Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 4269–4272

www.elsevier.com/locate/jeurceramsoc

Stability and oxygen transport properties of $Pr_2NiO_{4+\delta}$ ceramics

A.V. Kovalevsky [*], V.V. Kharton, A.A. Yaremchenko,
Y.V. Pivak, E.N. Naumovich, J.R. Frade

Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

Abstract

The oxygen permeability and stability of dense $Pr_2NiO_{4+\delta}$ ceramics have been appraised in comparison with K_2NiF_4-type lanthanum nickelate. In oxidizing atmospheres, $Pr_2NiO_{4+\delta}$ exhibit an extensive oxygen uptake and decomposition into the Ruddlesden–Popper-type $Pr_4Ni_3O_{10}$ and praseodymium oxide at temperatures below 900 °C. At 900–950 °C when the K_2NiF_4-type praseodymium nickelate is stable in the ceramic membranes placed under an oxygen partial pressure gradient, the steady-state oxygen permeability of $Pr_2NiO_{4+\delta}$ is similar to $La_2NiO_{4+\delta}$. The phase changes on cooling lead to considerably higher oxygen permeability, which becomes comparable to that of perovskite-type cobaltites, and to noticeable isothermal expansion. The stability of $Pr_2NiO_{4+\delta}$ in reducing atmospheres, estimated from the $p(O_2)$ dependencies of total conductivity and Seebeck coefficient, is lower than that of $La_2NiO_{4+\delta}$, probably due to a smaller size of the A-site cation.

Keywords: Ionic conductivity; Thermal expansion; Perovskites; Membranes; Praseodymium nickelate

1. Introduction

Due to relatively fast ionic and electronic transport and significant electrocatalytic activity rare-earth nickelates with K_2NiF_4-type structure are of substantial interest as a potential materials for the cathodes of intermediate-temperature solid oxide fuel cells (IT SOFCs) and oxygen-separation membranes.[1–5] For these systems, the maximum emphasis in literature was focused on lanthanum nickelate, $La_2NiO_{4+\delta}$, and its derivatives. The crystal structure of $La_2NiO_{4+\delta}$ is built of alternating rock-salt La_2O_2 and perovskite NiO_2 layers, and can accomodate a significant oxygen excess, charge-compensated by electron holes localized on nickel cations.[5] At the same time, $Pr_2NiO_{4+\delta}$ exhibits a larger range of the oxygen nonstoichiometry variations (and references therein),[4] due to smaller size of the A-site cations and, possibly, to the presence of a minor fraction of tetravalent Pr^{4+}. However, the effects of A-site cation radius on the oxygen transport properties are still unclear. In the case of isostructural cuprates, $Ln_2CuO_{4+\delta}$ (Ln = La, Pr, Nd), the ionic conduction was found to decrease with decreasing rare-earth cation size as La > Pr > Nd.[2] On the contrary, $Pr_2NiO_{4+\delta}$ was reported to exhibit the highest oxygen tracer diffusion coefficients in $Ln_2NiO_{4+\delta}$ series.[3] In particular, these contradictions may result from the metastability of the K_2NiF_4-type praseodymium nickelate phase at temperatures below 850 °C in oxidizing atmospheres.[4] The present work was aimed on the study of thermodynamic stability and oxygen transport properties of $Pr_2NiO_{4+\delta}$ in the vicinity of phase boundary; a particular attention was given to a comparative analysis of these properties with those of $La_2NiO_{4+\delta}$ in similar conditions.

2. Experimental

Powders of $Pr_2NiO_{4+\delta}$ and $La_2NiO_{4+\delta}$ were prepared via glycine–nitrate process; ceramic samples (hereafter called "as-prepared") with 95–98% density were sintered in air at 1320–1400 °C for 2–3 h and cooled down with a rate of 3–4 °C/min. As the processes of equilibration of the phase composition in ceramics are often kinetically stagnated, a series of $Pr_2NiO_{4+\delta}$ samples were annealed in air at 950 °C (24 h) or at 800 °C (50 h), or in flowing argon at $p(O_2) \approx 10^{-5}$ atm and at 950 °C (43 h) or at 800 °C (50 h) with subsequent quenching in liquid nitrogen followed by X-ray diffraction (XRD) analysis.

The XRD patterns were collected at room temperature using a Rigaku D/MAX-B diffractometer (Cu Kα, $2\Theta = 10–100°$, step 0.02°, 1 s/step); the structural parameters were refined employing the Fullprof program. A basic microstructural characterization was carried out using Hitachi S-4100 scanning

---

[*] Corresponding author. Tel.: +351 234 370263; fax: +351 234 425300.
E-mail address: akavaleuski@cv.ua.pt (A.V. Kovalevsky).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.136

electron microscope (SEM) with a Rontec UHV Detection system for the energy dispersive spectroscopy (EDS). Thermal expansion in air was studied using a vertical alumina Linseis L75V/1250 dilatometer; the measurement procedure included temperature cycling in the range 650–950 °C with the step of 50 °C and equilibration at each temperature during 3–7 h. Thermogravimetric analysis (TGA) was performed using a Setaram SetSys 16/18 instrument. Similarly to thermal expansion measurements, the TGA route included heating up to 950 °C in flowing dry air, and temperature cycling in the range 700–1000 °C with the step of 50 °C and equilibration at each temperature during 2–10 h.

The total conductivity (σ, 4-probe dc) and Seebeck coefficient (α) were measured as functions of the oxygen partial pressure varying in the range from 10^{-15} atm to 0.5 atm at 700–950 °C; the experimental technique was described elsewhere.[6] The technique to study oxygen permeation using a solid-electrolyte cell with an oxygen pump and sensor was also described in previous work.[7] In terms of thermal pre-history of the membranes, the procedure included heating (3 °C/min) up to softening of a glass sealant (1115 °C), dwell for 5 min, and cooling down to 950 °C when the isothermal measurements were started. Further route included temperature cycling in the range 1023–950 °C, with steps of 50 °C and equilibration at each temperature. The criterion for a steady-state achievement was formulated as independence of the sensor emf on time during 10 h, with an accuracy of 0.5–0.7%. After the determination of oxygen fluxes at 800–950 °C, all measurements were repeated two to four times in order to check reproducibility. The reproducibility error at temperatures far enough from the phase transition, such as 950 °C or 800 °C, was 5–7%. In the vicinity of phase transformation, temperature cycling resulted in a higher error, 20–30%.

3. Results and discussion

XRD analysis of the as-prepared materials showed the formation of single K_2NiF_4-type phases: namely, orthorhombic (SG *Bmab*) for $Pr_2NiO_{4+\delta}$ and tetragonal (SG *I*4/*mmm*) for $La_2NiO_{4+\delta}$, in agreement with literature data.[1,3,4,8] Corresponding XRD pattern of as-prepared praseodymium nickelate ceramics is presented in Fig. 1. Basic SEM inspection revealed high quality and low porosity of $Pr_2NiO_{4+\delta}$ ceramics, while no essential inhomogeneities and phase impurities were detected by energy dispersive spectroscopy.

Isothermal dilatometric studies and TGA tests of as prepared samples in air confirmed the metastability of Pr_2NiO_4-based solid solutions at low temperatures, as it was previously established in[4] and attributed to the phase decomposition at above 800 °C:

$$3Pr_2NiO_{4.14} \xrightarrow{O_2} Pr_4Ni_3O_9 + 2PrO_{1.71} \qquad (1)$$

and the backward reaction on further heating. At 900–950 °C the equilibrium sample length was attained during 0.1–0.3 h after cooling down to a given temperature, whilst an opposite behavior was observed at 700–850 °C (Fig. 2A). In particular, during testing at 800 °C for 6.5 h, the relative change in $\Delta L/L_0$ value was as high as 0.02%, what is considerably higher than the experimental error, and tends to further increase with time. The observed behavior may be explained taking into account the higher number of perovskite blocks in Ruddlesden–Popper-type $Pr_4Ni_3O_{10-\delta}$ compared to $Pr_2NiO_{4+\delta}$ and the fact that the thermal expansion of K_2NiF_4-type oxides is generally lower than that of perovskite-type oxides having the similar cation composition.[9] As for sample dimensions, the weight changes of powdered $Pr_2NiO_{4+\delta}$ exhibit a good reproducibility and fast equilibration on cycling at 925–950 °C (Fig. 2B). At lower temperatures, prolonged transient processes start at 900 °C and is accompanied with extensive oxygen uptake and noticeable increase in sample weight (Fig. 2C). Thus, within the limits of experimental uncertainties associated with stagnated kinetics of the phase changes, the temperature of decomposition of $Pr_2NiO_{4+\delta}$-based phase on cooling corresponds to 850–900 °C.

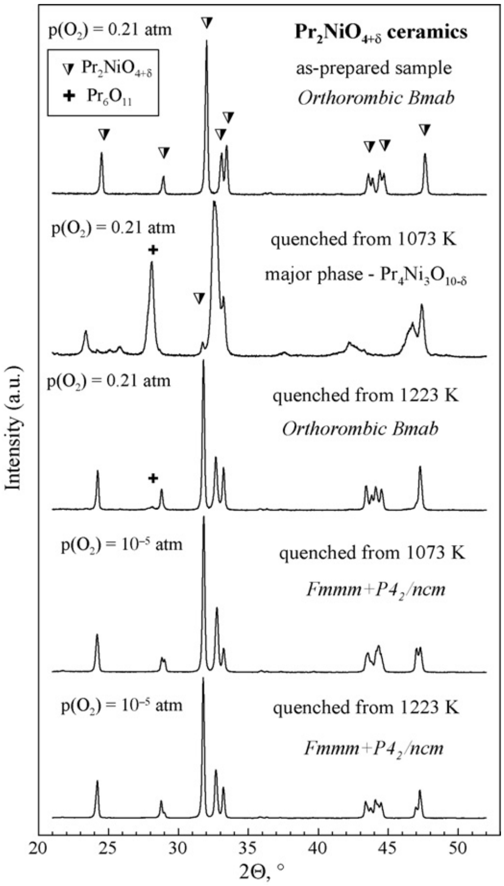

Fig. 1. XRD patterns of $Pr_2NiO_{4+\delta}$ quenched after annealing in air and argon (see text). The pattern of as-prepared $Pr_2NiO_{4+\delta}$ is given for comparison. In the cases when $Pr_4Ni_3O_{10-\delta}$ is major phase, all unmarked peaks correspond to this phase.

The above conclusions were further validated by XRD analysis. After annealing of as prepared sample at 800 °C in air and quenching, the major phases were identified as praseodymium oxide and $Pr_4Ni_3O_{10-\delta}$ (Fig. 1). After annealing of $Pr_2NiO_{4+\delta}$ at 950 °C in air, the K_2NiF_4-type phases were formed again: this material became almost single-phase. The presence of minor Pr_6O_{11} impurities is associated with kinetically stagnated phase

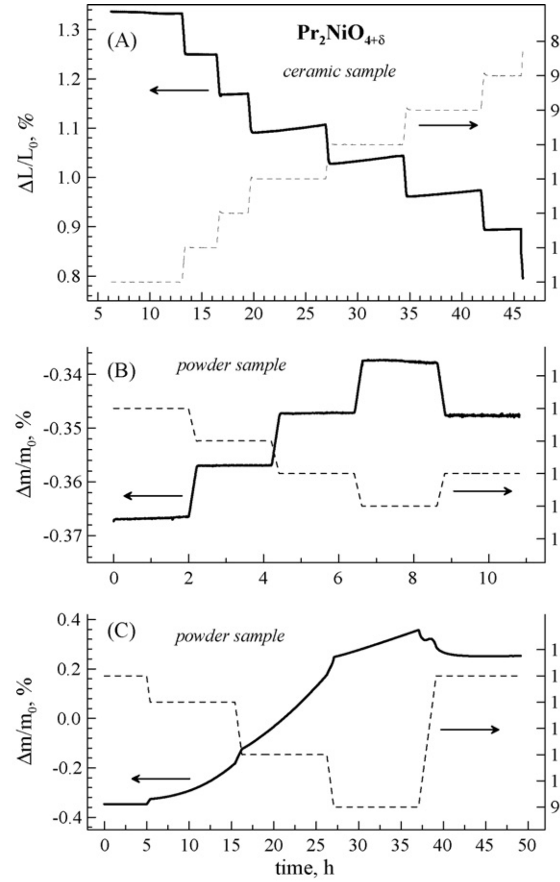

Fig. 2. Relative length (A) and weight changes (B and C) of as-prepared Pr_2NiO_4 during isothermal steps in air.

changes due to slow cation diffusion. Both quenching from 800 °C to 950 °C after annealing in argon ($p(O_2) \approx 10^{-5}$ atm) lead to formation of two K_2NiF_4-type phases. Although the symmetry of orthorombic $Pr_2NiO_{4+\delta}$ phases is known to depend on the oxygen content (e.g. Ref. 10), detailed neutron diffraction studies are necessary to determine exact effects of excess oxygen on the structure of Pr_2NiO_4-based solid solutions. Nevertheless, whatever the mechanism of structural changes, the XRD results confirm that the $Pr_2NiO_{4+\delta}$ is stable at moderate oxygen chemical potentials.

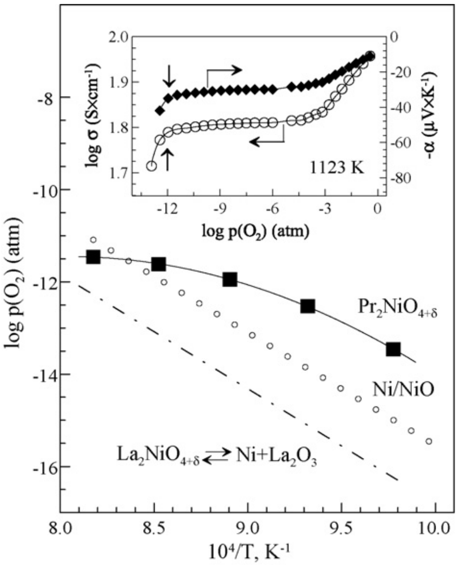

Fig. 3. Low-$p(O_2)$ stability limits of $Pr_2NiO_{4+\delta}$. Data on Ni/NiO phase boundary[13] and $La_2NiO_{4+\delta}$[11] are shown for comparison. Inset illustrates oxygen partial pressure dependencies of the total conductivity and Seebeck coefficient at 950 °C; bold arrows shows approximate limits of the K_2NiF_4-type phase existence domains.

The phase stability limits of $Pr_2NiO_{4+\delta}$ estimated from data on the total conductivity and Seebeck coefficient are presented in Fig. 3. The conductivity of $Pr_2NiO_{4+\delta}$ decreases with decreasing of oxygen partial pressure, while Seebeck coefficient has positive sign and increases (inset in Fig. 3), indicating a p-type electronic conduction within the phase stability domain. The decomposition of $Pr_2NiO_{4+\delta}$ occurs at oxygen chemical potentials higher than the stability limit of $La_2NiO_{4+\delta}$.[11] This trend well corresponds to literature data on other K_2NiF_4-type phases (e.g. Ref. 12 and references therein). In particular, thermodynamic stability of rare-earth cuprates with K_2NiF_4 structure also decreases with decreasing A-site cation radius.[12] At 900–950 °C the low-$p(O_2)$ stability limit of $Pr_2NiO_{4+\delta}$ is close to the Ni/NiO boundary,[13] but shifts towards higher oxygen partial pressures when temperature decreases (Fig. 3). This suggests a change in the decomposition mechanism and explains the observed deviations from the linear van't Hoff dependence, $\log p(O_2)$ versus $1/T$. Apparently, at high temperatures the decomposition of $Pr_2NiO_{4+\delta}$ occurs via formation of praseodymium oxide and metallic nickel, whilst below 877 °C the reduction should result in the binary oxides mixture, thus indicating a decrease in the thermodynamic stability of $Pr_2NiO_{4+\delta}$ compared to other phases of ternary Pr–Ni–O system.

Temperature dependence of steady-state oxygen permeation fluxes through $Pr_2NiO_{4+\delta}$ and $La_2NiO_{4+\delta}$ under a fixed oxygen chemical potential gradient is shown in Fig. 4. At temperatures higher or close to the phase transition, the levels of ionic transport in $Pr_2NiO_{4+\delta}$ and $La_2NiO_{4+\delta}$ are similar, as observed by the authors.[3] Although $Pr_2NiO_{4+\delta}$ is already metastable at 900 °C in air (Fig. 2C), XRD inspection of the membranes after testing at 900–950 °C did not reveal secondary phases. After temperature cycling, at 950 °C the oxygen permeation fluxes were reproducible with an accuracy of 5–7% (Fig. 4). The kinetic stabilization of K_2NiF_4-type nickelate might result from the

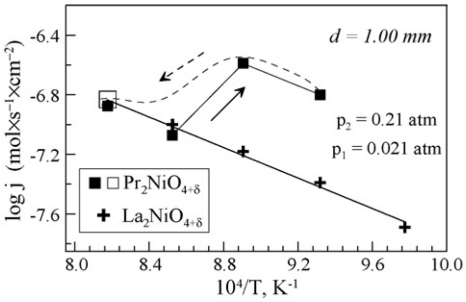

Fig. 4. Temperature dependence of steady-state oxygen permeation fluxes through $Pr_2NiO_{4+\delta}$ (open symbol corresponds to the reproducibility check) and $La_2NiO_{4+\delta}$ under a fixed oxygen chemical potential gradient.

presence of oxygen chemical potential gradient in the course of measurements, when the permeate-side oxygen pressure is lower than atmospheric.

Decreasing temperature down to 800–850 °C resulted in a slow increase in the oxygen permeability. The time necessary for stabilization was as long as 200–300 h. These processes can be undoubtedly ascribed to the partial decomposition in $Pr_4Ni_3O_{10-\delta}$ and PrO_x, confirmed by XRD. Although no systematic information on the ionic transport properties of the Ruddlesden–Popper-type $Pr_{n+1}Ni_nO_{3n+1}$ series is found in literature, the data on isostructural $(La,Sr)_{n+1}(Fe,Co)_nO_{3n+1}$ system[14] suggest that increasing the number of perovskite blocks (n) should increase oxygen diffusivity; $Pr_4Ni_3O_{10-\delta}$ is thus expected to possess a higher ionic conductivity compared to $Pr_2NiO_{4+\delta}$. A significant level of mixed ionic-electronic conductivity is also known for praseodymium oxide. Indeed, steady-state oxygen permeation fluxes through $Pr_2NiO_{4+\delta}$ ceramic membranes at 800–850 °C are four to five times higher than that of $La_2NiO_{4+\delta}$. In general, these results show, that the fast tracer diffusion and oxygen surface exchange of $Pr_2NiO_{4+\delta}$ ceramics at temperatures below 827 °C[3] may be partially contributed by $Pr_4Ni_3O_{10-\delta}$ and PrO_x, formed on partial decomposition of the K_2NiF_4-type praseodymium nickelate. The apparent activation energy (E_a) remains essentially unchanged, 98 kJ/mol for single-phase $La_2NiO_{4+\delta}$ and 97 kJ/mol for multiphase $Pr_2NiO_{4+\delta}$ ceramics, suggesting that the ionic transport mechanisms are still similar. However, the oxygen fluxes through praseodymium nickelate membranes are still lower than those through most permeable materials such as $Sr(Co,Fe)O_{3-\delta}$ perovskites.[7]

Acknowledgements

This work was supported by the FCT, Portugal (projects POCI/CTM/59197/2004 and SFRH/BPD/15003/2004), and by the NATO Science for Peace program (project 978002). Experimental assistance and helpful discussions, made by S. Yakovlev, A. Shaula and M. Patrakeev are gratefully acknowledged.

References

1. Kilner, J. A. and Shaw, C. K. M., Mass transport in $La_2Ni_{1-x}Co_xO_{4+\delta}$ oxides with the K_2NiF_4 structure. *Solid State Ionics*, 2002, **154/155**, 523–527.
2. Kharton, V. V., Viskup, A. P., Kovalevsky, A. V., Naumovich, E. N. and Marques, F. M. B., Ionic transport in oxygen-hyperstoichiometric phases with K_2NiF_4-type structure. *Solid State Ionics*, 2001, **143**, 337–353.
3. Boehm, E., Bassat, J.-M., Dordor, P., Mauvy, F., Grenier, J.-C. and Stevens, P., Oxygen diffusion and transport properties in non-stoichiometric $Ln_{2-x}NiO_{4+\delta}$ oxides. *Solid State Ionics*, 2005, **176**, 2717–2725.
4. Odier, P., Allançon, Ch. and Bassat, J. M., Oxygen exchange in $Pr_2NiO_{4+\delta}$ at high temperature and direct formation of $Pr_4Ni_3O_{10-x}$. *J. Solid State Chem.*, 2000, **153**, 381–385.
5. Kharton, V. V., Tsipis, E. V., Yaremchenko, A. A. and Frade, J. R., Surface-limited oxygen transport and electrode properties of $La_2Ni_{0.8}Cu_{0.2}O_{4+\delta}$. *Solid State Ionics*, 2004, **166**, 327–337.
6. Leonidov, I. A., Kozhevnikov, V. L., Mitberg, E. B., Patrakeev, M. V., Kharton, V. V. and Marques, F. M. B., High-temperature electrical transport in $La_{0.3}Sr_{0.7}Fe_{1-x}Ga_xO_{3-\delta}$ (x = 0–0.5). *J. Mater. Chem.*, 2001, **11**, 1201–1208.
7. Kharton, V. V., Tikhonovich, V. N., Shuangbao, L., Naumovich, E. N., Kovalevsky, A. V., Viskup, A. P. *et al.*, Ceramic microstructure and oxygen permeability of $SrCo(Fe,M)O_{3-\delta}$ (M = Cu or Cr) perovskite membranes. *J. Electrochem. Soc.*, 1998, **145**, 1363–1374.
8. Rodríguez-Carvajal, J., Fernández-Díaz, M. T. and Martínez, J. L., Neutron diffraction study on structural and magnetic properties of La_2NiO_4. *J. Phys. Condens. Matter*, 1991, **3**, 3215–3234.
9. Al Daroukh, M., Vashook, V. V., Ullmann, H., Tietz, F. and Arual Raj, I., Oxides of the AMO_3 and A_2MO_4-type: structural stability, electrical conductivity and thermal expansion. *Solid State Ionics*, 2003, **158**, 141–150.
10. Fernández-Díaz, M. T., Martínez, J. L. and Rodríguez-Carvajal, J., High temperature phase transformation of oxidized $R_2NiO_{4+\delta}$ (R = La, Pr and Nd) under vacuum. *Solid State Ionics*, 1993, **63–65**, 902–906.
11. Zinkevich, M. and Aldinger, F., Thermodynamic analysis of the ternary La–Ni–O system. *J. Alloys Compd.*, 2004, **375**, 147–161.
12. Kharton, V. V., Yaremchenko, A. A. and Naumovich, E. N., Research on the electrochemistry of oxygen ion conductors in the former Soviet Union, II. Perovskite-related oxides. *J. Solid State Electrochem.*, 1999, **3**, 303–326.
13. Charette, G. G. and Flengas, S. N., Thermodynamic properties of the oxides of Fe, Ni, Pb, Cu and Mn by EMF measurements. *J. Electrochem. Soc.*, 1968, **115**, 796–804.
14. Manthiram, A., Prado, F. and Armstrong, T., Oxygen separation membranes based on intergrowth structures. *Solid State Ionics*, 2002, **152/153**, 647–655.