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Synthesis and characterisation of a green NiO/La(Sr)$PO_{4-\delta}$ cermet anode for phosphate based solid oxide fuel cells

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Abstract

Cermets are commonly used as anode in fuel cells. Ni/La(Sr)$PO_{4-\delta}$ has not been synthesized before and it could be a good anode for high-temperature protonic fuel cells. In this article, the preparation of Ni/La(Sr)$PO_{4-\delta}$ by combustion synthesis using nitrates, ammonium phosphate and urea is described. In this preliminary work, we are more concerned to understand the calcined powder reduction pattern with in situ Electrochemical Impedance Spectroscopy (EIS) experiments. The as-prepared powder is structurally analysed by XRD, also after each calcination treatment in air and in reducing atmosphere, and before and after the electrical measurements were carried out. The electrical characteristics of a green pellet of NiO/La(Sr)$PO_{4-\delta}$ are studied by impedance spectroscopy as a function of temperature (50–800 °C) in a reducing atmosphere (10^{-20} atm). The reducing process of NiO to Ni is also followed by EIS. Finally, the morphology of this composite material analysed by EIS was observed by means of SEM/EDX. The morphology of this composite material indicates the presence of two compatible phases. One corresponds to the La(Sr)PO_4 phase and the second one to a Ni phase, according to EDX data. The low electrical conductivity values indicate that nickel agglomerates are not totally percolated in the calcined pellet as it was expected. Higher conductivity values are expected when total Ni percolation occurs after sintering.

Keywords: Composites; Impedance; Ionic conductivity; Fuel cells; Phosphates

1. Introduction

Composite materials are widely used in research and industrial materials as they combine the properties of each of the component phases. Examples of applications for this kind of materials can be found in resistors and sensors. Our interest is focused on a cermet, a biphasic composite made of a metal and a ceramic phase. Ni-based cermets are commonly used as anodes in solid oxide fuel cells (SOFCs). They offer good electronic and ionic conductivity and are good catalysts for the electrochemical oxidation of the fuel that takes place at the anode. A good electronic conductivity is necessary in order to collect the current produced by the fuel cell and, the protonic conductivity is of basic importance to have good transport properties from the fuel compartment through the anode to the electrolyte in a high temperature proton SOFC. Also Ni plays a relevant role, which is to provide the catalyst oxidation of the fuel. A typical cermet used in SOFC is Ni/YSZ[1] when the fuel is hydrogen. We propose the Ni/La(Sr)PO_4 cermet as candidate anode for proton high temperature SOFCs.

This work is a first approach to the synthesis of the Ni/La(Sr)PO_4 cermet. To our best knowledge, this material has not been synthesized before. For this reason, there are several basic points and problems to be analysed: the synthesis and characterisation of the powders, the chemical and physical compatibilities between the ceramic and the metal phase, the possible formation of second phases, the thermal stability, the percolation limit, etc. The work previously performed by the authors on the ceramic phase[2–5] is the base used to approach the subject together with a previous work by Mather et al.[6] The first choice is a phosphate based cermet because it would minimize the anode/electrolyte interface mismatch. The Ni/La(Sr)PO_4 (50 vol.%) was prepared by means of a one-step reaction, the combustion, and the subsequent reduction. This synthesis was successfully applied to obtain La(Sr)$PO_{4-\delta}$ in a previous work.[2] Combustion synthesis is a simple and fast synthesis and in the case of the cermet it would give the advantage of obtaining a composite material through a very simple process.

2. Experimental

The material preparation was made using the following powder precursors (analytical grade): $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$,

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$Ni(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_2HPO_4$ purchased from Panreac Química S.A., Barcelona, Spain. Urea was used as a fuel (analytical grade purchased from Aldrich, Germany). The precursors amounts were calculated to obtain a 5% Sr substitution in the $LaPO_4$ structure ($La_{0.95}Sr_{0.05}PO_{4-\delta}$), because this composition shows good values of conductivity.[4] Thus the following ratios were applied: 5 mol of $Sr(NO_3)_2$, 95 mol of $La(NO_3)_3{\cdot}6H_2O$ and 100 mol of $(NH_4)_2HPO_4$. Nickel nitrate was added to obtain a 50 vol.% of metal Ni in the final composite material. The precursors, stoichiometrical ratios for Ni/La(Sr)PO_4 (50/50 vol.%), were previously mixed in a wide-mouth vitreous silica basin employing a glass bar until a viscous liquid uniform mixture was formed. The fuel was added using the stoichiometric amount calculated in the same way as it was carried out in a previous work.[2] The basin was then placed on a hot plate and heated up to 100 °C for 10 min before the final treatment at 300 °C for 1 h. The reaction takes place in 5 min, leaving a green foam in the basin. The foam was crushed to obtain a fine powder which was easily sieved through a 100 μm sieve. The powder was finally calcined at 800 °C/12 h in air in order to increase the powder crystallinity and to eliminate the nitrate impurities.[2,3] A final sieve through 100 μm before compaction was performed. Pressed samples were reduced in a H_2/N_2 (10/90 vol.%) at 600 °C/2 h.

Phase identification of the as-prepared powder, also after each calcination treatment in air and in reducing atmosphere, and before and after the electrical measurements were carried out, has been performed by X-ray diffraction on a Siemens Powder diffractometer D-5000 operating at 50 kV and 30 mA using Cu Kα radiation and a Ni-filter in the range of $2\theta = 10$–80°. The scanning step was 0.05°, the time/step 1.5 s and the rotation speed 30 rpm. Particle morphology was observed by scanning electron microscopy and chemical analysed by energy-dispersive X-ray spectroscopy (SEM–EDS) on a Hitachi S-4700 microscope. The conductivity behaviour was examined by EIS (HP Agilent 4294A frequency analyzer model). The impedance spectra were collected every 50 °C in the 50–800 °C range, in two stages, heating and cooling, both in a reducing atmosphere (H_2/N_2, 10/90 vol.%, 10^{-20} atm). A frequency range of 40 Hz–1 MHz was applied.

Table 1

Relevant thermodynamic data. The elements and the compounds collected in the table are in their standard state (most stable physical state at 298 K and 1 atm)[7]

Compound	ΔH_f° (kJ mol^{-1})	C_p° (J mol^{-1} K^{-1})
$LaPO_4$	−1949	100.950
$(NH_4)_2HPO_4$	−1566.9	188.0
$Ni(NO_3)_2{\cdot}6H_2O$	−126.86	26.64
$Sr(NO_3)_2$	−978.2	149.9
$La(NO_3)_3{\cdot}6H_2O$	−3060.7	–
$CO(NH_2)_2$	−318.8	89.04
H_3PO_4	−1284.4	106.1
SrO	−592.04	45.4
La_2O_3	−1793.7	108.68
NH_4NO_3	−365.65	139.12
NH_3	−45.898	35.652
CO_2	−393.133	$43.22 + 0.011457T$[a]
H_2O	−241.587	$30.10 + 0.015057T$[a]
N_2	0	$27.17 + 0.004187T$[a]
O_2	0	$24.74 + 0.015057T$[a,b]

[a] T = absolute temperature.

[b] Calculated from discrete values.

3. Results and discussion

Standard thermodynamic properties of the compounds which might be involved in the combustion process are reported in Table 1.[7,8] The combustion reactions are described in Table 2 together with the ΔH° found in the literature.[7,8] The last reaction and most important one describes the total reaction, with all the involved precursors: the three nitrates, the phosphate and the urea (fuel). The reaction gives NiO, La(Sr)PO_4, NH_4NO_3 and the emission of $H_2O + N_2 + O_2$ as gases.

X-ray diffraction data are shown in Fig. 1. The first set of data are obtained from the as-prepared powders. Very broad peaks are easily detectable in the positions corresponding to the NiO and $LaPO_{4-\delta}$. The powder was then calcined at 800 °C, and the crystallisation of the monazite structure is produced. The result of the reduction process is indicated in the last set of data. The nickel oxide peaks are not observed while the metal Ni peaks are present. As it was expected the NiO was completely reduced to Ni.

Table 2

Equations describing some of the chemical reactions that might be involved in the combustion synthesis. ΔH° values are calculated from thermodynamic data listed in Table 1

Reaction	ΔH° (25 °C) (kJ mol^{-1})
R1 ($La(NO_3)_3{\cdot}6H_2O_{(c)} \Rightarrow 0.5La_2O_{3(c)} + 6H_2O_{(g)} + 1.5N_{2(g)} + 3.75O_{2(g)}$)	715.2
R2 ($Sr(NO_3)_{2(c)} \Rightarrow SrO_{(c)} + N_{2(g)} + 2.5O_{2(g)}$)	386.2
R3 ($(NH_4)_2HPO_{4(c)} + 3/4O_{2(g)} \Rightarrow H_3PO_{4(c)} + 1/2N_{2(g)} + 3/2H_2O_{(g)} + NH_{3(g)}$)	125.8
R4 ($2[La(NO_3)_3{\cdot}6H_2O]_{(c)} + CO(NH_2)_{2(c)} \Rightarrow 5La_2O_{3(c)} + CO_{2(g)} + 14H_2O_{(g)} + 4N_{2(g)} + 6O_{2(g)}$)	
R5 ($Sr(NO_3)_{2(c)} + CO(NH_2)_{2(c)} \Rightarrow SrO_{(c)} + CO_{2(g)} + 2H_2O_{(g)} + 2N_{2(g)} + O_{2(g)}$)	
R6 ($(NH_4)_2HPO_{4(c)} + CO(NH_2)_{2(c)} + O_{2(g)} \Rightarrow H_3PO_{4(c)} + CO_{2(g)} + 5H_2O_{(g)} + 2N_{2(g)}$)	
R7 ($2La_2O_{3(c)} + 3H_3PO_{4(c)} \Rightarrow 3LaPO_{4(c)} + La(OH)_{3(c)} + 3H_2O_{(g)}$)	
R8 ($2NH_4{}^+ + 2NO_3{}^- \Rightarrow 2NH_4NO_{3(c)}$)	
R9 ($[Ni(NO_3)_2{\cdot}6H_2O]_{(c)} \Rightarrow NiO_{(c)} + N_{2(g)} + 2.5O_{2(g)} + 6H_2O_{(g)}$)	520.41
R10 ($(1-s)La_2O_{3(c)} + 2H_3PO_{4(c)} + 2sSrO_{(c)} + 2sO_2 \Rightarrow 2La_{(1-s)}PO_4{:}Sr_{s(c)} + La_{(1-s)}PO_4{:}Sr_s{\cdot}xH_2O_{(c)} + 3H_2O_{(g)}$)	
R11 ($SrO_{(c)} + CO_{2(g)} \Rightarrow SrCO_{3(c)}$)	
R12 ($La(NO_3)_3{\cdot}6H_2O_{(c)} + nSr(NO_3)_{2(c)} + Ni(NO_3)_2{\cdot}6H_2O_{(c)} + (NH_4)_2HPO_{4(c)}$ $\Rightarrow La_{(1-s)}PO_4{:}Sr_{s(c)} + La_{(1-s)}PO_4{:}Sr{\cdot}xH_2O_{(c)} + NiO_{(c)} + 2NH_4NO_{3(c)} + H_2O_{(g)} + N_{2(g)} + 1/2O_{2(g)}$)	

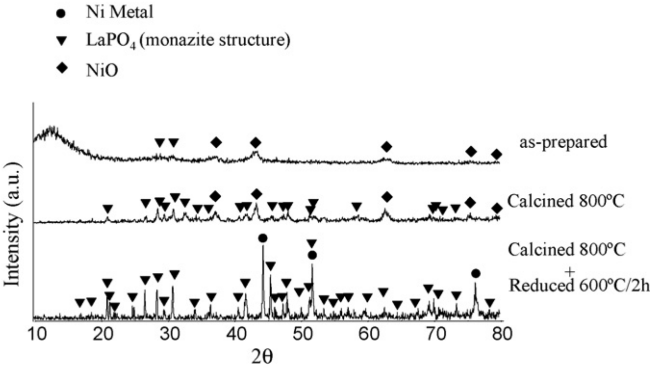

Fig. 1. XRD data of, respectively, as-prepared NiO/La(Sr)PO_4, calcined at 800 °C, reduced at 600 °C.

After reducing at 600 °C (and after the electrical measurements) a fresh fracture of the cermet pellet was observed by means of SEM. The micrograph (Fig. 2) shows two different types of agglomerates (∼200 nm size), one is white, the other one is dark. According to the atomic weight of the two phases (La(Sr)PO_4 and Ni) and to EDX analysis, the white agglomerates are attributed to the La(Sr)PO_4 phase and the dark ones are attributed to the nickel phase.

In Fig. 3 the experimental impedance spectroscopy data are shown. The sample is a green pellet calcined at 800 °C/12 h in air of NiO/$La_{0.95}Sr_{0.05}LaPO_{4-\delta}$ composition. The impedance spectra were collected every 50 °C in the 50–800 °C range under N_2/H_2 atmosphere. In this figure, two spectra for the heating stage and two spectra for the cooling stage are shown: at 200 and 600 °C in the heating stage and at 400 and 100 °C in the cooling stage under N_2 90 vol.%/H_2 atmosphere, respectively. Typical impedance arcs are obtained at low temperatures. At higher temperatures, a spike is observed instead of an arc. Fig. 4 was created using all the resistance data from all the impedance spectra.

It has to be outlined that at about 550 °C (point (a) in Fig. 4) the reduction of the NiO to metal Ni takes place. This fact is deduced by the conductance measurements done in situ during the reduction in H_2/N_2 atmosphere: from 450 to 550 °C the conductivity decreases, while at higher temperature it increases (Fig. 4). It is possible to attribute the decrease of conductivity to a volume change occurring during the phase transition and the following increase to the presence of the metal phase in the cermet, respectively. The total conductivity is relatively low for a cermet containing nickel. This might indicate that a part of the Ni enters into the La(Sr)$PO_{4-\delta}$ lattice[9] and/or a metal phase segregation takes place or, most probably that the nickel agglomerates inside the pellet are not percolated. This third factor has to be referred to the fact that the pellet in analysis is not sintered. The difference in the conductivity values, between heating and cooling, indicates a difference in the composition of the cermet due to the presence of NiO or Ni. XRD before and after the electrical measurements confirms the reduction process during the electrical measurements.

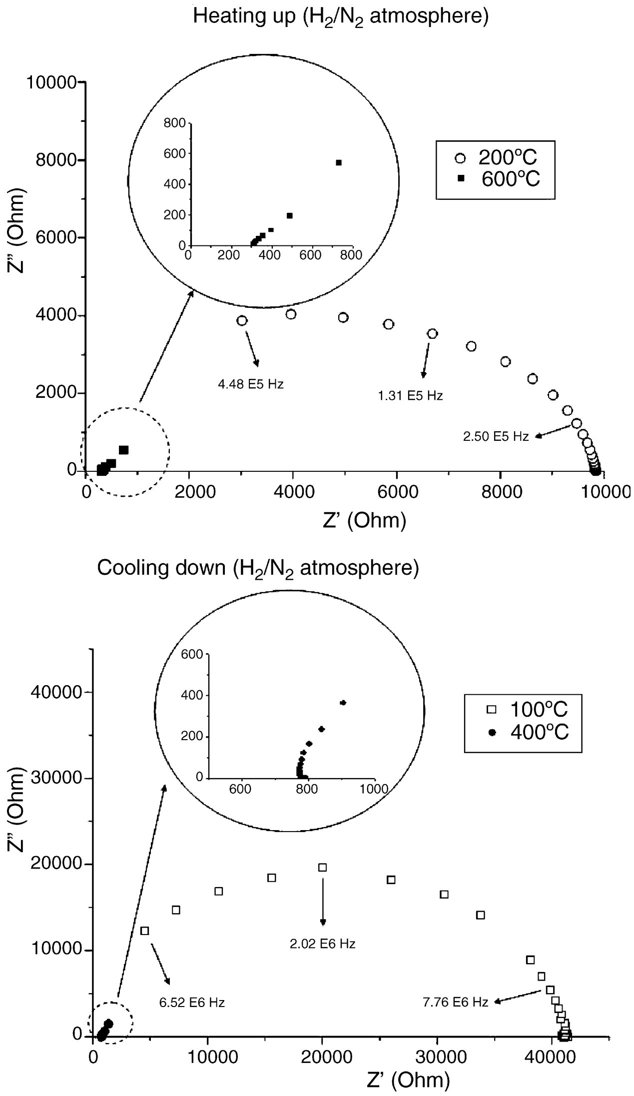

Fig. 3. Impedance spectra of NiO/La(Sr)PO_4 calcined at 800 °C in air. Two spectra are taken during heating (at 200 and 600 °C) and two during cooling (at 400 and 100 °C). Heating and cooling were both carried out under reducing atmosphere.

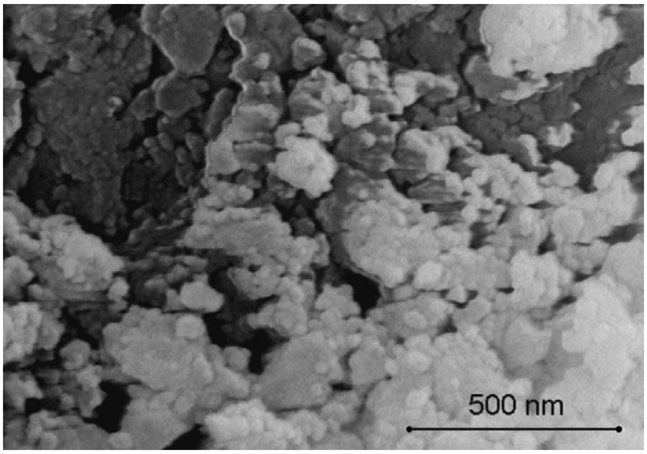

Fig. 2. SEM micrograph of a fresh fracture of the cermet pellet reduced at 600 °C (after the electrical measurements) in a H_2/N_2 atmosphere.

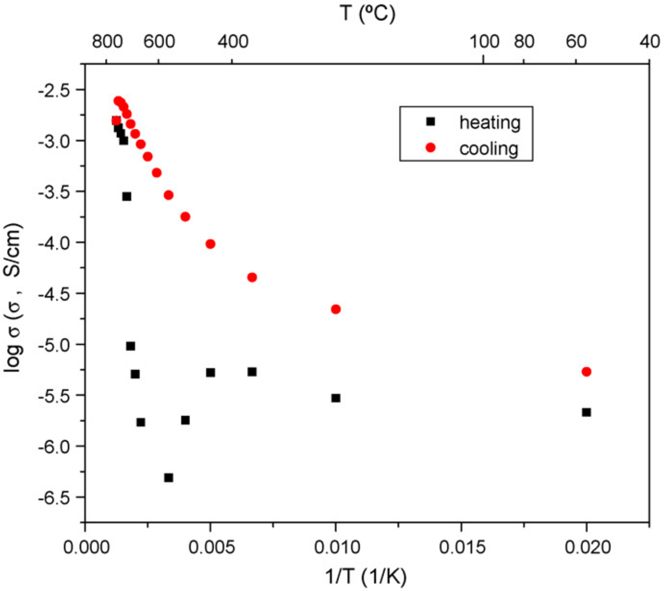

Fig. 4. Total conductivity obtained from impedance spectra (every 50 °C) of NiO/La(Sr)PO_4 calcined at 800 °C in air. First, heating from 50 to 800 °C, second cooling in the same range (Ni/La(Sr)$PO_{4-\delta}$). Heating and cooling were both carried out under reducing atmosphere.

4. Conclusions

It has been proved that combustion synthesis is a good preparation method in order to obtain a porous cermet of Ni/La(Sr)$PO_{4-\delta}$. By XRD and SEM, second phases were not detected and the metal and the ceramic phases seem to be compatible at least up to 800 °C. Also no indication of the presence of NiO after reduction was found, proving that all the oxide was reduced to the metal phase. The SEM micrographs indicate a distribution of two phases of both ceramic and metal. The impedance spectroscopy analysis performed on a pellet calcined at 800 °C in air indicate that the NiO reduction takes place at about 550 °C under N_2/H_2 (10/90 vol.%) atmosphere. The expected low conductivity values can be due to the fact that the pellet is constituted by calcined powders instead of sintered bodies. Higher conductivity values are expected when a total Ni percolation occurs after sintering.

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References

1. Ringuedé, A., Labrincha, J. A. and Frade, J. R., A combustion synthesis method to obtain alternative cermet materials for SOFC anodes. *Solid State Ionics*, 2001, **141/142**, 549–557.
2. Gallini, S., Jurado, J. R. and Colomer, M. T., Combustion synthesis of nanometric powders of $LaPO_4$ and Sr-substituted $LaPO_4$. *Chem. Mater.*, 2005, **17**(16), 4154–4161.
3. Gallini, S., Jurado, J. R. and Colomer, M. T., Synthesis and characterization of Sr:$LaPO_4$ prepared through coprecipitation. *J. Eur. Ceram. Soc.*, 2005, **25**, 2003–2007.
4. Gallini, S., Hansel, M., Norby, T., Colomer, M. T. and Jurado, J. R., Impedance spectroscopy and proton transport number measurements on Sr-substituted $LaPO_4$ prepared by combustion synthesis. *Solid State Ionics*, 2003, **162**, 167–173.
5. Gallini, S., Jurado, J. R. and Colomer, M. T., Preparation and characterization of $LaPO_4$ and Sr-doped $LaPO_4$ powders. In *Proceedings of the Workshop on Processing of and Microstructure–Property Relations in SOFC Components and Ceramic Gas-Separation membranes*, 2002, pp. 23–30.
6. Mather, G. C., Figueiredo, F. M., Jurado, J. R. and Frade, J. R., Synthesis and characterisation of cermet anodes for SOFCs with a proton-conducting ceramic phase. *Solid State Ionics*, 2003, **162/163**, 115–120.
7. D.R. Lide, D. R., ed., *CRC Handbook of Chemistry and Physics*. 84th ed. CRC Press, Boca Raton, Florida, USA, 2003–2004. pp. 5–1/5–106.
8. Thiriet, C., Konings, R. J. M., Javorský, P., Magnani, N. and Wastin, F., The low temperature heat capacity of $LaPO_4$ and $GdPO_4$, the thermodynamic functions of the monazite-type $LnPO_4$ series. *Chem. Thermodyn.*, 2005, **37**, 131–139.
9. Montel, J.-M., Devidal, J.-L. and Avignant, D., X-ray diffraction study of brabantite–monazite solid solutions. *Chem. Geol.*, 2002, **191**, 89–104.