MIXED IONIC ELECTRONIC CONDUCTING OXIDES: NEW MATERIALS FOR IT-SOFC CATHODES

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There is increasing interest in the development of Intermediate Temperature Solid Oxide Fuel cells (ITSOFCs). Decreasing the operating temperature should reduce problems with sealing and thermal degradation and allowed to use lower-cost interconnect materials (1). While improvement has been made today, reducing the operation temperature to 500-800°C without significantly decreasing the power density remains to be the challenge of this technology (2, 3). One of the major problems encountered is the large cathode overpotential due to reaction kinetics at lower temperatures. In order to solve this problem, Mixed Ionic and Electronic Conducting (MIEC) materials have been developed. It is believed that the improved electrode properties are due to the extended reaction sites from the traditional TPB (Triple Phase Boundary) region to the whole electrode surface (4-6).

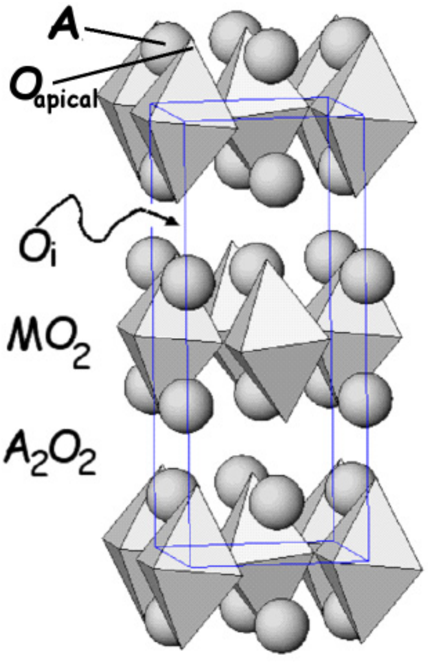

Fig. 1 *Structure of $Ln_2NiO_{4+\delta}$ materials: additional oxygen atoms are inserted into the Ln_2O_2 laver.*

Until now, most of the works concerning MIEC materials are oxygen deficient perovskite-type compounds. However, optimisation of the compositions seems to have been achieved. Recently, a new family of oxides has attracted much attention (7-13). Their general formulation is $Ln_2MO_{4+\delta}$ and they exhibit enhanced performances as cathodes.

We report the preparation and characterization of these oxides formulated $Ln_{2-x}A_xMO_{4+\delta}$, Ln = La, Pr, Nd; A = Ca,Sr; M = Ni, Cu. From a structural point of view, they correspond to the n = 1 member of the Ruddlesden-Popper series and crystallize with the K_2NiF_4 - type structure. The main feature of these oxides is the presence of additional oxygen atoms located in interstitial sites of the Ln_2O_2 layers of the structure (Fig. 1). The value of the oxygen excess δ depends on the nature of the A cation and on the temperature. It has been determined by both chemical and thermal-gravimetry analyses. A decrease of the oxygen content is observed with increasing temperature but this does not affect significantly their dilatometric properties. The thermal expansion coefficient (TEC) of these materials is about 13.10^{-6} K^{-1} and is

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consistent with the values of the usual SOFC electrolytes (TEC ≈ 10-12.10^{-6} K^{-1} for zirconia and ceria).

Due to the presence of the mixed valency Ni^{2+} / Ni^{3+}, these compounds show a high electronic conductivity (about 10^1-10^2 $S.cm^{-1}$ at 700°C), which meets the requirements for SOFC cathode materials. The oxygen diffusion properties have been studied using ^{18}O doping and SIMS (Secondary Ion Mass Spectroscopy) measurements. The oxygen diffusion coefficient D* as well as the surface exchange coefficient k have been determined at various temperatures. The D* and k coefficients of these nickelates as well as the oxygen ionic conductivity are, at 700°C, one order of magnitude higher than those of the best perovskite-type materials which are currently used (Fig. 2) (13-16).

Electrochemical measurements have been carried out using impedance spectroscopy in order to determine the polarization resistance Rp (or the ASR in Ω.cm²) of porous cathodes at various overpotentials (Fig. 3). The various contributions included in the polarization resistance, *e.g.* oxygen adsorption and dissociation on the cathode surface, oxygen diffusion in the cathode material, charge transfer between the cathode and the electrolyte are discussed.

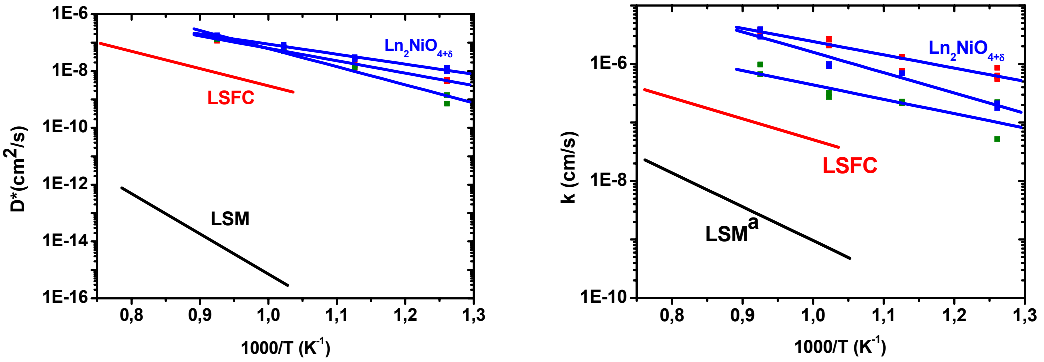

Fig. 2 *Thermal evolution of D* and k coefficients of* $Ln_2NiO_{4+\delta}$ *cathode materials compared with those of the perovskites* ($La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$) *and of LSM* ($La_{0.8}Sr_{0.2}MnO_3$).

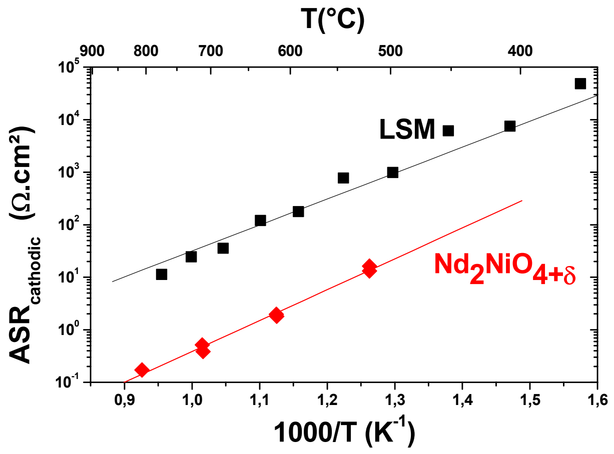

Fig. 3 *Thermal evolution of the cathodic ASR of* $Nd_2NiO_{4+\delta}$ *and LSM / 8YSZ half-cells.*

In addition, experiments concerned with the reactivity of these nickelates with zirconia and ceria have also been achieved. Some compositions show a good stability as a function of time.

These results show that these nickelates exhibit promising diffusion and electrocatalytic properties and especially in comparison with the performances of the best perovskite materials as $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$

(LSFC). This is discussed in terms of the 2D structural features of these materials.

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