Oxygen reduction on porous $Ln_2NiO_{4+\delta}$ electrodes

F. Mauvy*, C. Lalanne*, J.M. Bassat*, J.C. Grenier*, H. Zhao*[(a)], P. Dordor*, Ph. Stevens**

**ICMCB - CNRS - Université Bordeaux I - GDR "ITSOFC 700"*

87 Av. du Dr A.Schweitzer 33608 PESSAC Cedex - France

*** EDF - EifER Emmy-Noether-Strasse 11, 76131 Karlsruhe - Germany*

[(a)] Present address : College of Chemistry and Chemical Technology, Heilongjiang University, 150080 Harbin - China

Keywords : C: Electrical conductivity, Impedance, ionic conductivity, D : Transition metal oxides, E : Fuel cells

Abstract

$Ln_2NiO_{4+\delta}$ 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 O_2(g), $Ln_2NiO_{4+\delta}$ / zirconia porous electrodes in the temperature range 500 – 800°C, under air. In order to identify interfaces and electrode processes, a.c. 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 d.c. conditions with a three electrode cell. The polarisation curves allow to confirm that $Ln_2NiO_{4+\delta}$ 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 $Ln_2NiO_{4+\delta}$ and zirconia should be optimised by a better shaping because the interfacial resistance appears to be the most important

contribution to the total impedance. Ageing tests during one month under d.c. conditions show a reduction of the polarisation resistance and no significant reactivity between $Ln_2NiO_{4+\delta}$ and zirconia.

1 – Introduction

The mixed ionic and electronic conductors 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 $Ln_2NiO_{4+\delta}$ 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 $Ln_2NiO_{4+\delta}$ 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^{o}C for 4 hours 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.

$Ln_2NiO_{4+\delta}$ powders are prepared using the modified Pecchini 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 moles per mole of $Ln_2NiO_{4+\delta}$) ; 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 (1g powder per 1 ml etylene 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 5 times the thickness of the pellets. The cells are heated first at 500°C, for 4 hours, to burn out the organic binders and then sintered at 900°C for 2 hours, 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 analyzer (Autolab PGStat 30). The data are fitted using the Zview software.

3 – Results and discussion :

3-1 Electrochemical measurements under zero d.c. conditions :

The impedance spectra obtained for symmetrical two-electrode cells ($O_{2(g)}$ / $Ln_2NiO_{4+\delta}$ / electrolyte / $Ln_2NiO_{4+\delta}$ / $O_{2(g)}$) 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_{O2}, all impedance contributions are not simultaneously observable in the frequency range $10^6 – 10^{-3}$ Hz, which originates difficulties to identify them.

Figure 1 shows a typical Nyquist plot measured at 300 °C under air, for a symmetrical cell $La_2NiO_{4+\delta}$ / 8YSZ / $La_2NiO_{4+\delta}$. It is fitted on the basis of an equivalent circuit constituted of 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, $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.8}Sr_{0.2}Fe_{0.6}Co_{0.4}O_{3-\delta}$, $La_2NiO_{4+\delta}$) 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 grain boundary (HF^-) conductivities of the electrolyte; they do not show a significant dependence on the oxygen partial pressure [3], [4], [5]. Both arcs merge into a depressed semicircle at high temperatures. The calculated activation energy (Ea ≈ 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 ($La_2NiO_{4+\delta}$, 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 $La_2NiO_{4+\delta}$, 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 $Ln_2NiO_{4+\delta}$-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 ASR = $R_p \times S/2$, Rp 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 d.c. 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.

3-2 Electrochemical measurements under polarisation :

Electrochemical measurements under polarisation were made using a three electrode cell. Typical impedance diagrams measured for $Nd_2NiO_{4+\delta}$ 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 [5]. The low frequency range (LF), lower than 20Hz, 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 -1V/air, the charge transfer contribution is the most resistive which can be attributed to the not optimised microstructure of the interface between YSZ and $Nd_2NiO_{4+\delta}$.

The dc polarisation experiments were performed by chronoamperometry method. The overpotential is calculated according to the following relation : $\eta_{WE} = \Delta U_{WR} - iR_{el}$, where η_{WE} represents the cathode overpotential, 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 deposited on YSZ substrate. A comparison of the RI-free overpotential – current density curves of $Nd_2NiO_{4+\delta}$ with literature data for LSM and LSF is difficult because of the role of the microstructure (and the shaping) on the measurements. Nevertheless, one can observe that at 800°C, the $Nd_2NiO_{4+\delta}$ (this work) and $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (ref.[10]) exhibit nearly the same polarisation losses. It can be noticed in Fig.5 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 overpotential of 100mV, the current density through $Nd_2NiO_{4+\delta}$ is at least one order of magnitude higher than for LSM and can be compared to LSF. Because of the small reactivity of the neodymium nickelate with zirconia in the working temperature range T < 900°C, one can predict a good ageing behaviour for this material which is known to be the critical phenomenon of the ferrite perovskites [11].

4 – Conclusion

Electrochemical measurements were performed on $Ln_2NiO_{4+\delta}$ / 8YSZ / $Ln_2NiO_{4+\delta}$ cells under zero d.c. 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 $Nd_2NiO_{4+\delta}$ in particular, has been selected because of its low reactivity with YSZ and the interesting properties obtained under polarisation.

Acknowledgments : the authors are indebted to EDF and ADEME for their financial support.

References :

[1] J.M.Bassat, E.Boehm, J.C.Grenier, F.Mauvy, P.Dordor and M.Pouchard, YSZ - supported cathodes of rare-earth nickelates $Ln_2NiO_{4+\delta}$ for ITSOFC (650°C), In *5th European Solid Oxide Fuel Cell Forum* , ed. J.Huijsmans, 2002, pp.586-593

[2] F.Mauvy, J-M.Bassat, E.Boehm, J-P.Manaud, P.Dordor and J-C.Grenier, Oxygen electrode reaction on $Nd_2NiO_{4+\delta}$ cathode materials : impedance spectroscopy study. *Solid State Ionics*, 2003, **158**, 17-28

[3] E.J.L.Schouler, N.Mesbahi, G.Vitter, In situ study of the sintering process of yttria stabilized zirconia by impedance spectroscopy, *Solid State Ionics*, 1983, **9&10**, 989-996

[4] L.Desmond, Spectroscopie d'impédance des fissures dans la zircone cubique. PhD thesis, Institut National Polytechnique de Grenoble, Grenoble, France, 1992

[5] T.Wang, R.F.Novak, R.E.Soltis, A study of factors that influence zirconia/platinum interfacial impedance using equivalent circuit analysis, *Sensors and Actuators*, 2001, **B77**, 132-138

[6] B.C.H. Steele, Behaviour of porous cathodes in high temperature fuel cells. *Solid State Ionics*, 1997, **94**, 239-248

[7] R.J.Stafford, S.J.Rothman, J.L.Routbort, Effect of dopant size on the ionic conductivity of cubic stabilised ZrO_2, 1989, **37**, 67-72

[8] E.Siebert, A.Hammouche, M.Kleitz, Impedance spectroscopy analysis of $La_{1-x}Sr_xMnO_{3-y}$ yttria-stabilized zirconia electrode kinetics, *Electrochimica Acta*, 1995, **40**, 1741-1753

[9] R.A.De Souza, J.A.Kilner, Oxygen transport in $La_{1-x}Sr_xMn_{1-y}Co_yO_{3\pm\delta}$, *Solid State Ionics*, 1998, **106**, 175-187

[10] M.Krumpelt, J.Ralph, T.Cruse, J-M.Bae, Materials for low SOFCs, In *5th European Solid Oxide Fuel Cell Forum* , ed. J.Huismans, 2002, pp.215-224

[11] J.Holc, D.Huscer, M.Hrovat, S.Bernik, D.Kolar, Electrical and microstructural characterisation of $(La_{0.8}Sr_{0.2})(Fe_{1-x}Al_x)O_3$ and $(La_{0.8}Sr_{0.2})(Mn_{1-x}Al_x)O_3$ as possible SOFC cathode materials, *Solid State Ionics*, 1997, **95**, pp-259-268.

Figures

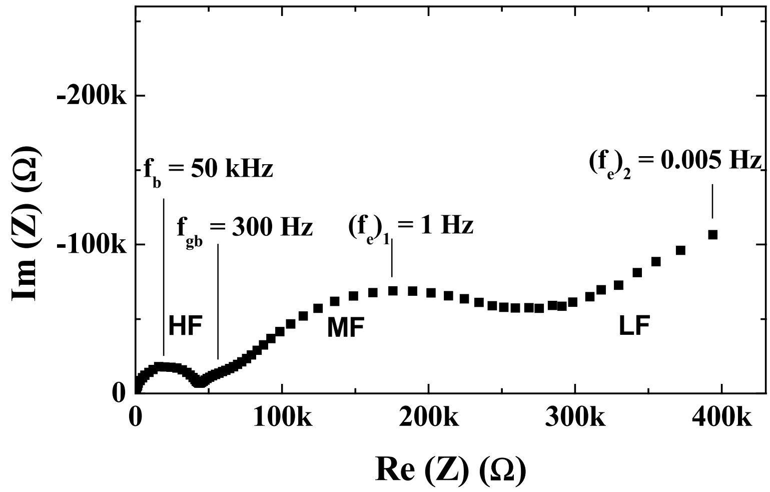

Figure 1 : Typical impedance spectrum obtained at T = 300°C, under air, for a symmetrical cell ($La_2NiO_{4+\delta}$ / 8YSZ / $La_2NiO_{4+\delta}$).

Figure 2 :

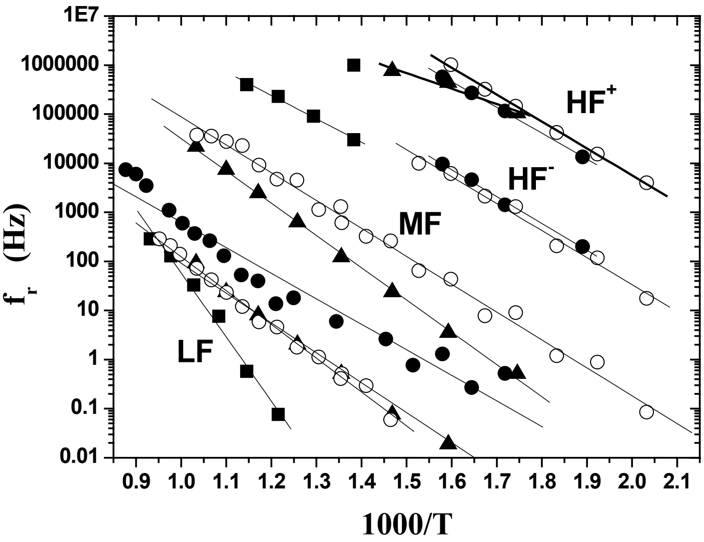

Figure 2 : Arrhenius plots of the relaxation frequencies for electrode / 8YSZ / electrode cells under air and zero d.c. conditions (HF, MF, LF corresponds to high, middle and low frequencies): !: Pt ; , : LSM ($La_{0.8}Sr_{0.2}MnO_3$) ; 7: LSCF ($La_{0.8}Sr_{0.2}Fe_{0.6}Co_{0.4}O_{3-\delta}$,) ; – : $La_2NiO_{4+\delta}$

Figure 3 :

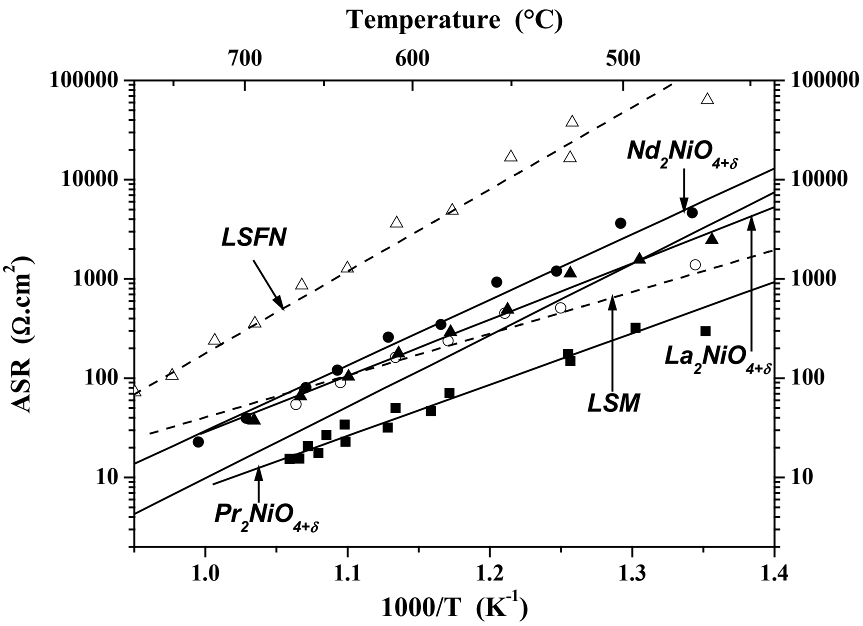

Figure 3 : Arrehnius plots of the ASR for $Ln_2NiO_{4+\delta}$ oxides (, : Nd, ! : Pr, 7 La) and – LSM ($La_{0.8}Sr_{0.2}MnO_3$) ; 8 : LSFN ($La_{0.6}Sr_{0.2}Fe_{0.8}Ni_{0.2}O_{3-\delta}$).

Figure 4 :

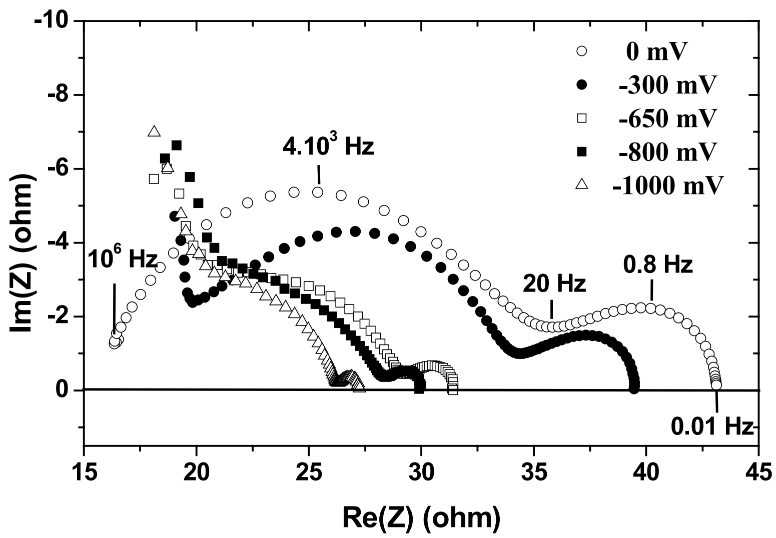

Figure 4 : Impedance plots for $Nd_2NiO_{4+\delta}$ as cathode material at different potentials under air (T = 718°C) (three-electrode cell)

Figure 5 :

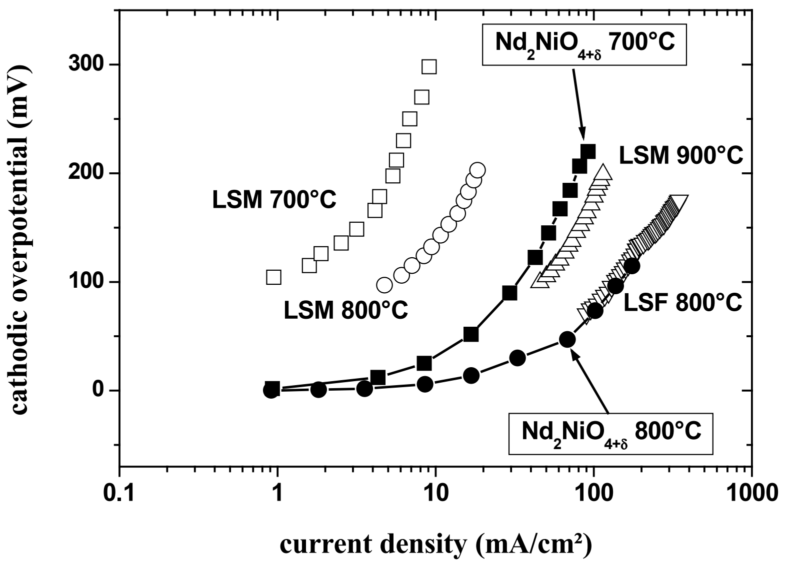

Figure 5 : Polarisation curves (RI-free, measured in air) for Nd_2NiO_4 cathodes (full symbols) and comparison with LSM and LSF (empty symbols) from ref.[10].