Symmetrical cells of $Pr_2NiO_{4+\delta}$ on electrolytes with the apatite-type structure. Fabrication of Microtubular Apatite-based SOFC

A. Orera , J. Silva, M.A. Laguna-Bercero, S. Poblador, R.I. Merino

Instituto de Ciencia de Materiales de Aragón

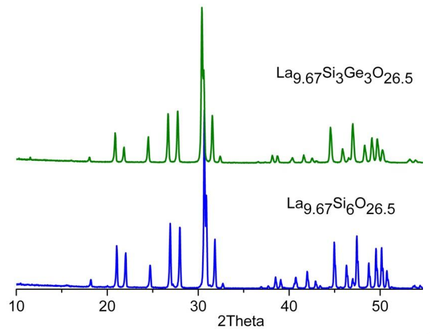
CSIC Consejo Superior de Investigaciones Científicas

ABSTRACT: Among the family of materials with the K_2NiO_4-type structure, Nd/Pr nickelates have extremely good performances as cathodes, especially at intermediate temperatures (700-800ºC), where the conventional oxygen conductor electrolytes like YSZ lose their supremacy. This intermediate temperature use, together with some chemical compatibility problems found with Zr based materials, make the combination of these nickelate cathodes with apatite electrolytes very interesting. The compatibility of two compositions, $Pr_2NiO_{4+\delta}$ and $Nd_{1.95}NiO_{4+\delta}$ with the electrolytes $La_{9.67}Si_6O_{26.5}$ (LSO) and $La_{9.67}Si_3Ge_3O_{26.5}$ (LSGO) has been proved at different temperatures and symmetrical cells of these pairs have been electrically evaluated. In order to study the SOFC performance , Ni-based anode supported microtubular cells have been fabricated with LSO as electrolyte and cathode layer of $Pr_2NiO_{4+\delta}$.

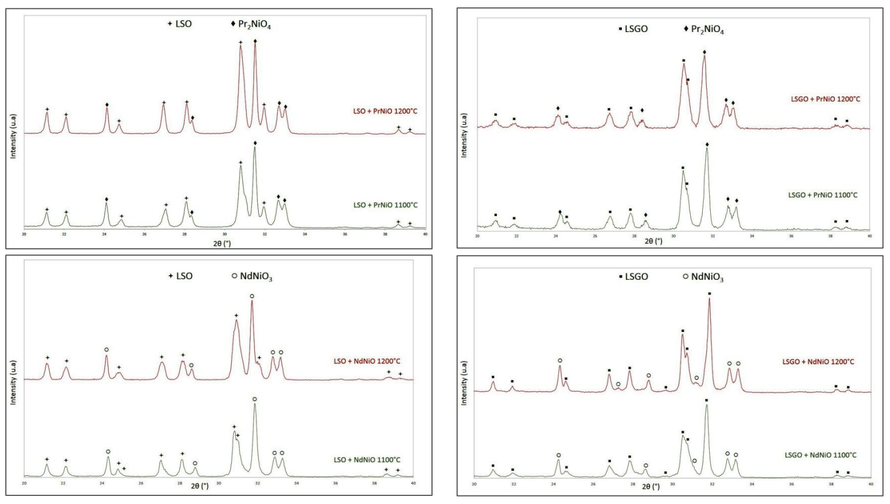
Materials

➢Single phase $La_{9.67}Si_6O_{26.5}$ and $La_{9.67}Si_3Ge_3O_{26.5}$ were prepared from a stoichiometric mixtures of the dried starting materials, La_2O_3, GeO_2 and SiO_2. The mixture was intimately ground in a ball mill for 6h in ethanol and then heated at 1500ºC for 4h. Phase purity was confirmed using XRD and Raman

➢Commercial powders of $Pr_2NiO_{4+\delta}$ and $Nd_{1.95}NiO_{4+\delta}$ (Marion Technologie) were used as cathode materials. Green NiO (Grade F Hart Materials Limited) was used in the anode mixtures



REACTIVITY TESTS



No reactivity has been observed between $Pr_2NiO_{4+\delta}$ / $Nd_{1.95}NiO_{4+\delta}$ and the silicate apatites $La_{9.67}Si_6O_{26.5}$ and $La_{9.67}Si_3Ge_3O_{26.5}$ at both 1100 and 1200ºC, Cosintering is not possible due the high temperatures required to obtained dense silicates and therefore a 2 step-sintering should be necessary

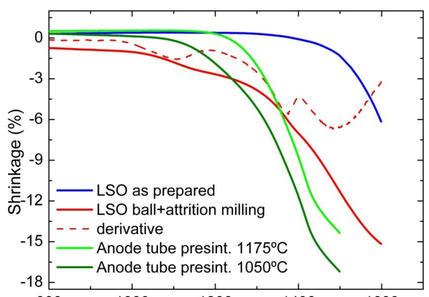
Sintering

Dilatometry experiments show the need of high sintering temperatures for both LSO and LSGO compounds in order to get densification.

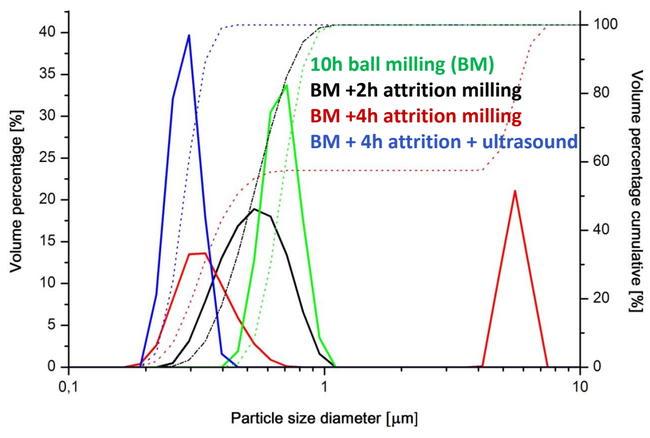
As prepared LSO was sintered at temperatures as high as 1575ºC for 2h, yielding densities of 92%. Ball milling and attrition milling processes reduced the grain size considerably (see bellow), allowing a decrease on the sintering temperature down to 1480ºC.

LSGO sintering is not so straightforward, since treatments at 1550ºC for short times (to avoid Ge volatilization) gave pellets 70% dense and. A milling treatment of the powder reduces the sintering temperature to 1430, yielding densities above 90%.

The presintering treatment of the anode supports was also modified in order to match the electrolyte shrinkage rate and temperature.



Particle Size Distribution



As prepared powder underwent different steps of ball-milling and attrition milling in order to decrease its particle size. The changes in particle size have drastic effects on the sintering temperature and densities achieved (see above)

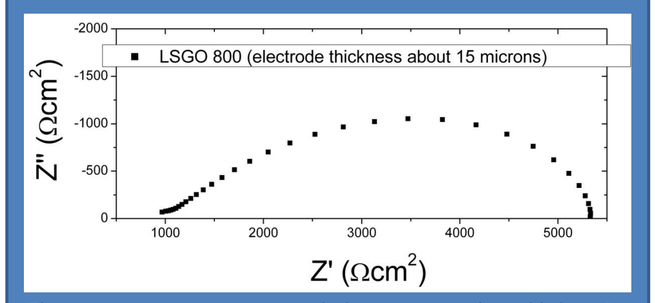
SYMMETRICAL CELL TESTS

Symmetrical cells of LSO and LSGO pellets with $Pr_2NiO_{4+\delta}$ cathodes on both sides have been electrochemically tested by means of Impedance Spectroscopy using a Solartron 1260. The table on the right shows the values of the ohmic and polarization ASR resistance for both electrolytes pellets at different temperatures in air. In the case of LSGO, an intermediate layer of the composite 80%PrNi-20%LSGO has been deposited between the electrolyte and the pure $Pr_2NiO_{4+\delta}$ cathode layer, decreasing significantly the polarization resistance at the electrode.

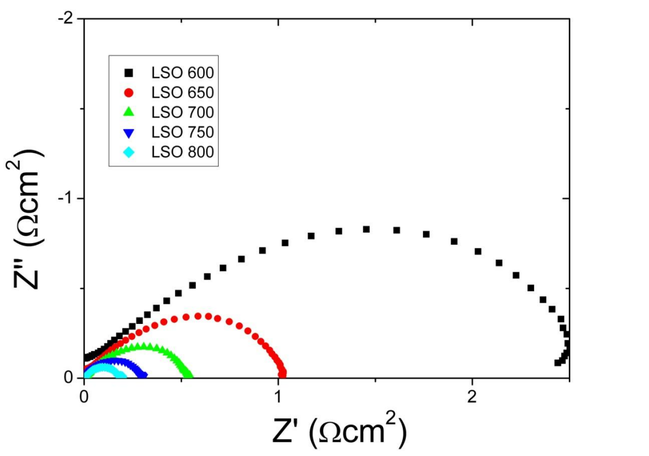
Sample	Temp. (ºC)	R_{ohm} (Ωcm^2)	R_{pol} (Ωcm^2)	C_{pol} ($x10^{-3}$ Fcm^{-2})
LSGO	600	83.62	2.19	4.05
LSGO	650	45.20	0.86	2.46
LSGO	700	27.80	0.40	1.88
LSGO	750	18.98	0.22	1.56
LSGO	800	14.24	0.14	1.43
LSO	600	42.04	2.30	2.94
LSO	650	26.13	0.95	2.02
LSO	700	19.04	0.49	1.63
LSO	750	14.90	0.27	1.56
LSO	800	11.59	0.17	1.18

Summary of EIS measurements for both samples under air atmosphere

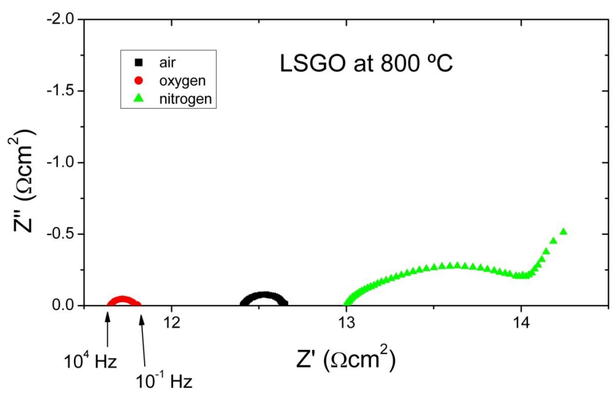
ELECTRODE THICKNESS



First, measurements were carried out on samples with just 4 immersions (~15μm). Such thin layers had very poor performances as current collectors, giving very high ohmic and polarization resistances and highlighting the need of thicker layers (~75μm) for the setup used. (~15μm).

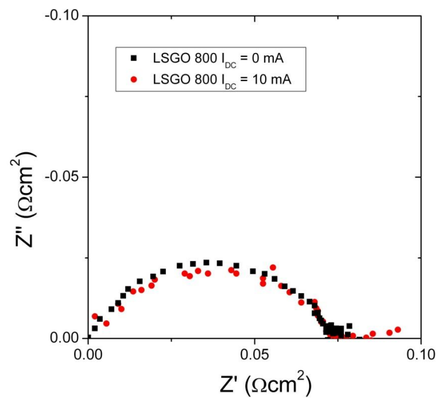


Evolution of the polarization resistance with temperature. Values given for one $Pr_2NiO_{4+\delta}$ electrode.



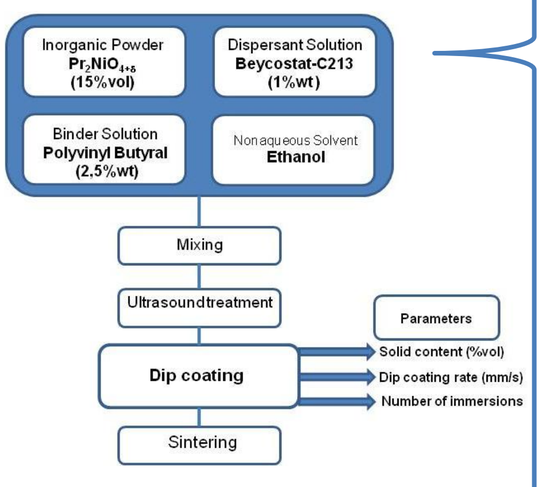
The performance of the cathode electrode improves clearly under oxygen, when both the ohmic and the polarization resistances decrease compared to air. In nitrogen, the electrode resistance increases and a new contribution probably due to the diffusion resistance is clearly seen. NOTE: a slight decrease on the ohmic resistance is also observed with time at high temperature under the same atmosphere, probably due to an improvement on the electrical contact.

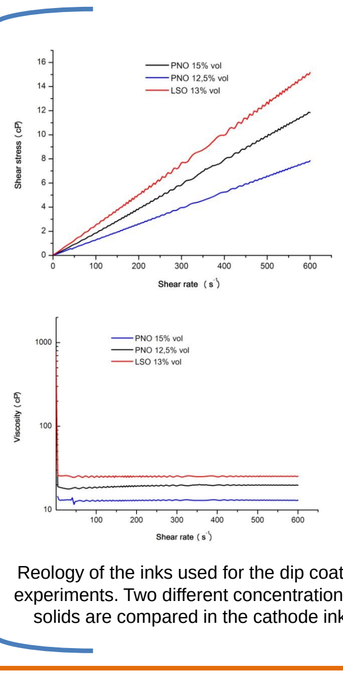
Preliminary measurements carried out under DC currents up to 80 mA show no significant changes on the polarization resistance of the electrode. Full fuel cell tests will be carried out in the near future in order to study these electrodes under operation conditions.



MICROTUBULAR FUEL CELL FABRICATION

Dip Coating Process





Reology of the inks used for the dip coating experiments. Two different concentrations in solids are compared in the cathode ink.

SEM picture of NiO-YSZ//YSZ//Pr_2NiO_4 microtubular cell. Inset: optical microscope picture highlighting the electrolyte sintering

- Good adhesion of the different layers.
- Very high densities are achieved in the apatite electrolyte layer.
- Homogeneous electrolyte layers of 10μm thickness are obtained
- Electrochemical characterization is being carried out

CONCLUSIONS

• $La_{9.67}Si_6O_{26.5}$, $La_{9.67}Si_3Ge_3O_{26.5}$ electrolytes show excellent compatibility with $Pr_2NiO_{4+\delta}$ and $Nd_{1.95}NiO_{4+\delta}$ cathode materials.

• A dip coating ink and process have been optimized in order to get homogeneous and stable electrode layers on both sides of dense apatite pellets. The layers show good adhesion on both systems and appropriate microstructure. Preliminary impedance spectroscopy studies on the symmetrical cells show the outstanding performance of these cathodes, with small polarization resistances that stay constant with applied DC currents.

•Powders of LSO and LSGO have been treated in order to make co-sinterization with the anode tubes viable. Microtubular SOFC supported on NiO-LSO anodes have been fabricated with LSO apatite electrolyte and $Pr_2NiO_{4+\delta}$ cathodes.

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