO interfaces are, respectively, $E_a=263 \pm 52$ kJ/mol and $E_a=212 \pm 52$ kJ/mol.

The transport data derived in this work by solid state reaction will be compared to similar data based on tracer- and inter-diffusion measurements. On these bases the transport mechanism will be discussed in more detail. Moreover, the cation diffusion in La₂NiO_{4+d} will be compared to other potential materials for oxygen separation membranes, e.g. perovskite-structured mixed oxide ion-electron conductors.

References

- [1] S. J. Skinner, J. A. Kilner, *Solid State Ionics*, **135**, 709 (2000)
- [2] C. Wagner, *Z. Phys. Chem. (B)*, **21**, 25 (1933); **34**, 309 (1936)