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Increasing Conductivity in Proton Conductors $BaCeO_{3-\delta}$ doped with Pr

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In $BaCeO_{3-\delta}$ perovskite, the oxygen vacancies could be hydrated, according to the following reaction:

$$V_O^{\bullet\bullet} + H2O \ + O_O^x \rightarrow 2OH^{\bullet} \quad (1)$$

Proton conductivity is due to the hopping of H^+ ions through O sublattice. This mechanism of ionic conductivity is characterized by their low activation energy [1] and the proton solubility increases as T decreases[2]. These features allow observing ionic conductivity at temperatures below 400 °C. Therefore, these kinds of oxides are suitable for application such as sensors, H-permeable membranes and electrolytes for Protonic Conductors Solid Oxide Fuel Cell (PC-SOFC) [2-3]. These applications are interesting because they improvethe energy conversion efficiency and allow the production of high purity H_2. However, the effort of materials science is yet devoted to develop new oxides with better properties, improving the ionic conductivity, the long term stabilities, and decreasing the cost of processing materials.

Reaction (1) depends on vapor pressure (pH_2O) and oxygen vacancies concentration ($V_O^{\bullet\bullet}$) in thesolid. Then, replacing Ce^{+4} for lanthanides ions Ln^{+3}, forces to $BaCeO_{3-\delta}$ to increase their oxygen vacancies concentration:

$$2Ce_{Ce}^{x} + O_O^{x} + Ln2O3 \rightarrow 2Ln_{Ce}^{'} + V_O^{\bullet\bullet} + 2CeO2 \quad (2)$$

The effect of different substitution in these compounds has been widely studied. It was found that the highest conductivities are achieved for Gd-doped compound [4]. This highest ionic conductivity is attributed to the fact that the Gd-doped composition exhibits the largest cell volume [5]. Therefore, some strategies involving multiple doping will be achieved in order to improve the electrolytes performances and extend the stability under CO_2 containing atmospheres. However, while in some cases the lanthanides co-dopant enhances the conductivity [6], in other cases, the doping hampers the proton conductivity. This is because proton conductivity is prevented when unit cell volume decreases [7] or when local symmetry around doped sites increases[8].

Hence, in this work we explore the effect of partial substitution of Ce for Pr ions in $BaCe_{1-x}Pr_xO_{3-\delta}$($0 \leq x \leq 0.8$) with the aim of increasing the oxygen vacancies concentration and H^+ charge carriers.

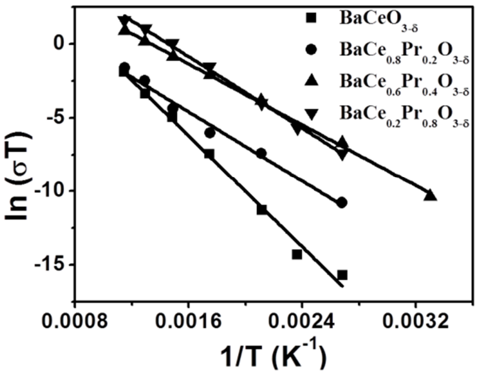

Figure 1.Arrhenius plot of conductivity, σ, in air between 75 and 600 °C.

The oxides were obtained by Pechini combustion method and sintered at 1350 °C. The Pr incorporation allows obtaining dense samples at this temperature. Decreasing the T of sintering is a key to avoid the Ba evaporation and improve the performance diminishing the bulk and grain boundary resistances. Crystal structure were studied by X-ray diffraction while morphology by FEG-SEM. The conductivity was characterized by Electrical Impedance Spectroscopy (EIS) under 20 % O_2/Ar and 10 % H_2/Ar with 2% humidity. We found that the Pr content diminished the stability of compound under reducing atmosphere.These results are in agreement with previous results in $BaZr_{0.9-x}Pr_xGd_{0.1}O_{3-\delta}$ (x= 0.3 and 0.6) compounds [9].

Figure 1 shows the Arrhenius plot of total conductivity obtained in synthetic air. It could be observed that while the activation energy for $BaCeO_{3-\delta}$ is 0.8 eV, in doped samples this values decrease until 0.5 eV evidencing a change of mechanism. Besides, as is shown in Figure 2 for 400 °C, the conductivity increases markedly with Pr doped level suggesting that this change will be due to the existence of non negligible fraction of electronic conductivity. Similar results were obtained for high Pr-doping $BaCe_{0.8-x}Pr_xGd_{0.2}O_{2.9}$, which was proposed as cathode materials due to their mixed H-ionic and electronic conductivities [10].

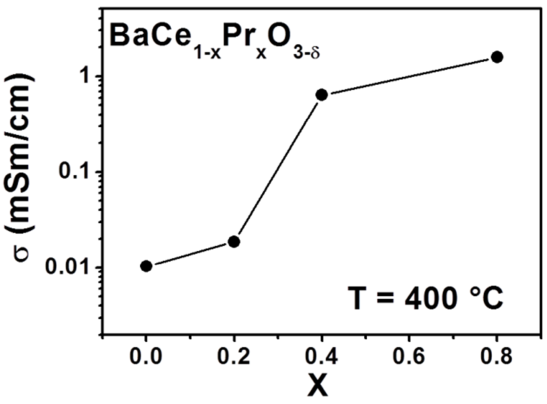

Figure 2.Variation of conductivity as a function of Pr content at 400 °C in air.

References

[1] A. Sammells, R. Cook, J. White, J. Osborne and R. MacDuff, Solid State Ionics52 (1992), p. 111.

[2] K.D. Keuer, Annu. Rev. Mater. Res. 2003. 33:333–59.

[3] Iwahara, H.; Uchida, H.; Ono, K.; Ogaki, K. J. Electrochem. Soc. 1988, 135(2), 529.

[4] M. Amsif, D. Marrero-López, J.C. Ruiz-Morales, S.N. Savvin, P. Núñez. J. Power Sources 196 (2011) 9154–9163.

[5] J. Kikuchi, S. Koga, K. Kishi, M. Saito, J. Kuwano, Solid State Ionics 179 (2008) 1413–1416.

[6] X.T. Su, Q-Z Yan, X-H Ma, W-F Zhang, C-C Ge Solid State Ionics 177 (2006) 1041–1045.

[7] C. Zhang, H. Zhao, Solid State Ionics 206 (2012) 17–21.

[8] F. Giannici, A. Longo, K-D Kreuer, A. Balerna, A. Martorana, Solid State Ionics 181 (2010) 122–

[9] A. Magrasó, C. Frontera, A. Gunnaes, A. Tarancon, D. Marrero-Lopez, T. Norby, R. Haugsrud; J. Power Sources 196 (2011) 9141-9147.

[10] R. Mukundan, P. K. Davies, and W. L. Worrell, J.Electrochem.Soc., 148 (1) A82-A86 (2001).