Structural properties and electrical conductivity of perovskite-type oxides in SOFCs

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Abstract. Structural properties and electrical conductivity of Sr₂MgMoO₆ (SMMO) and Sr₂MgMo₀.₉TM₀.₁O₆.₇ (TM = Co, Mn) compounds were analyzed for establishing the usefulness of these materials as Solid oxide fuel cells (SOFC) anode. SMMO and SMMTM were synthesized through combustion-solution method and annealing in air at temperatures between 1000 and 1200 ºC. SMMO and SMMCo with triclinic structures, and SMMMn with tetragonal structure at room temperature showed a cubic symmetry at 800 ºC, which are apparently coking-resistant. Mn-doping in SMMO is detrimental for electrical conductivity in diluted-H₂ environment, whilst the highest conductivity value was recorded for Co-containing sample on Mo-site of SMMO double perovskite. On the other hand, the oxygen reduction reaction of Pr₂₋ₓNdₓNiO₄⁺ₓʊ oxides with electrolyte materials is a serious drawback in their use as cathode in SOFC.

1. Introduction

The attractive structural and chemical flexibility displayed by perovskite type compounds has allowed its application as dielectric device, magnetic memory and electrolyte, anode and cathode in solid oxide fuel cells (SOFCs). The ideal simple perovskite (ABX₃), consisting of three-dimensional arrangement of corner-sharing octahedra with a central small cation (B) and a larger cation (A) situated in cuboctahedral cavity can be distorted giving rise to complex perovskites or double perovskites (A₂BB'X₆) [1-3], expanding the list of compounds crystallizing in perovskite structures and their utilities.

Double perovskites such as Sr₂MgMoO₆ (SMMO) [4] has raised the interest from researchers because of its thermal stability under reducing atmosphere and sulphur tolerance, which are crucial properties for a SOFC-anode [5,6] that work with light hydrocarbons (butane, hexane, etc) as fuel. Nevertheless, several research groups assumed the task of evaluating the effect of the partial substitutions of Sr by La and Sm [7,8], Mg by transition metals: Co, Ni, and Al [9-11]. In the case of Mo were implemented substitutional additions with Nb, V and W [12,13]. In this work 10% of Mo by Co and Mn in Sr₂MgMoO₆ oxide has been substituted with the aim of assessing the structural behaviour through X-ray diffraction studies, and the impact of each transition metal on conductivity values of SMMO double perovskite by using 4-probe DC method.
Regarding SOFC-cathode, Ln$_2$NiO$_{4+δ}$ oxides with K$_2$NiF$_4$-type structure are considered to be some of the most attractive electrodes [14]. Their crystal structure consists of LnNiO$_3$ perovskite layers having oxygen vacancies, stacked alternating with rock salt Ln$_2$O$_2$ layers which can accumulate O-interstitials ($δ$) of high mobility [15]. Some authors have reported a promising performance of Pr$_2$NiO$_{4+δ}$ (PNO) as oxygen reduction electrodes [16]. Nevertheless, other studies show that PNO is not thermally stable at temperatures below 900 °C [17]. Nd$_2$NiO$_{4+δ}$ (NNO) instead, shows thermal stability and chemical compatibility with a few electrolyte materials. Aiming to combine the good electrochemical features of PNO with the thermal stability and chemical compatibility of NNO, solid solutions between PNO and NNO such as Pr$_2$Nd$_x$NiO$_{4+δ}$ ($x=$0.3, 1 and 1.7) were studied by electrochemical impedance spectroscopy measurements (EIS).

2. Experimental

Sr$_2$MgMoO$_6$ (SMMO) and Sr$_2$MgMo$_{0.9}$TM$_{0.1}$O$_{6.6}$ (SMMTM) synthesis: SMMO and SMMTM powders were synthesized by combustion-solution (CS) method [18-20]. Stoichiometric amounts of SrCO$_3$ and Mg were dissolved in a diluted HNO$_3$ solution, whilst MoO$_3$ was dissolved in NH$_4$OH solution. For Mn- and Co-containing samples, metallic-manganese and cobalt powders were diluted in a HNO$_3$ solution. The resulting ashes were thermally treated under the optimised conditions of 1000 °C-12 h for SMMO and SMMMn, and 1200 °C-10 h for SMMCo.

Nickelates synthesis: PNNO powders were synthesised by hexamethylenetetramine (HMTA) method [17]. Stoichiometric amounts of precursors Pr$_6$O$_{11}$, Nd$_2$O$_3$ and Ni(CH$_3$COO)$_2$·H$_2$O were dissolved in acetic acid with HMTA and AcAc, in a (ligand: metal) 3:1 molar ratio. Precursor solution was refluxed and heated at 150 °C, which was then fired at 400 °C. The obtained powders were finally annealed at 1100 °C.

The phase purity for all samples (SMMTM and PNNO) was checked by X ray diffraction (XRD) using a Panalytical-Empyrean diffractometer equipped with a graphite monochromator and a 3D PIXcel detector. The high temperature - XRD studies were performed under oxidizing (air) atmosphere at 800°C making use of an Anton Paar HTK-1200N camera attached to the Empyrean diffractometer.

The electrical conductivity of all samples was measured by conventional four probe DC method by using an Agilent 3497 A scanner-multimeter. Dense samples were obtained by uniaxial pressing of SMMTM powders followed by a thermal treatment in air at 1300 °C during 4 h. Pt wire and Ag paste were used to make the electrical contacts. The measurement conditions have previously reported [20].

Symmetrical cells fabrication: La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.85}$ (LSGM) electrolyte pellets were formed by pressing uniaxially LSGM powder and then sintering at 1500 °C for 4 h. PNNO powders were suspended with polyvinyl butyral (2wt%), polyethylene glycol (1 wt%), ethanol (30 wt%) and α-terpinine (27 wt%); the resulting ink was then deposited onto the LSGM pellets by spin coating. These electrodes were allowed to dry before being fired at 1000 °C for 1 h in laboratory air. Gold metal grids were used as current collectors for electrochemical testing [21,22]. The microstructures of top surfaces of the electrodes and PNNO/LSGM cross-sections were examined by scanning electronic microscopy (SEM) using a SEM-FEG Nova Nano SEM 230 microscope.

Electrochemical characterization: EIS was used to study the mechanism of ORR and to follow the evolution in time of the total cathode polarization resistance of the samples. These measurements were performed with a frequency response analyzer (FRA) coupled to an AUTOLAB potentiostat, measuring between 0.2 mHz and 1 MHz, with 50 mV of amplitude and 0 V of bias potential. The spectra at different temperatures were collected each 50 °C by increasing temperature from 500 °C to 700 °C under synthetic air flow (20% O$_2$-Ar).

3. Results and discussions

3.1. Sr$_2$MgMo$_{0.9}$TM$_{0.1}$O$_{6.6}$ (TM = Co, Mn) double perovskites as anodes in SOFCs

The SMMO and SMMMn samples thermal treated at 1000 °C – 12 h and 1200 – 10 h respectively, exhibited a triclinic structure (s.g: I–I) at room temperature, whilst Mn-containing powders, annealing...
at 1000 °C – 12 h, showed a tetragonal structure (s.g: I4/m). These results were previously reported [18-20]. Furthermore, DRX patterns of SMMO and SMMTM powders, collected in air atmosphere at 800 °C, indicated that SMMO and SMMTM double perovskites present a cubic symmetry (s.g Fm3m). Figure 1 shows DRX patterns at RT and 800 °C of Co-containing sample. Inset Figure 1 displays a magnification between 25° and 35° of DRX patterns for SMMCo compound, where can be observed the SrO impurity. Then, the possible distortions that would be present on MgO6 and Mo(TM)O6 octahedrons at RT, disappear at 800 °C, broadened results have already been reported [20].

![DRX patterns of SMMCo powders at room temperature (RT) and 800 °C.](image)

Electrical conductivity measurements under reducing atmosphere (10%H2 – Ar) at temperatures of between 500 °C and 800 °C revealed that SMMO and SMMTM samples exhibit a linear dependence of conductivity, which is indicative of a semiconductor behavior. Figure 2 shows the Arrhenius-type plots of electrical conductivity ($\sigma$), with $\sigma = \left(\frac{A}{T}\right) \exp\left(-\frac{E_a}{k_B T}\right)$, where $k_B$: constant of Boltzman, $E_a$: activation energy and A: pre-exponential factor for Mn-containing sample. Table 1 presents conductivity and activation energy values for SMMO and SMMTM double perovskites. It can be observed that Mn presence was detrimental to electrical conductivity of SMMO double perovskite, since $\sigma$ decrease from 0.67 S/cm (SMMO) to 0.25 S/cm (SMMMn), whilst conductivity of SMMCo was the highest value registered 0.8 S/cm. A complete discussion on electrical conductivity of SMMO and SMMTM double perovskites are available in Reference [20].

![Arrhenius-type plots of electrical conductivity of SMMMn sample.](image)
Table 1. Electrical conductivity and activation energy of SMMO and SMMTM compounds.

| Compound | $\sigma$ (S/cm) | $E_a$ (eV) |
|----------|----------------|------------|
| SMMO     | 0.67           | 0.18       |
| SMMCo    | 0.80           | 0.27       |
| SMMn     | 0.25           | 0.91       |

The coking-resistance is one of the essential characteristics that a SOFC anode must fulfil, that is why SMMO and SMMTM powders, synthesized in this research, and Ni-GDC commercial powders were subjected an annealing under 10%CH$_4$-Ar atmosphere for 10 h, the results are display in Figure 3. DRX patterns before (pre-CH$_4$) and after (pos-CH$_4$) thermal treatment in diluted-CH$_4$ for Ni-GDC commercial powders (Figure 3(a)) showed that this material does not retain its phase once it is exposure to CH$_4$ atmosphere and additionally it accumulates carbon-deposits, as indicated by graphite-peak. Meanwhile, XRD patterns of SMMCo sample revealed an apparent resistance to coking on part of this double perovskite (Figure 3(b)).

3.2. Study of Pr$_2$-xNd$_x$NiO$_{4+\delta}$ ($x=0.3, 1$ and $1.7$) oxides as cathodes in SOFCs

Figure 4 shows representative impedance spectra recorded at 700 °C in synthetic air flow for the symmetrical cell Au/PNNO/LSGM/PNNO ($x=1$)/Au cell and comparing to the spectrum of NNO sample [14,21]. The data are normalized to the geometric area of the electrodes in the symmetrical cell. Contrary to the expected outcomes, the polarization resistance increased with the increment of the Pr amount, two reasons are possible to explain the observed in this work. The microstructure of the electrode affects in a significant way its electrochemical performance. Considering this fact, the larger polarization resistance of the PNNO samples respect to NNO can be related to NNO microstructure with smaller particles than those of PNNO samples [22]. Nonetheless, this reason does not explain the rise of the polarization resistance with the decrease of Nd content in PNNO samples. On the other hand, it has been reported that the thermal and chemical stability have an important effect in the electrical transport properties. Accordingly, the XRD pattern of PNNO electrodes surface deposited on LSGM, before and after EIS measurements were compared, the results for PNNO ($x=0.3$) are shown in Figure 5(a) (similar results were observed for the other two samples). Only the peaks of NPNO and one small peak in
$2\theta=32.3$ corresponding to LSGM can be observed in the XRD patterns, before and after EIS measurements. This result indicates that PNNO are stable with these operation conditions (time, temperature and atmosphere). However, the chemical compatibility between PNNO and LSGM electrolytes was checked by performed a reactivity essay. Equal amounts of nickelate and electrolyte powders were mixed; the mixture was grinded and annealed at 1000 °C for 72 h with the target of producing an accelerated aging. In previous works, similar tests with NNO showed that below 1050 °C there are not chemical reactivity between NNO and LSGM materials. XRD patterns of the annealed mixtures between PNNO and LSGM are shown in Figure 5(b) afterwards the heat treatment, peaks corresponding to LSGM are observed, meanwhile the NPNO phases are decomposed. The new phases, which is product of the chemical reactivity could not be indexed. The magnitude of the chemical reactivity increases as the content of Pr augment.

![EIS spectra for NPNO cathodes collected at 700 °C in air.](image)

**Figure 4.** EIS spectra for NPNO cathodes collected at 700 °C in air.

![XRD pattern of the NPNO (x=0.3) cathodes before and after EIS measurements. XRD patterns of PNNO and LSGM powders mixtures after thermal treatment at 1000°C for 72 h.](image)

**Figure 5.** (a) XRD pattern of the NPNO (x=0.3) cathodes before and after EIS measurements. (b) XRD patterns of PNNO and LSGM powders mixtures after thermal treatment at 1000°C for 72 h.

The results of the reactivity tests would indicate that PNNO electrodes may have reacted with the electrolyte at the adhesion temperature and is possible that other phases coexist on the electrode/electrolyte interface. These extra phases would affect the electrical transport properties of the PNNO cathodes. This outcome is the reason of the larger polarization resistance in the samples that contained Pr.
4. Conclusions
Sr$_2$MgMo$_{0.9}$Co$_{1}$O$_{6.5}$ (SMMC0) and Sr$_2$MgMo$_{0.9}$Mn$_{1}$O$_{6.5}$ (SMMMn) synthesized by combustion method achieved a double perovskite phase at room temperature with triclinic (1I) and tetragonal (14/m) structures respectively. These structures change to cubic symmetry at 800 °C. The electrical conductivity measurements displayed that the partial substitution of Mo by Co in Sr$_2$MgMoO$_6$ structure improve its electrical response, because conductivity value increases from 0.67 S/cm for SMMO to 0.8 S/cm for SMMC0. DRX studies after a thermal treatment in diluted-CH$_4$ of SMMO and SMMTM powders showed that these materials are coking-resistant. Then, SMMTM double perovskites could be considered a promising SOFC-anode.

Contrary to the expected results, EIS measurements of Pr$_2$-Nd$_{x}$NiO$_{6.5}$ (x=0.3, 1 and 1.7) oxides revealed that, the addition of Pr in the oxides does not improve the electrochemical performance of the PNNO cathodes. The results of the reactivity-test between PNNO and LSGM, displayed that the presence of Pr in the cathodes, increase the chemical reactivity on electrode/electrolyte interface, leading to a decrease in transport properties of the PNNO cathodes. The chemical reactivity with electrolyte materials is a serious drawback of the PNNO in their utilities as cathode materials.

Acknowledgments
This work was financially supported by Comisión Nacional de Energía Atómica (CNEA), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de Cuyo (UNCuyo) and ANPCyT.

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