Ionic Transport Modification in Proton Conducting $\text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta}$ with Transition Metal Oxide Dopants

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Abstract

Proton conducting $\text{BaCe}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCZY63) pellets were fabricated by the solid-state reactive sintering method whereby a small extra amount of a metal oxide additive (5 mol%) was included in the precursor mixture before sintering. The effect of the addition of six different metal oxide additives (CuO, ZnO, Fe_2O_3 , MnO_2 , PdO, and Cr_2O_3) on the transport properties of BCZY63 was investigated. Although most additives (e.g. ZnO, Fe_2O_3 , MnO_2 , Cr_2O_3) led to a decrease (sometimes minor) in conductivity, CuO and PdO dopants yielded an increase in total conductivity compared to the BCZY63 control. The enhancement in the total conductivity is found to be related to two factors: 1) the additive can act as a sintering aid to produce larger grain size; 2) substitutional doping of the BCZY structure by metal ions from additives can lead to increased bulk proton concentration. Due to its excellent sinterability and moderately improved proton conductivity, CuO-doped BCZY63 was subsequently applied as the dense electrolyte layer in protonic ceramic fuel cells utilizing a recently developed single firing step fabrication technique to produce high quality single cells that showed exceptional performance and long-term stability.

Keywords: proton conduction, electrical properties, reactive sintering, fuel cells

1. Introduction

Proton conducting perovskite ceramics are currently being studied for a number of electrochemical device applications including protonic ceramic fuel cells, steam electrolyzers, hydrogen sensors, and hydrogen permeation membranes as they have unique ionic conduction properties at moderate temperatures [1-5]. The proton conductivity of these oxides is created by the dissociative absorption of water into oxygen vacancies (created extrinsically by doping). In Kröger-Vink notation, this reaction is given as:

The hopping of a proton between adjacent oxygen sites is the origin of proton conductivity. Improved performance of electrochemical devices employing proton conducting perovskite oxides, such as fuel cells, requires new materials or composites that can provide higher proton conductivity (for electrolytes) or mixed protonic-electronic conduction (for electrodes) [6-8]. For the electrolyte, it is necessary to have a fully dense structure (to mitigate gas intermixing) as well as high ionic conductivity and low electronic conductivity to prevent charge leakage across the layer. Unfortunately, barium-zirconate based proton conducting electrolytes typically require high temperatures and long annealing times to obtain full density, which can have side effects that

negatively impact the proton conductivity [9]. We recently clarified the beneficial sintering and densification effects associated with the solid state reactive sintering method (SSRS) whereby a small extra amount of a sintering additive enables the direct solid-state reaction, densification, and grain growth of precursor powders in a single firing step, thereby overcoming many of the issues associated with the otherwise refractory nature of these materials [10-11]. However, the effect of the dopants on the conduction properties of these protonic oxides is still unclear.

Here, our goal is to clarify these issues by studying the effect of several metal oxide additives (CuO, ZnO, Fe₂O₃, MnO₂, PdO, and Cr₂O₃) on the conductivity of the proton conducting ceramic BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-δ} (BCZY63). We have deliberately chosen to avoid the study of NiO doping as there are already many prior studies investigating the effect of NiO on the electrical properties of BCZY and related materials [6,11,21]. Partial substitution of Zr for Ce in BCZY was chosen to obtain electrolytes with both high proton conductivity and good chemical stability. We find that many of the additives (such as Fe₂O₃ and MnO₂) lead to only minimal improvements in the pellet grain size and actually cause a decrease in total conductivity. ZnO, while proving to be an excellent densification aid, also produces pellets with a minor decrease in total conductivity (a similar null/negative effect has also been observed by others) [12]. CuO and PdO dopants were the only additives to yield a total conductivity exceeding the BCZY63 control. Of these two, only CuO also acts as an enhancer of grain growth and densification. In contrast, PdO addition to the bulk powder results in similar small grain size and relative density as the control sample. Herein, we discuss possible mechanisms leading to the observed behavior associated with these various dopant additives. Finally, we apply the Cu-BCZY63 composition as an electrolyte layer in protonic ceramic fuel cell utilizing a recently developed single firing step fabrication technique to produce high performance button-cell fuel cells.

2. Experimental

2.1 Fabrication of proton conducting ceramic pellets by SSRS

BCZY63 pellets were prepared via the SSRS method. All the chemicals used in this study were purchased from *Alfa Aesar* without any further purification. BaCO₃, ZrO₂, Y₂O₃, and CeO₂ were the primary components in the synthesis of the BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-δ} (BCZY63) pellets examined in this study. The metal oxides (MO_x) of ZnO, CuO, MnO₂, Fe₂O₃, Cr₂O₃, and PdO were used as sintering additives with a concentration of 5mol% *as an addition* to the normal BCZY63 stoichiometry. These BCZY63-MO_x precursors were added into 300mL of isopropanol and the resulting slurries were ball milled using 400 g of 3mm yttria stabilized zirconia (YSZ) balls for 48 h until the precursor powders were homogeneously mixed. The slurries were then dried in an oven at 80 °C for 48 h. The resulting BCZY63-MO_x precursor powders were pressed into pellets of 19.5 mm diameter with a press of 25,000 lbs for 2 min. The green pellets were put into alumina crucibles and heated at a rate of 2 °C/min until they achieved the final sintering temperatures of 1450-1650 °C, where they were held for a period of 12 h. Our proton conducting button cell was fabricated utilizing a new processing methodology (detailed experimental methodology is reported elsewhere [1]). The first step involves the preparation and firing of an anode/electrolyte structure from raw precursor oxides at intermediate sintering temperatures (1450°C). Lastly, the cathode is screen printed on the sintered heterostructure and fired at a lower temperature (900°C) in order to maintain a porous and active nanostructure framework. The composition of our fuel cell is as follows: anode - 40wt.% BCZY63 + 60wt.% NiO | electrolyte - BCZY63 +5mol% CuO | cathode – BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ}.

2.2 Characterization of the pellets

The crystal structure of the sintered proton conducting ceramic pellets after impedance analysis in wet UHP Ar and 5% H₂ were analyzed by a Philips X'pert X-ray Diffractometer (Almelo, the Netherlands) (XRD, CuK α radiation) with 0.008° step size and 5 s per step time in 2 theta range 10-120 °. The microstructure and morphology of the sintered proton conducting ceramic pellets were characterized by observing fractured cross sections using field-emission scanning electron microscopy (FE-SEM, JEOL 7000, Peabody, MA). Average grain size was established using a modification of the ASTM standard methodology whereby the electron microscope ruler tool was used to generate lines that intersected grain boundaries in the SEI image [13].

Pellets for electrochemical impedance spectroscopy (EIS) measurements were polished with sand paper of increasing grit number until the surface became mirror-like. Ag paste was applied to each side and cured in a furnace in air to 800°C for 1 h to form a symmetric cell. Electrical measurements were performed in either wet UHP Ar (Ar + ~2.5% H₂O) or wet 5% H₂ in Ar (Ar + 5% H₂ + ~2.5% H₂O) using a Gamry Reference 600 potentiostat/galvanostat/ZRA. The EIS spectra were recorded over a frequency range of 1 MHz to 0.01 Hz, with a signal amplitude of 10 mV. A stabilization time of ~1 h was applied between each temperature change.

3. Results and Discussion

3.1 Structure Stability

We have reported previously on the crystal structure and potential impurities found in SSRS synthesized pellets with these transition metal oxide dopants [10]. The X-ray diffraction patterns for samples doped with CuO, ZnO, PdO, MnO₂, and Fe₂O₃ showed a single-phase perovskite material after sintering. We found traces of CeO₂ impurities in specimens doped with the Cr₂O₃ additive. In order to evaluate the stability of phase-pure samples over a typical measurement period, several BCZY63-Cu pellets were first exposed to an atmosphere of 5% H₂ in Ar at 650°C for 24 h and the phase composition of the resulting specimens was investigated by XRD (**Figure 1**).

Figure 1: XRD for BCZY63-Cu samples that were first annealed in 5% H_2 in Ar at 650°C for 24 h (top pattern) and subsequently annealed in UHP Ar at 650°C for an additional 24 h (bottom pattern)

Subsequently, the remaining pellets were re-oxidized in UHP Ar at the same annealing conditions, and again the specimens were powderized and their phase was analyzed. The XRD spectra show the main perovskite phase material with no additional impurities detected. We conclude the presence of any Cu/CuO precipitates, as well as any additional impurities generated in the annealing process, are too small to be detected by XRD for this set of annealing conditions.

3.2 Microstructure

Ceramic pellets with and without dopants were sintered at a variety of temperatures (1450-1650 °C) for 12 h and further characterized using FE-SEM (**Figure 2A-D**). A large variation in sintering temperature was necessary to produce pellets with a high relative density which would be suitable for impedance measurements.

Figure 2: Cross-sectional FE-SEM images for BCZY63 pellets doped with various transition metal oxides at different sintering temperatures for 12 h hold. A) CuO – 1450°C, B) ZnO – 1450°C C) Fe₂O₃ – 1600°C, D) Cr₂O₃ – 1600°C, E) PdO – 1600°C F) Control – 1650°C.

The cross section image (**Fig. 2A**) of the sintered BCZY63 pellet with 5mol% CuO (1450°C for 12 h) shows high relative density and large grain size (~6.2 μm). Similar density, grain size, and microstructure were observed for the BCZY63 pellets modified by ZnO (**Fig. 2B**). For ease of comparison, we classify CuO and ZnO as group 1 dopants. Pellets doped with 5mol% Fe₂O₃ (**Fig. 2C**) required higher sintering temperatures (1600°C for 12 h) to produce high density pellets and resulted in a microstructure with few pores but smaller grain size than their group 1 counterparts (~3.3 μm). MnO₂ required similar sintering conditions to achieve high relative density and had similar grain size; thus these two dopants (Fe₂O₃ and MnO₂) are further referred to as group 2 dopants. Finally, the sintering additives Cr₂O₃ (**Fig. 2D**) and PdO (**Fig. 2E**), group 3 dopants, produced microstructures that were similar, or worse, than the BCZY63 control sample, despite having similar sintering conditions (1600°C for 12 h). PdO is thought to create a small increase in point defect concentrations, a hypothesis which we along with others have previously proposed [14-17]. Thus we expect its grain size and density to be comparable or slightly better than the control. Indeed, the PdO doping resulted in a pellet with a grain size of 1.4 μm vs. ~1.3 μm for the control sample (**Fig. 2F**), which was sintered at even higher temperatures (1650 °C for 12 h). Conversely, Cr₂O₃ had a negative impact on the sinterability of BCZY63 and specimens with these additives had small grain sizes on the order of 350 nm (**Fig. 2D**).

3.3 Electrical Transport Properties

The transport properties of the materials were analyzed by EIS using symmetric cells.

Samples doped with group 1 and 2 additives had high relative densities and were therefore not subjected to corrections in conductivity. However, samples doped with group 3 additives and the control had some residual porosity even after sintering at high temperatures. Increasing the sintering temperature or dwell time in these cases could lead to barium volatilization which could have negative effects on the conductivity. Thus the total conductivity of these samples was corrected for their slightly lower relative density ~90% vs. >95%.

Three different contributions are discernible in the impedance spectra in the low temperature range, which are attributed to the grain interior (bulk), grain boundary, and the electrode responses (**Figure 3**).

Figure 3: Typical Nyquist plots for A) BCZY63 control sample under wet 5% H₂ and wet UHP Ar, B) Cu-doped BCZY63 sample wet 5% H₂ and wet UHP Ar. All measurements at 100°C. Wet H₂ plots offset vertically (on the y-axis) for comparison.

Fig. 3A shows typical Nyquist plots for the BCZY63 control sample in both measurement atmospheres (wet 5% H₂ in Ar and wet UHP Ar) at low temperature (100°C). These spectra were fitted with an equivalent circuit of R-CPE elements in series (**Fig. 3**), where R is the resistive element and CPE is a constant phase element typically used to represent imperfect capacitors. The grain boundary and grain interior processes were studied separately at low temperatures, where both processes were distinguishable. The temperature at which the processes overlap into a single electrolyte arc varies between samples; however, these two processes are generally not discernable above 350°C. **Fig. 3B** shows the impedance spectra of the Cu doped BCZY63 pellet under the same measurement conditions as the control specimen in **Fig. 3A**. Both plots maintain the same scale for easy comparison. Comparison of **Fig. 3A** vs. **3B** reveals a great reduction in the second arc (grain boundary contribution) while the first arc (bulk contribution) remains for the most part, unmodified.

The Arrhenius plots of the total conductivity under humidified 5% H₂ and UHP Ar for the temperature range of 650-100°C are shown in **Figure 4**.

Figure 4: Total conductivity as a function of temperature of all doped samples and control in both UHP Ar and 5% H₂ in Ar.

Fig. 4 is separated into three sections according to same groups 1-3 used above in **Fig. 2** to rank their sinterability. As expected, the BCZY63 control sample (without sintering aids) shows similar conductivities in both wet 5% H₂ and UHP Ar, with a slightly higher conductivity in the wet 5% H₂ atmosphere (due to higher proton concentration). As shown in **Fig. 4**, most additives (ZnO, Fe₂O₃, MnO₂, Cr₂O₃) lead to a decrease in total conductivity. Only the CuO and PdO dopants yield a higher total conductivity compared to the BCZY63 control. Most notably, the grain boundary resistance in Cu doped BCZY63 samples is almost an order of magnitude lower than that of the control. In order to evaluate the normalized effects of the sintering aids on the grain boundary

behavior of these samples, the specific grain boundary conductivity was estimated by taking into account differences in average grain size using the standard “brick layer” model [18]. The temperature dependence of the specific grain boundary and bulk conductivities is displayed in **Figure 5**.

Figure 5: A) Specific grain boundary and B) grain bulk conductivities for selected representatives of groups 1-3 and control sample in UHP Ar. C) Specific grain boundary and D) grain bulk conductivities for all doped and control BCZY63 samples in wet 5% H_2 .

As shown in **Fig. 5**, the *specific* (i.e., normalized per unit area of grain boundary) grain boundary conductivity for the CuO and PdO-doped samples are revealed to have similar values to the parent compound, indicating that they do not significantly alter the intrinsic grain boundary conduction properties of these samples (despite the presence of nanoparticles decorating the grain boundaries after reduction – see supplementary section – **Figure S1**). The other sintering additives yield large decreases in the specific grain boundary conductivity— sometimes up to several orders of magnitude (i.e., in the case of Cr_2O_3). The bulk conductivity of the PdO-modified BCZY63 in the two humidified atmospheres was higher than the unmodified control. In this case, it is likely that the introduction of Pd^{2+} cations into the bulk lattice leads to the formation of additional oxygen vacancies, which subsequently have the ability to react with water to form additional protonic defects. Pd may also modify the uptake of protons into the bulk matrix due to its high catalytic activity towards hydrogen dissociation.

3.4 Fuel Cell Performance

Because of its excellent densification and conduction properties, the as-synthesized

BCZY63+5mol% CuO composition was applied as an electrolyte material in an anode-supported “button cell” proton conducting ceramic fuel cell (PCFC). A recently developed fabrication approach was applied, based on solid-state reactive sintering, that allowed the anode/electrolyte portion of the cell to be created in a single intermediate temperature (1450°C) firing step directly from the raw precursor oxides [1]. The completion of the cell is accomplished with the screen printing of the cathode and firing the structure at a low temperature (900°C). **Figure 6** shows a cross-sectional FESEM image from a typical PCFC button cell fabricated by this method after fuel cell testing. The cell was operated in humidified H₂ fuel while the cathode was exposed to ambient air. While metallic nanoparticles were observed in reduced pellets, they were not observed in the fuel cell electrolyte layer after long term cycling.

Figure 6: Cross-section FESEM image of 40wt.% BCZY63 + 60wt.% NiO | BCZY63 +5mol% CuO | BCFZY0.1 fuel cell after performance test.

Figure 7 shows the steady-state I-V and I-P polarization curves of the PCFC button cell incorporating the BCZY63 +5mol% CuO electrolyte in the 450-750°C temperature range. Open circuit voltages (OCVs) between 1.0 and 1.2 V were achieved under the given measurement conditions and are comparable to those observed in literature [1,19,20]. The measured OCVs of the cell at lower temperatures (450-600°C) match closely with the theoretical Nernst potential of ~1.2V suggesting that the addition of the Cu dopant did not significantly increase the electronic charge transfer number. At temperatures $\geq 650^\circ\text{C}$, the measured OCV decays until it reaches a minimum value around 1.0V at 750°C. A comparison of the measured OCV versus the theoretical Nernst Potential at these higher temperatures suggest that thus the electronic contribution to the total conductivity may increase to as much as 15% at the highest temperature. However, it is unclear if the Cu dopant or the p-type conductivity arising from the dehydration of the cell (above 650°C) is the major culprit for this decrease in the OCV. The electrolyte contribution to the cell resistance was found to have similar values to the symmetric cell pellets presented in **Fig. 4** (see supplementary – **Figure S2**). The cell performance did not degrade even during long term testing (>500 h) at 500°C, suggesting that any Cu metal precipitates forming in the electrolyte layer do not create a continuous pathway for electronic conduction. Peak power densities varied from ~200-600 mW/cm² in the 450-750°C temperature range and are comparable to some of the best previous PCFC results published in the literature [1,19].

Figure 7: A) I-V curves and the corresponding power densities of 40wt.% BCZY63 + 60wt.% NiO | BCZY63 + 5mol% CuO | BCFZY0.1 at 450-750 °C under H₂/Air operation B) Stability of BCZY63 cell at 500 °C on hydrogen

Conclusions

The effect of the addition of six different metal oxide additives (CuO, ZnO, Fe₂O₃, MnO₂, PdO, and Cr₂O₃) on the transport properties of BCZY63 was investigated. When the metal oxides of CuO and PdO are added to the proton conducting perovskite oxide BCZY63, the resulting structures (synthesized by solid state reactive sintering) are found to have a higher total conductivity than the unmodified control sample. This enhancement in the electrical properties is shown to be due to a combination of larger grain size and enhanced bulk conductivity (likely due to an increase in the number of oxygen vacancies). The other investigated oxide additives (ZnO, Fe₂O₃, MnO₂, and Cr₂O₃) all led to a decrease in total conductivity. At these low doping concentrations, it is unlikely that electrical conduction contributes significantly to the total

conductivity of any of the samples. However, some of these transition metal oxide dopants might be useful in the electrode portion of a full protonic ceramic fuel cell if their doping concentration is increased. Due to the excellent morphology of the CuO doped pellets, this additive was further utilized in the synthesis of a ceramic fuel cell device that showed exceptional stability over long testing durations.

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