(Digital Presentation) **Ni-Doped $PrBaFe_2O_{5+\delta}$ As Symmetrical Electrode for Solid Oxide Cells**

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Abstract Text:

The development of new redox stable electrode materials for Solid Oxide Cells (SOFs) have attracted great attention in recent years, since finding suitable compositions to operate efficiently in both fuel cell and electrolyzer modes is crucial for their wide commercialization [1]. For this reason, research on new doping strategies [2] and advanced deposition techniques [3] for symmetrical electrode materials have significantly increased with the aim of simplifying cell fabrication and extending cell durability. In this sense, double perovskites are gaining great interest due to their excellent electrical properties and high redox and long-term stability in different atmospheres [4].

In this study, the double-perovskite $(PrBa)_{0.95}Fe_2O_{5+\delta}$ (PBF) is proposed as symmetrical electrode for SOCs [5]. Two different strategies are implemented: on the one hand, Ni-doping in order to improve the electrical properties under reducing atmosphere and, on the other hand, the preparation of nanostructured electrodes in one-step by spray-pyrolysis deposition. A thorough characterization of the material is performed regarding its crystal structure, microstructure and electrochemical properties in both oxidizing and reducing atmospheres.

With that purpose, PBF and $(PrBa)_{0.95}Fe_{2-x}Ni_xO_{5+\delta}$ ($PBFN_x$) powders are prepared by the freeze-drying precursor method. XRD patterns show the formation of a single perovskite-type phase in both air and H_2 atmospheres, without the presence of any secondary phases. As for conductivity tests, they reveal increased values for the Ni-doped material over the pristine PBF material in air and 5% H_2 at 600 ºC. These materials were thereafter screen-printed onto $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{2.85}$ (LSGM) electrolyte and calcined at 1100 ºC for 1h to ensure adequate adhesion to the electrolyte.

Alternatively, spray-pyrolysis deposition method is employed to infiltrate $PBFN_x$, with a 0.02 M precursor solution of the corresponding nitrate salts, into a porous $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) layer previously fixed onto LSGM electrolyte ($PBFN_x$-CGO). SEM images reveal that the screen-printed $PBFN_x$ has a thickness of 30 µm and a particle size of around 1 µm, while the same composition deposited by spray-pyrolysis shows a nanometric particle size and it is well-infiltrated in the 10 µm-thick CGO layer (**Figure 1a**). These electrode microstructures are maintained after ongoing a reduction process, where exsolved Ni particles are observed on the surface.

The impedance spectra show lower polarization resistance (R_p) values for $PBFN_x$ with respect to PBF, *i.e.* 0.47 and 0.62 Ω cm^2 at 650 ºC in air, respectively. But most significantly, further R_p reduction is observed for $PBFN_x$-CGO prepared by spray-pyrolysis, values as low as 0.17 Ω cm^2 at 650 ºC in air (**Figure 1b**). In reducing atmosphere, the $PBFN_x$-CGO electrode also has lower R_p values (0.23 Ω cm^2 at 650 ºC) when compared to the pristine PBF (0.52 Ω cm^2 at 650 ºC).

All in all, the nanostructured Ni-doped PBF electrodes exhibit high redox stability and low polarization resistance values under both oxidizing and reducing atmospheres, demonstrating their potential application as symmetrical electrodes for SOCs. These findings show that the optimization of the electrode composition but mostly its microstructure is key when developing new electrode materials for solid oxide cells.

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Figure 1. a) $PBFN_x$-CGO electrode deposited by spray-pyrolysis onto LSGM electrolyte: (i) Low magnification image of the electrode and electrolyte; (ii) Zoomed image of the pure PBFN top layer and the $PBFN_x$ layer infiltrated in CGO; and (iii) Zoomed image of $PBFN_x$ particles infiltrated on CGO scaffold. b) Polarization resistance (Rp) in air of PBF, $PBFN_x$ and $PBFN_x$-CGO electrodes as a function of temperature (450-800 ºC).