

Intermediate temperature SOFC single cell test using $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ as cathode

C. Lalanne^a, F. Mauvy^{a,*}, E. Siebert^b, M.L. Fontaine^c, J.M. Bassat^a,
F. Ansart^d, P. Stevens^d, J.C. Grenier^a

^a ICMCB-CNRS, Université Bordeaux I, 87 Av. Schweitzer, 33608 Pessac Cedex, France

^b LEPMI-ENSEE, 1130 rue de la piscine, BP75, 38402 Saint-Martin d'Hères Cedex, France

^c CIRIMAT, Université P. Sabatier, Bât. 2R1, 118 route de Narbonne, 31062 Toulouse Cedex, France

^d EDF-EijER Emmy-Noether-Strasse 11, 76131 Karlsruhe, Germany

Available online 11 April 2007

Abstract

This work deals with SOFC single cell tests using neodymium nickelate $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ as cathode material. This MIEC oxide exhibits high values of both surface exchange coefficient (k) and oxygen diffusion coefficient (D^*), as well as high electronic conductivity, which result in an enhanced electrochemical activity with respect to classical materials. The SOFC cells were fabricated from an anode-supported electrolyte half-cell provided by InDEC B.V. Corporation, with a 36 mm diameter. The $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ cathode was prepared as a two-stage electrode consisting of a thin interlayer of several hundred nanometers covered by a thicker layer of dozens microns. The $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ oxide powders were synthesized using different routes in order to reduce the final annealing temperature, and to subsequently obtain submicronic powders. I – V characteristics of the single cells were investigated under hydrogen–air conditions. The power densities versus current densities curves are reported and the results of impedance spectroscopy measurements performed under these operating conditions are discussed.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Transition metal oxides; Fuel cells; Mixed conducting oxides

1. Introduction

The state-of-the-art SOFC materials are based on yttria-stabilised cubic zirconia (YSZ) as electrolyte material and Ni-YSZ cermet as anode material. LSM is mostly used as cathode material despite the fact that this oxide is a poor oxygen ionic conductor. So that, high working temperature of around 1000 °C is required to achieve satisfactory power density. Decreasing the temperature leads to a lower ionic conductivity of the solid electrolyte and higher polarization resistance of the electrodes. This is particularly highlighted at the cathode side. Depending on materials, several issues are therefore explored to keep high cell performance at reduced working temperature (600–700 °C). Concerning the electrolyte material, two solutions are considered: reducing its thickness or finding a new material exhibiting an ionic conductivity higher than that of the classically used yttria-stabilised zirconia. For the electrode, the cathodic over-

potential may be reduced by increasing the active area for the oxygen reduction from the triple phase boundary (TPB) between gas, electrode and electrolyte to the whole surface of the cathode. A conceivable solution is to use mixed ionic and electronic conductors (MIEC). The A_2MO_4 materials have been studied with this aim. Among those materials, $\text{Ln}_2\text{NiO}_{4+\delta}$ have shown a wide range of oxygen overstoichiometry (δ). The additional oxygen atoms occupy interstitial sites in the lattice so that the structure is stabilised, and are also involved in an interstitial oxygen diffusion mechanism.¹ Moreover, in these oxides, part of Ni^{2+} cations are oxidised into Ni^{3+} cations. As a consequence, both ionic and electronic conductivities are enhanced compared to those of classical perovskite-type materials for which the ionic conduction results from a vacancy mechanism of higher activation energy.² The excellent electrochemical performance of the nickelates has already been demonstrated on cathode/YSZ/cathode symmetrical half cells while measuring under zero d.c. conditions.^{3,4} The present work deals with SOFC single cell tests using these cathode materials deposited onto commercial anode/YSZ half cells. Polarization and impedance spectroscopy measurements were performed in order to quantify their performance.

* Corresponding author. Tel.: +33 540002517; fax: +33 540008373.
E-mail address: mauvy@icmcb-bordeaux.cnrs.fr (F. Mauvy).

2. Experimental

2.1. Preparation of $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$

The $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ oxides were prepared using three different routes. The first one is based on solid-state reaction. A stoichiometric mixture of rare-earth oxide (Nd_2O_3 , Strem, 99.99%) and nickel oxide (NiO, Aldrich, 99.9%) was annealed at 1300°C and then thoroughly grounded using a milling attritor. After this treatment, the obtained average particle size was around $1\ \mu\text{m}$. The second route was based on a nitrate–citrate process. A stoichiometric mixture of single oxides was first dissolved in nitric acid. Citric acid was then added in a molar ratio 1:1:1. The resulting solution was heated until a self-combustion of the precipitates occurs. The final material was obtained after an annealing at 1000°C . In this case, the average particle size reached $1\ \mu\text{m}$ after the attrition step. To reduce the annealing temperature and to obtain submicronic powders, a third synthesis route was therefore developed and was based on a polyacrylamide gel route.⁵ Individual aqueous solutions of each cation were prepared from nitrate salts. The cations were then chelated by adding either ethylenediaminetetraacetic (H_4EDTA) or triammonium citrate ($(\text{NH}_4)_3\text{Cit}$) (pH controlled via NH_4OH addition). Solutions of chelated cations were mixed in a stoichiometric ratio. The organic gels were made using monomers of acrylamide to form chains and the cross-linker N,N' -methylenebis-acrylamide. α,α' -Azobisisobutyronitrile (AIBN) dissolved in a few millilitre of acetone was used as a polymerisation initiator. The gel was transferred to a porcelain bowl and heated in a ventilated furnace at $3^\circ\text{C}/\text{min}$, up to 800°C , for 1 h. A final annealing at 1000°C was required to obtain the single phase $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$. The average particle size was finally about $0.6\ \mu\text{m}$ after an attrition stage. The polyacrylamide gel route was selected for SOFC cathode application because of the small particle size obtained by this way.

Oxide powders prepared by these three synthesis routes were characterized by X-ray diffraction using a Philips 1710 diffractometer ($\text{Cu K}\alpha$ radiation). All samples revealed a single-phase material exhibiting the K_2NiF_4 -type structure.

2.2. Fuel cell construction

SOFC tests were performed on single cells of anode–electrolyte–cathode systems. The samples were constructed from an anode supported electrolyte half-cell produced by InDEC B.V. Corporation, having a diameter of 36 mm. The sample consists of an anode-supported substrate coated with a dense 8YSZ electrolyte layer of 3–10 μm . The cathode was prepared as a two stages electrode consisting of a thin $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ interlayer of approximately 500 nm coated onto the electrolyte, covered by a thicker $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ layer of about 20–50 μm . The former layer was prepared by a polymeric route derived from Pechini's work.^{6,7} The polymeric sol was dip-coated two times onto the half cell and the resulting green layer was annealed in air at 1000°C for 2 h. A heating rate of $50^\circ\text{C}/\text{h}$ was used to prevent the formation of cracks during the thermal decomposition of organic compounds. The annealed layer was crystallized

and exhibited the K_2NiF_4 -type structure as shown by XRD analysis. The thick layer was prepared by the coating of a colloidal ceramic suspension made of $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ powder dispersed in ethylene glycol. The slurry was painted onto the thin interlayer by means of a brush. The green layer was annealed in air at 1200°C for 20 min to ensure a strong adhesion between the two cathodic layers. The whole electrode thickness was about 20–50 μm and the geometric area was $3.8\ \text{cm}^2$.

2.3. I – V characteristics

The morphology of the powders and the microstructure of the sintered cells were characterized by scanning electron microscopy (SEM) using a JEOL JSM 6360A apparatus.

I – V characteristics of the SOFC cell assembly were investigated by monitoring the current and the terminal voltage under various loads at fixed temperature in reducing atmospheres and air. Current collectors were gold grids welded to platinum wires. The electrical contact between gold grids and electrode materials were obtained by mechanical pressure. The gastightness between the anodic and the cathodic sides was ensured by use of a glass sealant. The YSZ–NiO cermet reduction was realized at 800°C in agreement with InDEC standard process, which consists in introducing an Ar-H_2 (5%) gas mixture and slowly increasing the hydrogen ratio. Electrochemical measurements were realized under the next conditions:

- Cathodic compartment: under air with a flow rate of 300 mL/min or 70 mL/min.
- Anodic compartment: under pure hydrogen with a flow rate of 100 mL/min or 30 mL/min, or under argon/hydrogen mixtures.
- Working temperatures: 800, 750, 700, 650 $^\circ\text{C}$ successively.

The impedance of the cell was recorded under operating conditions using a frequency response analyzer Solartron 1260 and a potentiostat Solartron 1287.

3. Results and discussion

The cross-section SEM picture of $\text{Nd}_{1.95}\text{NiO}_{4+\delta}/\text{YSZ}$ supported SOFCs, which was fired at 1200°C during 20 min has been performed. A good adhesion between dense electrolyte and the two porous electrodes has been observed.

The open circuit voltage (OCV) of the cell was firstly measured. In agreement with the Nernst law, the OCV values were found to be in-between 1.1 and 1.2 V, depending on the working conditions. This observation allows us to conclude that both sides of the cell were efficiently sealed. Then the gas flows were fixed at 30–35 mL/min for hydrogen and 70 mL/min for air. The polarization curve obtained at 700°C is reported in Fig. 1. At 800 mV, the current density is around $85\ \text{mA cm}^{-2}$. By extrapolation, the current density can be estimated at about 100–120 mA cm^{-2} under 700 mV.

In order to identify the resistances associated to the polarization curve, impedance spectroscopy measurements have been performed when the cell discharged through a variable load.

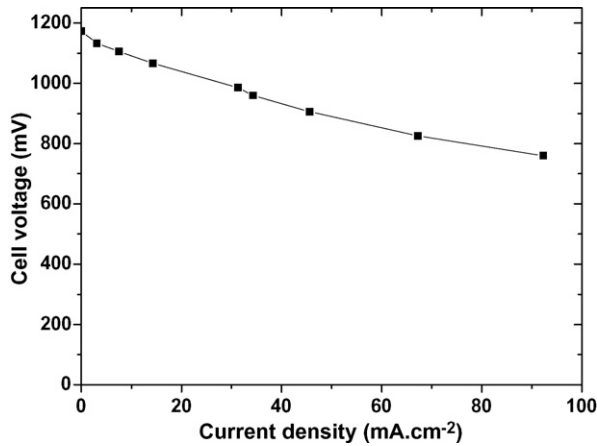


Fig. 1. Current–voltage behaviour of $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$ cathode single cell operated at 700°C (with 30 mL/min H_2 and 70 mL/min air).

In these measurement conditions, it can be considered that the assembly anode/electrolyte/cathode nearly acts as a working SOFC single cell. Under open circuit conditions, impedance diagrams have been decomposed into a high frequency self part, a resistance and two capacitive loops, respectively named high frequency (HF) and low frequency (LF), associated in series. A typical impedance spectrum is shown in Fig. 2. The associated electrical equivalent circuit is reported in Fig. 3. The parameters values of the different impedance spectra recorded on the polarization curve are shown in Table 1. It can be seen that the first resistance series R_s is the most important resistive component. This impedance was not been clearly identified but may be attributed to an insufficient contact between the single cell and the current collectors. Indeed, the mechanical pressure applied for the set-up was lower than the value recommended by InDEC in the measurements process with anode-supported cells.

The resistances R_{HF} and R_{LF} of the capacitive loops decreased versus current. This shows that these resistances are attributed to anodic and cathodic polarization resistances. Nevertheless, it is difficult to identify which semi-circle is related to the cathodic contribution. Indeed, according to previous studies,^{8,9,10} both capacitive effects $C \sim 0.01\text{ F}$ and $C \sim 0.3\text{ F}$ associated respectively to the high frequency (HF) and the low frequency (LF) impedances, can be identified as electrode processes. Generally, the capacitive effects are more important in triple phase boundaries (TPB) electrodes, such as YSZ-Ni cermet, and are lower in internal diffusion (ID) electrodes, as for $\text{Nd}_{1.95}\text{NiO}_{4+\delta}$. One

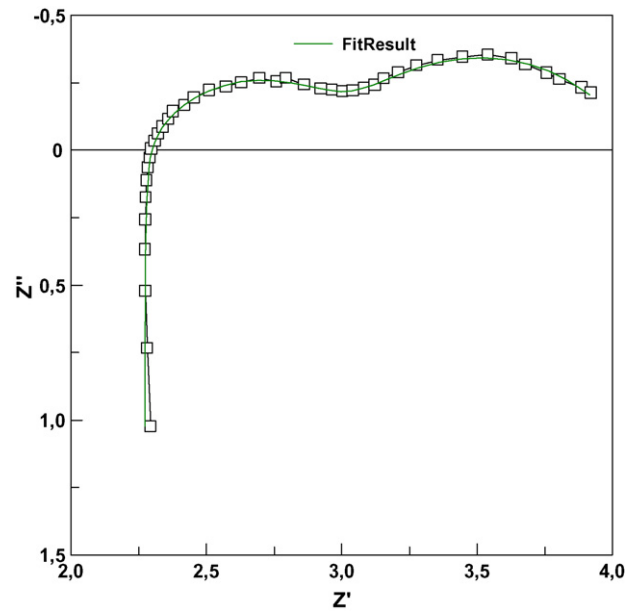


Fig. 2. Typical complex impedance spectrum of the cell recorded at 700°C under open circuit conditions.

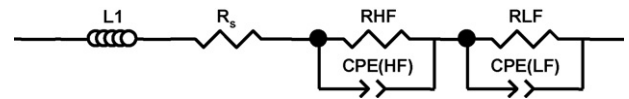


Fig. 3. Equivalent circuit used to identify the Fig. 2 spectrum.

can therefore assume that the HF resistance may be attributed to the cathodic response while the LF one may rather be assigned to the anodic contribution. Results show that for low current density (high voltage), the HF resistance is the lowest contribution whereas and with further increase in current, the LF resistance forms the majority impedance. This indicates that, apart from the high resistance R_s presumably related to weak contact between the current collectors and the electrodes, the predominant polarization resistance in the cell may be attributed to the anode. This suggests an improvement in the cell materials with respect to the usual major cathodic contribution measured on conventional SOFC cells made of TBP cathodic electrode.

The power density versus current density curves are reported in Fig. 4 for $750\text{--}700\text{--}675^\circ\text{C}$. It can be noticed that for low polarization, the temperature increasing did not affect the cell performance. For current densities higher than 20 mA cm^{-2} , the electrical properties increases and a power density of

Table 1
Cell voltage and fitted values of the different parameters associated to the equivalent circuit reported in Fig. 3

Diagram	E (mV)	L (H)	R_s (Ω)	R_{HF} (Ω)	C_{HF} (F)	R_{LF} (Ω)	C_{LF} (F)
700.1	1161	2.52×10^{-6}	0.969	0.744	0.01246	1.070	0.3652
700.2	1121	2.53×10^{-6}	0.965	0.797	0.01447	1.012	0.3712
700.3	1071	2.49×10^{-6}	0.934	0.643	0.01260	0.825	0.4334
700.4	943	2.38×10^{-6}	0.872	0.543	0.01239	0.582	0.5942

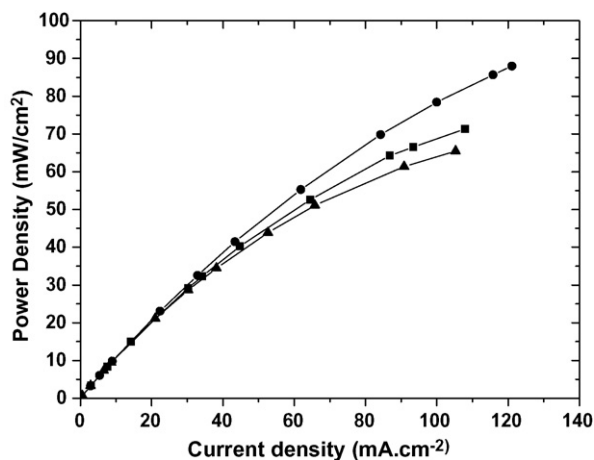


Fig. 4. Power density vs. current density for single cell operated at 750 °C (●), 700 °C (■) and 675 °C (▲).

140 mA cm⁻² under 700 mV is obtained. At 750 °C, the power density is about 90 mW cm⁻².

4. Conclusion

Accordingly, the power density demonstrates in this study on nickelate-based SOFC cell is low and unexpected with respect to the intrinsic properties of nickelates materials (high oxygen diffusion coefficient, high surface exchange coefficient and good electronic conductivity) and the good electrochemical performance already demonstrated on half asymmetrical cell. This poor performance may therefore rather be assigned to a weakness in the set up design as suggested by the high resistance R_s

and to an inadequate cell shaping. These both parameters have to be further optimized to benefit from the good intrinsic properties of neodymium nickelate oxides.

References

1. Goodenough, J. B. and Manthiram, A., Crystal chemistry and superconductivity of the copper oxides. *J. Solid State Chem.*, 1990, **88**, 115–139.
2. Bassat, J. M., Boehm, E., Grenier, J. C., Mauvy, F., Dordor, P. and Pouchard, M., YSZ-supported cathodes of rare-earth nickelates $\text{Ln}_2\text{NiO}_{4+\delta}$ for ITSOFC (650 °C). In *Proceedings of the 5th European solid oxide fuel cell forum*, 2002, pp. 586–594, ISBN 3-905590-10-X.
3. Mauvy, F., Bassat, J.-M., Boehm, E., Manaud, J.-P., Dordor, P. and Grenier, J.-C., Oxygen electrode reaction on $\text{Nd}_2\text{NiO}_{4+\delta}$ cathode materials: impedance spectroscopy study. *Solid State Ionics*, 2003, **158**, 17–28.
4. Boehm, E., Bassat, J. M., Dordor, P., Mauvy, F. and Grenier, J. C., Oxygen transport properties of $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ mixed conducting oxides. *Solid State Sci.*, 2003, **5**, 973–981.
5. Douy, A., Polyacrylamide gel: an efficient tool for easy synthesis of multi-component oxide precursors of ceramics and glasses. *Int. J. Inorg. Mater.*, 2001, **3**, 699–707.
6. Pechini, US patent, 3.330.687.
7. Fontaine, M.-L., Laberty-Robert, C., Ansart, F. and Tailhades, P., Elaboration and characterization of $\text{La}_2\text{NiO}_{4+\delta}$ powders and thin films via a modified sol–gel process. *J. Solid State Chem.*, 2004, **177**, 1471–1479.
8. Mitterdorfer, A. and Gauckler, L. J., Identification of the reaction mechanism of the Pt, $\text{O}_2(\text{g})$ /yttria-stabilized zirconia system. Part II. Model implementation, parameter estimation, and validation. *Solid State Ionics*, 1999, **117**, 203–217.
9. Mauvy, F., Lalanne, C., Bassat, J. M., Grenier, J. C., Zhao, H., Dordor, P. et al., Oxygen reduction on porous $\text{Ln}_2\text{NiO}_{4+\delta}$ electrodes. *J. Eur. Ceram. Soc.*, 2005, **25**, 2669–2672.
10. Lalanne, C., Mauvy, F., Bassat, J. M., Grenier, J. C., Pordor, D., Pouchard, M. et al., Electrochemical behaviour of porous $\text{Nd}_2\text{NiO}_{4+\delta}$ electrodes. In *Proceedings of the 6th European solid oxide fuel cell forum*, 2004, pp. 1351–1359, ISBN 3-905592-15-0.