

Oxygen reduction on porous $\text{Ln}_2\text{NiO}_{4+\delta}$ electrodes

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Abstract

$\text{Ln}_2\text{NiO}_{4+\delta}$ based materials (Ln=La, Nd or Pr), show very good electrocatalytic performances as SOFC cathode: the oxygen diffusion coefficient D^* and the surface exchange coefficient k measured by isotopic exchange are several orders of magnitude higher than that of the standard LSM cathode material. They are good mixed ionic and electronic conductors (MIEC) due to the mixed valence of the transition metal cation M and to the presence of mobile additional oxygen atoms. Therefore, the O_2 reduction is not limited by a charge transfer process occurring usually at the one-dimensional “three-phase boundary” interface between gas, electrode and electrolyte characteristic of metallic cathodes.

This study aims to characterise the reaction kinetics at $\text{O}_2(\text{g})$, $\text{Ln}_2\text{NiO}_{4+\delta}$ /zirconia porous electrodes in the temperature range 500–800 °C, under air. In order to identify interfaces and electrode processes, ac electrochemical impedance spectroscopy was used under zero bias conditions with symmetrical cells. Using the Schouler method, the electrode/electrolyte interface impedance has been clearly identified as the limiting step. Furthermore, electrode properties have also been measured under non-zero dc conditions with a three-electrode cell. The polarisation curves allow to confirm that $\text{Ln}_2\text{NiO}_{4+\delta}$ oxides are promising materials for SOFC cathode. The observed overpotentials are lower than those observed for LSM under the same current and temperature conditions. Nevertheless, the interface between $\text{Ln}_2\text{NiO}_{4+\delta}$ and zirconia should be optimised by a better shaping because the interfacial resistance appears to be the most important contribution to the total impedance. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

The mixed ionic and electronic conducting oxides (MIEC) have attracted interest for use in a wide range of applications such as cathodes for solid oxide fuel cell (SOFC), electrodes for electrically driven ceramic oxygen generators (COG) or dense membranes for pressure driven oxygen separators. The $\text{Ln}_2\text{NiO}_{4+\delta}$ oxides can be good candidates for these types of applications because of the high level of their electronic and ionic conductivities. In fact, previous measurements of oxygen diffusion and surface exchange coefficients employing isotope exchange techniques with secondary ion mass spectroscopy analysis, have shown that these over-stoichiometric oxides exhibit an oxygen mobility higher than that of the

perovskite oxides.¹ Furthermore, they are good electronic conductors due to the mixed valence of the nickel cations. In this paper, we report an electrochemical characterisation of $\text{Ln}_2\text{NiO}_{4+\delta}$ oxides used as SOFC cathode deposited on yttrium stabilised zirconia (YSZ) electrolytes.

2. Experimental

2.1. Sample preparation

Cells for electrochemical measurements are made of YSZ pellets on which are deposited electrodes of the studied materials. Fine powder of YSZ (Tosoh Co.) is dried, then pressed under 2T to form green pellets, which are sintered at 1350 °C for 4 h and then slowly cooled down. The density is about 95% of the theoretical value. The surface of the pellets is then roughened with #600 grid paper and cleaned with an ethanol solution.

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$\text{Ln}_2\text{NiO}_{4+\delta}$ powders are prepared using the modified Pechini method. The required amounts of the starting oxides are dissolved into nitric acid to form metal ion solution. Then citric acid is added into the solution, in a large excess (3.3 mol/mol of $\text{Ln}_2\text{NiO}_{4+\delta}$); the obtained clear solution is then slowly heated up to 120 °C to obtain a viscous brown gel, which is burned at 600 °C. A final heating at 1000 °C, for 12 h, leads to the final products whose purity is checked by XRD. For the preparation of cathode pastes, the as-prepared powders are first milled and the particle size distribution is found to be in the range of 1 μm by SEM. The fine powders are then dispersed into acetylene glycol (1 g powder ml^{-1} ethylene glycol) to form a paste. The paste is then brush painted on both sides of a YSZ pellet, in a symmetrical configuration. For the three-electrode cells, the platinum reference electrode is deposited by painting on the same side as the working electrode. The distance between the cathode and this reference electrode is over five times the thickness of the pellets. The cells are heated first at 500 °C, for 4 h, to burn out the organic binders and then sintered at 900 °C for 2 h, which leads to porous electrodes well stuck on the electrolyte.

2.2. Electrochemical measurements

The cell is pinched on an alumina ceramic support, Pt mesh being used as electrical collectors. All the electrochemical experiments are performed from 300 °C up to 800 °C, under different oxygen partial pressures. The impedance spectra are measured by an impedance analyser (Autolab PGStat 30). The data are fitted using the Zview software.

3. Results and discussion

3.1. Electrochemical measurements under zero dc conditions

The impedance spectra obtained for symmetrical two-electrode cells ($\text{O}_{2(\text{g})}$ /MIEC/electrolyte/MIEC/ $\text{O}_{2(\text{g})}$) may exhibit various contributions. Some of them are assigned to intrinsic properties of the materials, the others being attributed to phenomena occurring at the electrode/electrolyte or electrode/gas interfaces.² For a cell made of given materials, two ways allow to separate these contributions, either by varying the geometrical cell factors or by changing the operating oxygen partial pressure. The resistance and capacitance of the cell are directly correlated to the first ones. It is also well known that the properties of YSZ do not significantly depend upon the oxygen partial pressure while the interface polarisation is strongly affected. At steady temperature and p_{O_2} , all impedance contributions are not simultaneously observable in the frequency range 10^6 Hz to 10^{-3} Hz, which originates difficulties to identify them.

Fig. 1 shows a typical Nyquist plot measured at 300 °C under air, for a symmetrical cell $\text{La}_2\text{NiO}_{4+\delta}/8\text{YSZ}/\text{La}_2\text{NiO}_{4+\delta}$. It is fitted on the basis of an equivalent circuit constituted of

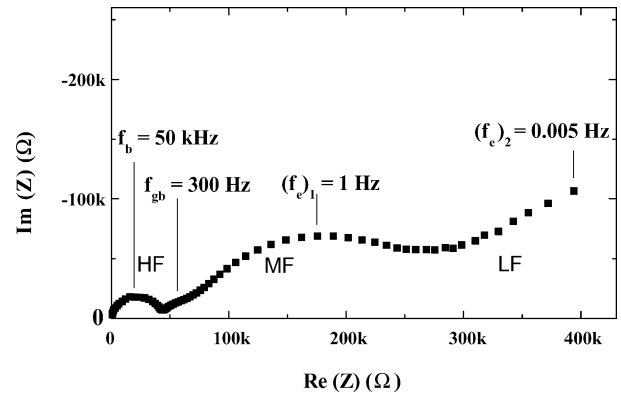


Fig. 1. Typical impedance spectrum obtained at $T = 300$ °C, under air, for a symmetrical cell ($\text{La}_2\text{NiO}_{4+\delta}/8\text{YSZ}/\text{La}_2\text{NiO}_{4+\delta}$).

several R-CPE elements in parallel associated in series. Each resistance or CPE can be assigned to the resistance or capacitance associated to a specific electrochemical process which are calculated by fitting the experimental data. Usually there exist two arcs more or less overlapped in the high frequency range (HF) and two other ones in the lower frequency range (LF).

On the basis of the fitted data, we used the Schouler-type representation, which consists to plot the relaxation frequency of each contribution as a function of temperature.³ Such a graph can be considered as a reference for interpreting an impedance diagram, even if all the contributions do not appear at a fixed temperature. The results are shown in Fig. 2 for different kinds of cells made of two symmetrical electrodes (Pt metal, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$ (LSFC), $\text{La}_2\text{NiO}_{4+\delta}$) and 8YSZ as electrolyte. From the results obtained for the Pt/8YSZ/Pt cell which agree with those reported in previous works, the high frequency arcs can be assigned to the bulk (HF^+) and

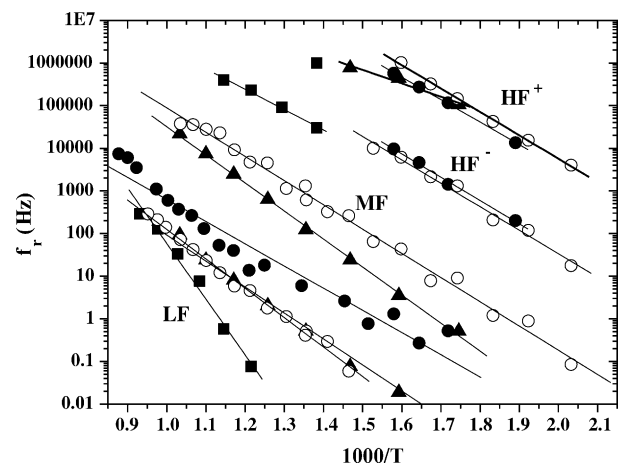


Fig. 2. Arrhenius plots of the relaxation frequencies for electrode/8YSZ/electrode cells under air and zero dc conditions (HF, MF, LF corresponds to high, middle and low frequencies): (■) Pt; (●) LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$); (▲) LSFC ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.6}\text{Co}_{0.4}\text{O}_{3-\delta}$); (○) $\text{La}_2\text{NiO}_{4+\delta}$.

grain boundary (HF^-) conductivities of the electrolyte; they do not show a significant dependence on the oxygen partial pressure.^{3–5} Both arcs merge into a depressed semicircle at high temperatures. The calculated activation energy ($E_a \approx 1$ eV) and the ionic conductivity of the electrolyte are in good agreement with previously reported values.^{6,7}

Concerning the MF contribution, the amplitude of the semicircle decreases with increasing temperature, and completely disappears above 700 °C. It is quite insensitive to oxygen partial pressure. One should also point out that this MF contribution exists only for electrodes made of O^{2-} ionic conducting oxides ($\text{La}_2\text{NiO}_{4+\delta}$, LSFC) whereas it is absent for the Pt metal electrode. In previous studies, a similar middle frequency arc has also been observed.⁸ In addition, the higher the ionic conduction, the higher the relaxation frequency (f_r), which would mean that the ion transfer at the interface electrode/electrolyte is enhanced.

Concerning the LF contribution, the Pt metal has the lowest frequency relaxation, which agrees with the fact that Pt has a slow oxygen reduction kinetics. For LSFC and $\text{La}_2\text{NiO}_{4+\delta}$, the thermal behaviours of f_r are almost similar (Fig. 2). In addition, LSM seems to have only one contribution in between the MF and LF contributions, which can be related to the very small ionic conductivity of this compound.⁹

The kinetics of the oxygen reduction on the surface of $\text{Ln}_2\text{NiO}_{4+\delta}$ -type oxides can be characterised through the polarisation resistance of the electrode. Fig. 3 shows the thermal variation of the area specific resistivity (ASR) which is calculated by the relation $\text{ASR} = R_p S/2$, R_p being the sum of the real parts of the impedance at MF and LF and S the surface area of both electrodes. For attrited powders, the ASR decreases by two orders of magnitude. Under zero dc conditions, Pr_2NiO_4 is the most efficient electrode but this compound has a poor lifetime with respect to the electrolyte. Actually, neodymium compounds, which do not significantly react with the electrolyte, appear to show the best performances. Subsequently, following studies were performed on this compound.

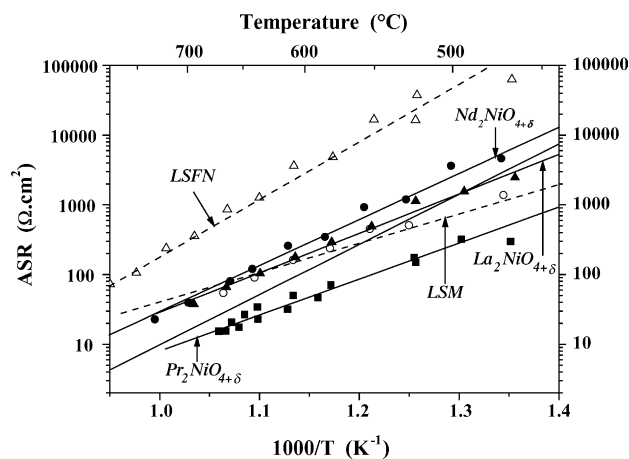


Fig. 3. Arrhenius plots of the ASR for $\text{Ln}_2\text{NiO}_{4+\delta}$ oxides: (●) Nd, (■) Pr, (▼) La; and (○) LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$); (△) LSFN ($\text{La}_{0.6}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$).

3.2. Electrochemical measurements under polarisation

Electrochemical measurements under polarisation were made using a three-electrode cell. Typical impedance diagrams measured for $\text{Nd}_2\text{NiO}_{4+\delta}$ as cathode, at 718 °C, under air, for different applied potentials are reported in Fig. 4. In the potential range 0, -1 V/air, the impedance response shows two main contributions. At high frequencies (HF), the YSZ electrolyte impedance is not observed. The middle frequency (MF) range, centred on 4 kHz, is usually assigned to the charge transfer process occurring at the electrode/electrolyte interface. The low frequency range (LF), lower than 20 Hz, is the complex contribution of non-charge-transfer processes including oxygen surface exchange, solid-state diffusion, and gas-phase diffusion through the cathode. It can be noticed that the electrolyte resistance is nearly stable whereas both MF and LF impedance decrease versus potential. Under -1 V/air, the charge transfer contribution is the most resistive which can be attributed to the not optimised microstructure of the interface between YSZ and $\text{Nd}_2\text{NiO}_{4+\delta}$.

The dc polarisation experiments were performed by applying step by step a steady potential. The over-potential is calculated according to the following relation: $\eta_{\text{WE}} = \Delta U_{\text{WR}} - iR_{\text{el}}$, where η_{WE} represents the cathode over-potential, ΔU_{WR} is the applied voltage between the working electrode and the reference electrode, i is the current intensity flowing through the cell and R_{el} is the resistance of the electrolyte obtained from impedance spectrum. Fig. 5 shows Ri-free polarisation curves of various cathodes (LSM and LSF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$)) deposited on YSZ substrate. A comparison of the Ri-free over-potential–current density curves is difficult because of the influence of the microstructure (and of the shaping) on the measurements. Nevertheless, one can observe that at 800 °C, $\text{Nd}_2\text{NiO}_{4+\delta}$ (this work) and exhibit nearly the same polarisation losses. It can be noticed that the neodymium nickelate has a better electrochemical activity than LSM at 700 °C or 800 °C. For example, at 800 °C, under a cathodic over-potential of 100 mV, the current density

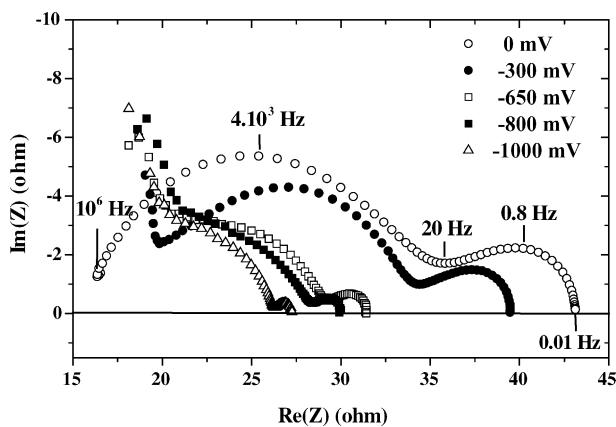


Fig. 4. Impedance plots for $\text{Nd}_2\text{NiO}_{4+\delta}$ as cathode material at different potentials under air ($T = 718$ °C) (three-electrode cell).

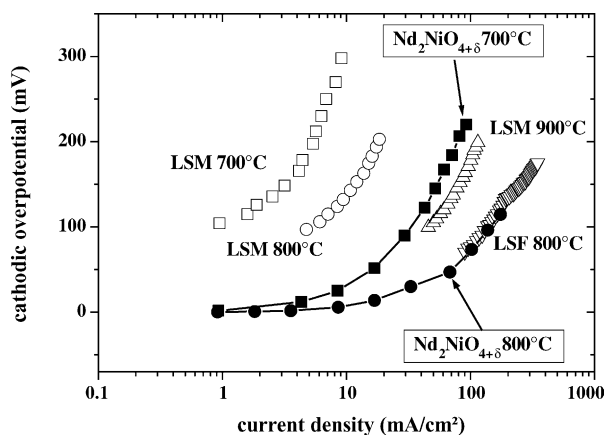


Fig. 5. Polarisation curves (R_i -free, measured in air) for Nd_2NiO_4 cathodes (full symbols) and comparison with LSM and LSF (empty symbols) from Ref. ¹⁰.

through $\text{Nd}_2\text{NiO}_{4+\delta}$ is at least one order of magnitude higher than for LSM and is similar to that of LSF (Ref. ¹⁰).

In addition, the reactivity of the neodymium nickelate with YSZ was performed by mixing and heating powders in the temperature range 700–900 °C. Neither pyrochlore phase (like $\text{Nd}_2\text{Zr}_2\text{O}_7$) nor new phases could be observed by XRD. Therefore, one can predict a good ageing behaviour for this material, which is known to be the critical phenomenon for the ferrite perovskites.¹¹

4. Conclusion

Electrochemical measurements were performed on $\text{Ln}_2\text{NiO}_{4+\delta}/8\text{YSZ}/\text{Ln}_2\text{NiO}_{4+\delta}$ cells under zero dc conditions and also under polarisation. Thanks to a Schouler-type analysis of the impedance spectra, electrode and electrolyte contributions were deconvoluted. The area specific resistivities of the nickelate cathodes and the cathodic polarisation curves were measured; good performances were observed in a large operating temperature. The compound $\text{Nd}_2\text{NiO}_{4+\delta}$ in particular, has been selected because of its low reactivity

with YSZ and the interesting properties obtained under polarisation.

Acknowledgments

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