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Oxygen transport in $La_2NiO_{4+\delta}$: Assessment of surface limitations and multilayer membrane architectures

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ABSTRACT

The steady-state oxygen permeation through dense $La_2NiO_{4+\delta}$ ceramics, limited by both surface exchange and bulk ambipolar conduction, can be increased by deposition of porous layers onto the membrane surfaces. This makes it possible, in particular, to analyze the interfacial exchange kinetics by numerical modelling using experimental data on the oxygen fluxes and equilibrium relationships between the oxygen chemical potential, nonstoichiometry and total conductivity. The simulations showed that the role of exchange limitations increases on reducing oxygen pressure, and becomes critical at relatively large chemical potential gradients important for practical applications. The calculated oxygen diffusion coefficients in $La_2NiO_{4+\delta}$ are in a good agreement with literature. In order to enhance membrane performance, the multilayer ceramics with different architecture combining dense and porous components were prepared via tape-casting and tested. The maximum oxygen fluxes were observed in the case when one dense layer, ~60 μm in thickness, is sandwiched between relatively thin (<150 μm) porous layers. Whilst the permeability of such membranes is still affected by surface-exchange kinetics, increasing thickness of the porous supporting components leads to gas diffusion limitations.

1. Introduction

Mixed-conducting materials derived from K_2NiF_4-type $La_2NiO_{4+\delta}$ are of substantial interest for high-temperature electrochemical applications, in particular, cathodes of solid oxide fuel cells (SOFCs) and ceramic membranes for oxygen separation and natural gas conversion reactors [1–11]. The advantages of La_2NiO_4-based compositions include relatively high oxygen ionic and p-type electronic conductivities, moderate thermal and chemical expansion, and high electrocatalytic activity. The oxygen permeability of dense nickelate membranes is essentially limited by kinetics of surface redox processes [1,3,6,10], which prevents bulk decomposition and enables stable operation under air/CH_4 gradients up to temperatures as high as 1173 K [4]. At the same time, partial reduction of the nickelate surface exposed to reducing atmosphere results in the formation of porous La_2O_3-supported Ni catalyst layer, providing a high selectivity towards partial oxidation of methane [5]. One promising concept for the ceramic membrane developments relates to asymmetric configurations where a thin dense highly-permeable layer is sandwiched between two porous sheets made of similar compositions [12–14]. The porous components enhance specific surface area and exchange rates, and may simultaneously act as the membrane and catalyst supports and, when necessary, protective diffusion barriers preventing surface poisoning and reductive decomposition. The present work was focused on the evaluation of surface contributions to the oxygen chemical potential drop across $La_2NiO_{4+\delta}$ membranes, and on the assessment of multilayer nickelate ceramics with porous layers, prepared using tape-casting.

2. Experimental

The powder of $La_2NiO_{4+\delta}$ was synthesized by glycine-nitrate process (GNP), followed by annealing in air at 1070–1370 K for 2–4 h and subsequent ball-milling. X-ray diffraction (XRD) analysis confirmed the formation of single K_2NiF_4-type phase (space group *I4/mmm*, unit cell parameters: $a=3.8646(4)$ Å, $c=12.691(4)$ Å). The disk-shaped samples, hereafter referred to as "standard", were uniaxially pressed at 150–200 MPa and sintered at 1590 ± 5 K for 2 h in air. The density of the standard $La_2NiO_{4+\delta}$ membranes was 98 ± 1% of their theoretical density calculated from XRD data; the thickness (L) varied in the range 0.6–1.0 mm. For the fabrication of multilayer ceramics via tape-casting, slurries containing the as-prepared $La_2NiO_{4+\delta}$ powder without or with

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graphite pore-forming additive (3 wt.%), ethanol, butyl acetate, butyral resin and a plasticizer were introduced in an injection-molding machine and a series of 30 ± 1 μm thick tapes were fabricated; then the membranes with different architecture were prepared by laminating various sets of these tapes and sintering at 1570 ± 5 K for 2 h. In this work, data on four types of the tape-casted membranes are compared. The first two are based on single-layer dense ceramics with $L = 0.35$ mm without or with feed-side surface modification. In the latter case, porous layers of $La_2NiO_{4+\delta}$ (sheet density of 2–4 mg/cm^2) were deposited onto the feed side surface of the sintered single-layer ceramics. Hereafter these membranes are denoted as "1-layer" and "1-layer activated", respectively. Fig. 1A illustrates the morphology of porous activating layer, evaluated by scanning electron microscopy (SEM). The 3-layer membranes of another group comprised a dense layer with $L \approx 60$ μm and two porous layers, 50 and 140 μm, as displayed by Fig. 1B. Similar membranes with thicker porous components were obtained sandwiching the as-laminated 3-layer compact between two additional layers made of $La_2NiO_{4+\delta}$ powder, graphite (15 wt.%) and polyvinyl acetate (3–5 wt.%). The resultant microstructure of the sintered 5-layer ceramics, tested in order to assess impact of the relatively thick membrane/catalyst supports, is shown in Fig. 1C. In selected cases, the porous supports were additionally modified infiltrating a very small amount of praseodymium oxide, known for its high catalytic activity in electrochemical reactions involving molecular oxygen [6,12], into the pores by impregnation with a diluted $Pr(NO_3)_3$ solution in ethanol and subsequent thermal decomposition at 800–900 K. The equipment and procedures used for microstructural characterization, oxygen permeation tests, total conductivity measurements and numerical modelling, were described elsewhere (see Refs. [3,4,6,15–17] and references cited). All data on steady-state oxygen permeability presented in this work correspond to the feed-side oxygen partial pressure, $p(O_2)_{feed}$, equal to atmospheric; the permeate-side oxygen pressure, $p(O_2)_{perm}$, varied in the range 5×10^{-3} to 0.2 atm. The reproducibility error of the oxygen permeation fluxes through dense $La_2NiO_{4+\delta}$ membranes was less than 10–12%; in the case of multilayer ceramics where the permeability is strongly affected by minor microstructural differences and defects in the porous supports, this error achieved 25–30%.

3. Results and discussion

Fig. 2 compares the oxygen permeation fluxes (j) through mono- and multilayer $La_2NiO_{4+\delta}$ membranes, shown as a function of the oxygen pressure gradient at 1123 and 1223 K. The deposition of porous layers leads to a substantially higher permeation, thus confirming that the overall oxygen transport is affected by surface exchange kinetics, in agreement with literature data revealing that the role of interfacial exchange as a permeation-limiting factor increases when temperature or oxygen partial pressure decreases [1,3,6,10]. A similar conclusion on non-negligible impact of the surface processes can be drawn analyzing the membrane thickness dependence of oxygen fluxes through the standard $La_2NiO_{4+\delta}$ ceramics without surface activation (Fig. 3). Note also that reducing permeate-side oxygen pressure leads to a smaller difference between the membranes with different thicknesses. Another necessary comment is that the effect of surface modification on the permeability of monolayer tape-casted membranes with $L = 0.35$ cm is almost invisible, comparable to the experimental error at 1223 K, but becomes obvious at 1123 K (Fig. 2).

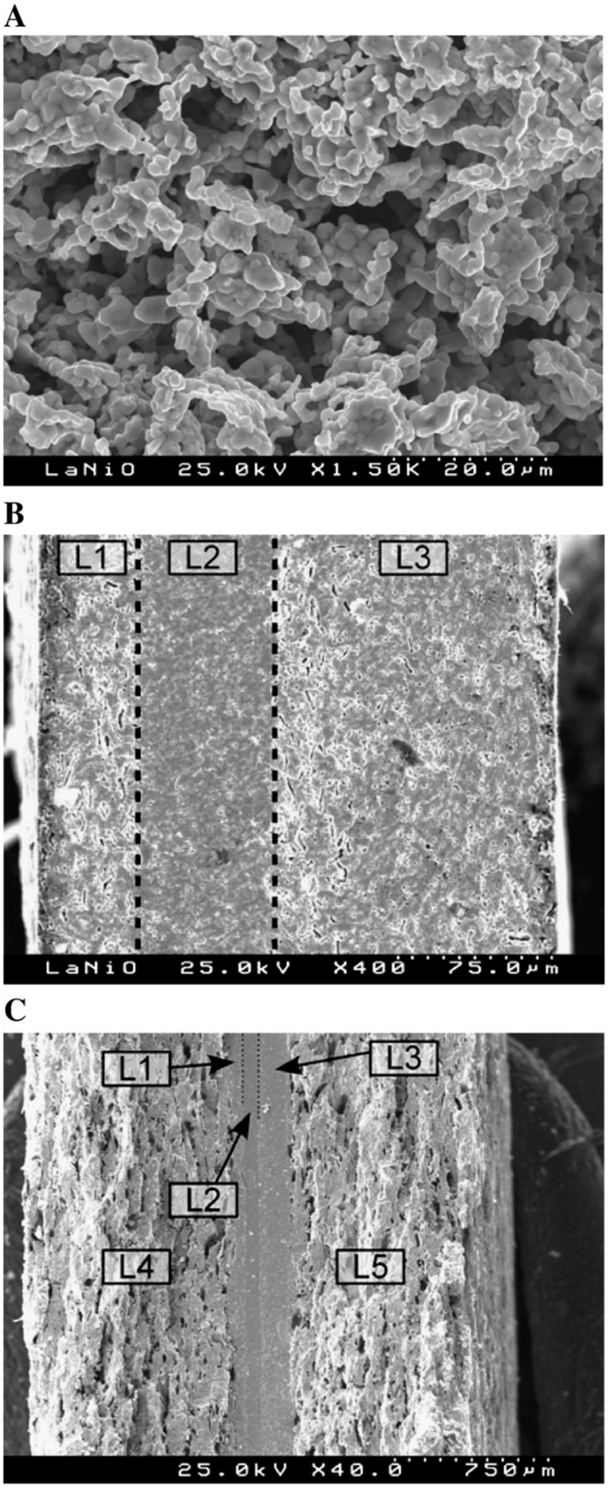

Fig. 1. SEM micrographs of the activated feed-side surface of monolayer $La_2NiO_{4+\delta}$ membrane (A), and cross-sections of 3-layer (B) and 5-layer (C) ceramics. For (B) and (C), L2 corresponds to the dense central layer; L1 and L3 are thin porous layers. L4 and L5 in (C) correspond to the additional porous layers.

This behavior makes it possible to model all rate-determining steps of the oxygen transport process by splitting the overall oxygen chemical potential gradient across $La_2NiO_{4+\delta}$ membranes into three parts, which correspond to the membrane bulk ($\Delta\mu_{bulk}$) and to the permeate-side ($\Delta\mu_{perm}$) and feed-side ($\Delta\mu_{feed}$) surfaces. The bulk contribution is determined by the partial ionic and electronic conductivities according to the Wagner equation:

$$j = \frac{1}{16F^2L}\int_{\mu^s_{perm}}^{\mu^s_{feed}} \sigma_{amb}\, d\mu = \frac{RT}{16F^2L}\int_{\mu^s_{perm}}^{\mu^s_{feed}} \sigma_O\left(1-\frac{\sigma_O}{\sigma}\right)d\mu \qquad (1)$$