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BOOK OF ABSTRACTS

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Abstract Title: Investigation of Ni and Cu doping effects on the sintering and proton conducting behaviour of BaZr0.7Ce0.2Y0.1O3-δ

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Abstract: BCZY (BaZr0.7Ce0.2Y0.1O3-δ), a commercial protonic electrolyte, was modified by doping with CuO or NiO (1 wt.%), aiming to improve the sintering behaviour of the electrolyte. As expected, the transition metals acted as sintering aids. Due to their presence, the sintering occurred at 1350 °C (with Cu) and 1450 °C (with Ni) at six h. A greater degree of densification was observed for the modified materials but not for the pristine BCZY at the same conditions. The electrical results reveal that the protonic conduction characteristic was maintained for the Ni-dopped material. Meanwhile, the electronic and anionic conduction seems predominant for the Cu-doped one.

Keywords: BZCY, protonic electrolyte, transition metal doping, SOFC, SOEC.

Introduction and Objectives: As an excellent alternative for electric energy generation, the use of ethanol in fuel cells, which can either work as a solid oxide fuel cell (SOFC) or as a solid oxide electrolysis cell (SOEC), has been seen as a significant advance. Despite the advantages of clean energy and environmental friendliness provided by these systems, the need to operate at high temperatures (800-1000 °C) instigates efforts to optimise and improve their energy conversion efficiency.

Nowadays, most conventional solid oxide electrolytes are oxygen-ion conductors, which can only reach sufficient ionic conductivity at high temperatures. Accordingly, the interest in proton-conducting electrolytes has increased due to their relatively lower activation energy and higher conductivity at intermediate low temperatures (400-700 °C).

Currently, the main protonic electrolytes known are the metal oxides with perovskite structure of the type A2+B4+O3, in which the A2+ sites are occupied by divalent cations (such as Ca2+, Ba2+ and Sr2+), and the B4+ sites are occupied by tetravalent cations (such as Zr4+ and Ce4+; respectively known as zirconates and cerates). Among these two classes, ceramics based on cerates have the highest proton conductivity at intermediate temperatures (400-800°C) despite presenting low chemical stability. On the other hand, zirconates, although having good chemical and thermal stability, show conductivity values not as high as the ones offered by the prior compounds at the same conditions. Merging the advantages of cerates and zirconates, solid solutions of BaCeO3 BaZrO3 have been developed to balance conductivity and chemical

stability. Examples of these types of materials are compounds with the general formula BaZrxCeyYzO3-δ, e.g., BaZr0.7Ce0.2Y0.1O3-δ. Notwithstanding the improvements achieved by the combination of Ce and Zr, some issues are still to be addressed, such as high grain boundary resistance and elevated sintering temperatures for densification. In this scenario, this work aims to investigate the optimization of the sintering behavior and electrochemical characteristics of the commercial electrolyte BaZr0.7Ce0.2Y0.1O3-δ (BZCY) through its modification by the addition of sintering aids.

Methodology: To prepare the modified materials, pristine BZCY (BZCY721, FuelCell Materials) and 1 wt.% of NiO (99.8%, Aldrich) or CuO (97.8%, Aldrich), were wet ground in a zirconia mortar using isopropanol as the medium. The obtained powders were pressed into pellets under 196 MPa using a 19 mm diameter stainless steel die. The pellets were sintered in air at 1450 °C (for NiO) and 1350 °C (for CuO) for 6 h. Standard pellet samples were prepared in the same conditions, but in the absence of sintering aids (NiO or CuO), with 100% of pristine BZCY, and were sintered at 1350 and 1450 °C for comparison purposes. It is worth mentioning that, for the sintering process, each pellet was embedded with powders of the same type to prevent elemental volatilization. Samples of BZCY721 (as received) and BZCY721 containing 1 wt.% of NiO or 1 wt.% of CuO are noted as BZCY, BZCY Ni and BZCY Cu, respectively. The physical characteristics of the samples were investigated by scanning electron microscopy (SEM). The electrical properties of the BZCY-Cu and BZCY-Ni were assessed by electrochemical impedance spectroscopy. The AC impedance spectra were obtained at a 400 800 ºC and under dry-H2 and wet-H2 atmospheres.

Preliminary results: After the sintering process at each respective temperature, the BZCY (1350 and 1450 °C), BZCY Cu (1350 °C) and BZCY Ni (1450 °C) materials presented average sintering values of 10.2%, 15.2%, 25.5% and 26.8%, in this order. These values indicate that the electrolyte exhibits higher thermal contraction behaviour in the presence of the transition metals Cu and Ni. Agreeing to that, the cross-sectional SEM images revealed that the BZCY, without any sintering aid, developed smaller grains and presented larger pores compared to the BZCY Cu and BZCY Ni. Additionally, the SEM data confirm that the temperature also plays an important role in the densification of the BZCY. For the BZCY sintered at 1450 ºC, grain growth and decrease in porosity were favoured compared to the BZCY sintered at 1350 ºC. Besides the slightly larger shrinkage value presented by BZCY-Ni, compared with BZCY-Cu, its microscopy images indicate more significant densification for this material.

The conductivities (σ) for the BZCY Cu and BZCY Ni materials were calculated from the AC impedance spectrum. For both of them, the total conductivity values under wet-H2 atmosphere were higher than those under dry-H2. At 600 ºC, BZCY-Cu exhibited σ = 3.87 mS cm-1 (wet-H2) and σ = 3.36 mS cm-1 (dry H2), whereas BZCY-Ni showed σ = 2.45 mS cm-1 (wet-H2) and σ = 0.24 mS cm-1 (dry-H2). As represented by these values, the difference between the conductivity under wet and dry H2 atmospheres was greater.

Analyzing the activation energy (Ea), determined from the Arrhenius plot of the total conductivity data for BZCY-Ni, a decrease in Ea is observed under H2 atmosphere containing

water: Ea,wet = 0.12 eV < Ea,dry = 0.31 eV. This result, associated with increased conductivity under the same atmosphere, confirms that BZCY-Ni is mainly a proton conductor material in these conditions. On the other hand, for the BZCY-Cu under wet-H2, the Ea value is slightly larger than the one in dry atmosphere (Ea,wet = 0.13 eV > Ea,dry = 0.16 eV), indicating that, for this material, electron-hole and oxygen vacancies are likely to be the main charge carriers in this environment.

Preliminary conclusions: According to the preliminary results, the addition of CuO and NiO, even in concentrations as small as 1 wt.%, is capable of favouring the sintering process, allowing the BZCY721 to achieve a higher degree of densification at relatively lower temperatures. In the case of the BZCY-Ni material, the electrical investigation returned an increase in conductivity followed by a decrease in the activation energy. Such observation confirms that, despite the Ni addition, the electrolyte BZCY-Ni maintained its proton conductivity behavior under humidified H2 atmosphere. Conversely, BZCY-Cu, under wet-H2, presented only a moderately larger conductivity associated with a slight increase in the activation energy, which might be related to electronic and anionic conduction.

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Innovation (23.1.8493.1.9), hosted by the University of São Paulo (USP), sponsored by FAPESP – São Paulo Research Foundation (2020/15230-5), and sponsored by TotalEnergies, and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&DI levy regulation.

Abstract Title: Wind potential improvement through the study and mitigation of generation deviations and failures.

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Abstract: This research project aims to improve the use of the wind resource by achieving the following objectives: (i) production of artificial intelligence (AI) tools to characterize deviations between forecast and generation, identifying their probable causes, (ii) production