Cathodes Materials for Intermediate Temperature Solid Oxide Fuel Cells

J.-C. Grenier*, J.-M. Bassat, C. Lalanne, F. Mauvy
ICMC Bordeaux-CNRS, Univ. de Bordeaux, 87. Av. du Dr Schweitzer,
F-33608 Pessac cedex, France
*grenier@icmcb-bordeaux.cnrs.fr

Abstract

Nowadays, most cathode materials used in high temperature solid oxide fuel cells (SOFC) are mixed electronic ionic compounds (MEIC oxides), usually perovskite-type compounds, AMO$_{3-\delta}$, whose characteristics is oxygen deficiency. Recently, a new family of oxides, formulated A$_2$MO$_{4+\delta}$ with A = La, Nd, Pr, Sr and M = Ni, Cu, has been investigated. Their main feature is their oxygen overstoichiometry, Due to their basic properties (large $D*$ and $k$ coefficients, high electrical conductivity), the nickelate compounds, especially Nd$_2$NiO$_4$ and Pr$_2$NiO$_4$, exhibit very promising electrochemical properties down to temperature as low as 600 °C, as SOFC-O$_2$ as well as SOFC-H$^+$ cathodes. This is confirmed by encouraging cell tests. Thus, it appears that these materials show an extremely high flexibility for being used as air electrode in very different conditions in terms of oxygen partial pressure or/and water content. This is explained on the basis of structural features of these materials and the great ability of these compounds for accommodating the oxygen non-stoichiometry.

Keywords: solid oxide fuel cell; cathode materials; mixed electronic-ionic conductivity; lanthanide nickelate; electrochemical impedance spectroscopy;

1. Introduction

Nowadays, most efforts are devoted to the development of Intermediate Temperature Solid Oxide Fuel cells (ITSOFCs) operating at temperatures ranging from 500 to 700 °C); these temperatures are expected to allow using low-cost metallic interconnects and reducing the ageing process kinetics. However, the main challenge remains not to decrease significantly the power density of these systems due to slower kinetics of the electrode reactions at lower temperatures and decreased ionic conductivity of the electrolytes. However, the most crucial problem is the increase of the cathode overpotential. In order to overcome this problem, new materials have to be developed.

Early cathodes that have been industrialized for SOFC, were composite electrodes made of an electronic conducting oxide, the perovskite LSM (La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$) mixed with an ionic conducting oxide electrolyte (usually doped zirconia or ceria) with the aim to increase the number of TPB (Triple Phase Boundary). They were efficient only at operating temperatures higher than 900 °C [1].

At lower temperatures, Mixed Electronic and Ionic Conducting (MEIC) oxides that exhibit simultaneously high electronic and ionic conductivities are a way to improve the electrode properties as it is believed that they extend reaction sites from the traditional TPB (Triple Phase Boundary) region to the whole electrode surface.
From a general viewpoint, MEIC oxides can be formulated \((A, A')_n(M, M')_mO_x\pm\delta\) where \(A\) and \(A'\) are either rare-earth or alkaline earth cations of large size and \(M\) and \(M'\) are 3d elements. According to the \(n/m\) ratio, various structural types can be formed, as for instance perovskite, or derived compounds (as brownmillerite), Ruddlesden-Popper type, pyrochlore,… By varying the nature of \(A\) and \(A'\) cations and the \(A/A'\) ratio, as well as the nature of \(M\) and \(M'\), it results, first, a mixed valences of the \(M, M'\) cations, which confers usually a p-type electronic conductivity, and secondly either sub- or over oxygen stoichiometry, which can induce ionic conductivity. These properties can be easily modulated and lead to interesting properties fulfilling the requirements for cathode materials.

2. Perovskite compounds

During the last two decades, most studies have been devoted to perovskite-type compounds that can be formulated \(AMO_3\pm\delta\). Compounds, such as \(La_0.6Sr_0.4CoO_3\pm\delta\) (LSC), \(La_0.6Sr_0.4Fe_0.8Co_0.2O_3\pm\delta\) (LSFC), are considered as excellent SOFC cathode materials, as they show high surface exchange kinetics and high oxygen diffusivity [2, 3]. Their structure consists of an infinite succession of layers of corner- sharing \(MO_6\) octahedra along all directions (Fig. 1).

The biggest cation \(A\) (\(r_A > 110\) pm) is located in the central cuboctahedral site and the smallest one, \(M\) (\(r_M < 70\) pm), in octahedral sites. The creation of oxygen vacancies lead to the formation of [5] and [4] fold coordinated (pyramidal and tetrahedral) sites.

Provided \(\delta\) is not too large (< 0.20), at high temperature, the structure usually adopts a cubic symmetry and the oxygen vacancies are randomly distributed.

Fig. 1. Structure of \(AMO_3\pm\delta\) perovskite showing the location of the oxygen vacancies
3. Ln$_2$MO$_{4+\delta}$ oxides: basic properties

A new family of oxides belonging to the so-called Ruddlesden-Popper series $A_{n+1}M_nO_{3n+1}$ ($n = 1, 2, 3,$ ) has been investigated during the last few years. The $n = 1$ term, i.e. the compounds formulated $A_2MO_{4+\delta}$ with $A = La$, Nd, Pr, Sr and $M = Ni$, Cu, Co have been more especially studied [4-8]. The main feature of most of these compounds is that they show some oxygen overstoichiometry associated with a mixed valence of the transition metal cation, $M$ [6-10]. Their structure ($K_2NiF_4$ - type) is made up of sheets of (MO$_6$) elongated octahedra sharing corners, interleaved by $A_2O_2$ layers of NaCl-type in which additional oxygen atoms, $O_i$, can be inserted (Fig. 2). The amount of inserted oxygen atoms ($\delta$) may reach values as high as 0.22 as for Nd$_2$NiO$_{4+\delta}$ or even 0.25 for electrochemically oxidized La$_2$NiO$_{4+\delta}$ [4, 9]. They are located in tetrahedral sites, (O$_i$A)$_4$ (Fig. 1).

![Fig. 2. Structure of A$_2$MO$_{4+\delta}$ compounds showing the location of interstitial oxygen atoms](image)

Compared to the perovskite compounds, the oxygen transport in these materials is supposed to be quite different with respect to the oxygen non-stoichiometry-type that involves interstitial oxygen atoms instead of oxygen vacancies.

Basic properties of these materials have been studied; using the isotopic $^{18}$O/$^{16}$O exchange, it has been evidenced that these materials exhibit indeed larger oxygen bulk diffusion ($D^*$) and surface exchange ($k$) coefficients than classical perovskite compounds (Fig. 3) [10, 11].
Fig. 3. Thermal evolution of the diffusion coefficient \( D^* \) and of the surface exchange coefficient \( k \) for various MEIC oxides

The \( D^* \) values are one order of magnitude higher than those of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta} \) (LSFC) and \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta} \) (LSFN), the best perovskite cathodes and eight orders of magnitude larger than for LSM. In addition, their activation energy (\( \approx 0.8 \) eV) is lower than the ones of the perovskite MEIC oxides. The oxygen ionic conductivity of the \( \text{Ln}_2\text{NiO}_{4+\delta} \) compounds calculated using the Nernst-Einstein relation is of the same order of magnitude than the one of the yttrium stabilized zirconia, so called 8YSZ. A similar feature is observed for the surface exchange coefficient \( k \) (Fig. 3). One can conclude that the lower the temperature, the better the expected gain in terms of relative performances for these materials.

Finally, the electronic conductivity of these oxides is about 70 – 120 S/cm and their thermal expansion coefficients about 11-12 \( 10^{-6} \) K\(^{-1} \), close to the ones of the usual electrolytes.

Electrochemical experiments as well as cell tests confirm these promising basic properties.

4. Nickelate compounds as cathodes of SOFC (\( \text{O}^2- \) or \( \text{H}^+ \))

Impedance spectroscopy and voltammetry measurements were performed on various kinds of symmetrical cells.

The first studies were performed under air, with anionic electrolytes. The results with \( \text{Ln}_2\text{NiO}_{4+\delta}/8\text{YSZ/Ln}_2\text{NiO}_{4+\delta} \) cells show that values of area specific resistances (ASRs) at 600 - 700°C fulfil the targets for an application in complete cells (Fig. 4). Currently, the slightly cation deficient Pr nickelate exhibits the lowest value, which makes possible these cathodes to be used even at temperatures as low as 600 °C. Moreover it has been observed that the addition of an interfacial CGO layer significantly improves the ASR as well as the mechanical properties.
Tests cell have been reported showing high values of current densities and power densities. For instance, for cathodes of Nd$_2$NiO$_4$, screen-printed on anode-supported 8YSZ/Ni-8YSZ commercial half cells (HTceramix$^\text{®}$), values up to 1.31 A.cm$^{-2}$ @ 0.70 V, at 800 °C, have been measured leading to a power density of 0.31 W.cm$^{-2}$ at 0.7 V average cell voltage, at 700°C, for a 5-cell stack (250 cm$^2$), the electrical efficiency being 33 % (fuel flow: 5 ml/min/cm$^2$) [12].

The best performances, more than 2 W.cm$^{-2}$ at 800 °C, have been reported by Laberty $et$ $al.$ for a cell made of composite cathodes (La$_2$NiO$_4$-Sm$_{0.2}$Ce$_{0.8}$O$_{1.90}$) [13].

On the other hand, impedance spectroscopy measurements were performed with symmetrical cells using the protonic electrolyte BaCe$_{0.9}$Y$_{0.1}$O$_{3-δ}$ (so called BCY10) under air/3 % H$_2$O atmosphere. The Area Specific Resistances (ASR) are reported in Fig. 5 and again, Pr$_2$NiO$_{4+δ}$ exhibits the lowest value among the investigated compositions.
Following these promising results, a Ni-BCY10/BCY10/Pr2NiO4+δ single cell has been operated at 550–650 °C [14]. The results of I-V characteristics show a power density value of about 100 mW.cm⁻² at 600 °C, which is of the same order than previous results reported by Lin et al. using the perovskite compound BSCF [15].

5. Discussion about the Ln₂NiO₄+δ compounds

Previous examples have pointed out the interest to use the Ruddlesden-Popper compounds, Ln₂NiO₄ nickelates as air electrode in different configurations. Such interesting properties will be discussed on the basis of some basic features of these compounds: i) their stability in dry air as well as in moist atmosphere, which is a requirement for the use in SOFC-H⁺ cells,  ii) their behaviour under different oxygen partial pressures, studied by TGA measurements: these oxides can exchange reversibly some additional oxygen atoms and remain stable in such conditions which is of interest with respect to their behaviour under polarization. One can expect that the material will “breathe” whatever the overpotential, iii) their structural features: the 2D layered structure (anisotropy of the oxygen diffusion [16, 17]), the presence of vacant sites in the A₂O₂ layer, allowing water molecules to be inserted, and to induce some protonic conductivity which would explain the good performances of these nickelates as SOFC-H⁺ cathodes. Last item is concerned with the relation, iv) the last feature of these compounds is concerned with some peculiar structural aspects, i.e. the competing mechanical effects between the sizes of the Ln₂O₂ layer and of the NiO₂ plane, correlated to the redox Ni²⁺/Ni³⁺ couple and the δ value.

Thus it appears that these compounds are really flexible for being used in different systems, which is illustrated by their outstanding good performances.

References
