Soft Chemical Route Improving IT-SOFC Cathode Performance: The lanthanum barium cobaltites case.

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Different cobaltites with perovskite related structures have been proposed as materials for high and intermediate temperature electrochemical applications [1-4]. The high mixed, ionic and electronic conductivity of these materials and also their good oxygen exchange properties make them suitable to substitute conventional oxygen electrodes and works in Intermediate Temperature Solid Oxide Fuel Cell (IT-SOFC).

In this work we explore the 50%Ba-50%La substitution on A sites of a Co-rich perovskite with nominal composition La0.5Ba0.5CoO3. In recent works shown that, it is possible to change the phase structures of this composition controlling the synthesis parameter. Therefore, whereas in air atmosphere at 1100 °C a cationic disordered phase with cubic structure (La0.5Ba0.5CoO3)δ is obtained, under inert gas Ar at 1150 °C a cationic order phase with laminar structure and tetragonal symmetry is obtained (LaBaCoO4)δ [5-7]. These different structures could be obtained because the difference between ionic radii of both cations (rBa2+ = 1.36 Å and rCo3+ = 1.61 Å) and the unlike capability to accommodate oxygen vacancies of these compounds.

In this work, besides the La0.5Ba0.5CoO3δ obtained at 1100 °C in air (LBC-1100 °C/Air) and the LaBaCoO4δ obtained at 1150 °C in Ar (LBC-1150 °C/Ar) we essayed a new chemical route involving a gel formation by polymerization of AcetylAetone and HMTA. In this case we obtained a phase with mixed characteristic between the high temperature cationic ordered and disordered phase but at lower temperature, 900 °C in Ar (LBC-900 °C/Ar). The microstructure of oxides obtained at 1100 °C in air and at 1150 °C in Ar are similar between them but quite different to that obtained by chemical route at 900 °C in Ar (See Figure 1).

Recently, S. Pang et al. found that, while the electrical conductivity for cationic disordered La0.5Ba0.5CoO3δ phase is higher than for the ordered LaBaCoO4δ, the ASR is lower [8-10]. For the latter, the ASR reaches values of 0.0086 Ωcm2 for ordered [9] and 0.013 Ωcm2 for disorder [10] at 800 °C in air. In this work we explore the mechanism working on electrode reaction for LBC-1100 °C/Air, LBC-1150 °C/Ar and LBC-900 °C/Ar samples. We use Electrochemical Impedance Spectroscopy (EIS) on symmetrical cells LBC/GDC/LBC (GDC, Gadolinium-Doped Cerium). The measurements were performed at 700 °C changing oxygen partial pressure (pO2) between 0.9 and 5 10-4 atm. Figure 2 shows the impedance spectrum of samples at different pO2. As could be noted, the polarization resistance of sample obtained by chemical route decreases almost one order of magnitude at higher pO2 respect to that obtained by convention solid state reaction method. In three samples at least two contributions could be noted. The dependence of polarization resistance with pO2 and the activation energy allows propose the nature of different process. The high frequency contributions could be associated to oxygen bulk diffusion with some grade of co-limitation by oxygen surface exchange, depending on sample microstructure and temperature. The low frequency process changes depending on sample microstructure and structure. While for LBC-1100 °C/Air and LBC-900 °C/Ar samples the dependence with pO2 is -1, assigned to oxygen gas diffusion; for LBC-1150 °C/Ar sample it depends with pO2-2/3, suggesting that the LaBa perfectly layered distributed induces a surface dissociative adsorption process limiting the electrode mechanism for this sample.

Figure 1. FEG/SEM images of resulting samples. a) LaBaCoO4δ at 1150 °C in Ar b) La0.5Ba0.5CoO3δ obtained at 1100 °C in air (LBC-1100 °C/Ar) and LaBaCoO4δ obtained at 1100 °C in air (LBC-900 °C/Ar).

Figure 2. EIS spectra at 700 °C and different pO2.

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