Electrical Properties of $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ Proton-conducting Electrolyte Prepared by a Combustion Method

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$\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ (BCN18), regarded as a promising proton-conducting electrolyte material for solid oxide fuel cells, is usually synthesized by a solid-state reaction because of the limited choice of Nb precursors. This study presents a wet chemical route for preparing BCN18 powders that were then sintered into pellets. Electrochemical impedance spectroscopy studies indicated that BCN18 pellets show proton conductivity, since their total conductivity in wet air was significantly larger than that in dry air. However, a detailed analysis showed that only the BCN18 bulk behaves as a proton conductor, while its grain boundary conductivity did not increase in wet air.

Introduction

High temperature proton conductors (HTPCs) are regarded as good electrolyte candidates for intermediate-temperature solid oxide fuel cells (SOFCs) due to their low activation energies compared with oxygen-ion conductors (1-5). Furthermore, SOFCs with proton-conducting electrolyte generate water at the cathode side, which will not dilute the fuel at the anode chamber (6). Although most of the researches for the HTPCs are focused on ABO_3 type perovskite materials, the search for new proton-conducting oxides is still continuing (7). Some complex perovskite oxides have been found to show proton conductivity at intermediate temperatures and $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9-\delta}$ (BCN18) is the most representative material, as it was reported to show conductivity almost equal to that of doped BaCeO_3 , which is regarded as the most conductive polycrystalline proton-conducting oxide. Fuel cells with the BCN18 electrolyte show a power output even larger than that of fuel cell using BaCeO_3 -based electrolytes (8). BCN18 also has a great advantage over doped BaCeO_3 since it shows good chemical stability in CO_2 and H_2O containing environment, making it very interesting as a potential electrolyte material for proton-conducting SOFCs (9, 10). However, although the good chemical stability of BCN18 is well recognized, the conductivity results for BCN18 are scattered in the different studies, with differences reaching even two orders of magnitude (11). Such a huge difference in conductivity is mostly attributed to different preparation parameters, such as the calcination temperature and the purity of the starting materials (11, 12).

Although it is recognized that different preparation routes may have a great influence on the electrical properties of the final BCN18 samples, the BCN18 powders are usually synthesized by solid-state reaction, due to the limited choice of Nb precursors for wet-chemical synthesis. However, the incomplete reaction, the possible introduction of

impurities, or the loss of given amounts of starting materials during the repeated milling and annealing process in the solid-state reaction would affect composition and thus influence the electrical properties of the final samples. This might be the reason for the scattered conductivity results for the BCN18 materials reported in the literature.

In contrast, wet chemical routes involve the mixture of different starting materials at a molecular level, resulting in more homogeneous and fine oxide powders. Studies on the preparation of BCN18 powders using wet chemical routes are scarce. Sol-gel has been used to prepare BCN18 samples that showed proton conductivity in both bulk and grain boundaries (13). These results are different from those reported for BCN18 samples prepared by solid-state reaction, which showed that the main charge carriers at grain boundaries are not proton (11), implying that the synthesis route plays an important role for the electrical performance of BCN18.

With the aim of further studying the wet-chemical synthesis of BCN18, in this paper we used $C_4H_4NNbO_9$ as the starting Nb source to prepare BCN18 powders using a self-combustion method. The electrical performance of the BCN18 samples was analyzed. Furthermore, a detailed analysis was given to separate the contribution of bulk and grain boundary from the total conductivity, in order to unravel the proton-conduction behavior of the BCN18 samples.

Experimental Procedure

$Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$ (BCN18) powders were synthesized by a self-combustion method. The most difficult part for preparing Nb-containing oxides by wet chemical routes is the selection of proper Nb precursors. In this study, $C_4H_4NNbO_9$ was used as the starting Nb source. $C_4H_4NNbO_9$ was precipitated with a NH_4OH solution, leading to the formation of a white slurry. The white slurry was filtered and collected, followed by washing with NH_4OH solution and water. Then, the white slurry was dissolved in a citric acid water solution under stirring, setting the molar ratio of citric acid/Nb ion at 1.5, obtaining the final solution made of Nb-citric acid complex solution. The exact Nb concentration in this solution was determined using an inductively coupled plasma optical emission spectrometer (ICP-OES).

Stoichiometric amounts of $Ba(NO_3)_2$, $Ca(NO_3)_2$ and Nb-citric acid complex were dissolved in distilled water. $Ba(NO_3)_2$ and $Ca(NO_3)_2$ were prepared by dissolving $BaCO_3$ and $CaCO_3$ in nitric acid. Citric acid was then added as a complexing agent, setting the citric acid/total metal ions molar ratio at 1.5. NH_4OH was added to adjust the pH value at around 8. The solution was heated under stirring to evaporate water until it changed into a viscous gel and finally ignited to flame, resulting in an ash. The ash was annealed at 1000 °C for 6 h to form the BCN18 powder.

The BCN18 powders were uniaxially pressed at 100 MPa to form green BCN18 pellets, which were sintered at 1400, 1500 and 1600 °C for 10 h, respectively, having a final thickness of about 1 mm. Scanning electron microscopy (SEM) was used to observe the morphology of the BCN18 pellets sintered at different temperatures. The phase composition of the as-prepared BCN18 pellets was confirmed using X-ray diffraction (XRD) measurements. To prepare the electrodes for electrochemical tests, silver paste

was painted on both sides of the BCN18 sintered pellets and then fired at 700 °C for 2 h. Conductivity measurements were performed using a multichannel potentiostat (VMP3 Bio-Logic Co.) in the 0.1 Hz - 1 MHz frequency range, using an AC voltage amplitude of 100 mV.

Results and Discussion

Morphology and phase identification of sintered BCN18 pellets

Figures 1a, 1b, and 1c show the SEM micrographs of the BCN18 pellet fracture surface after sintering for 10 h at 1400 °C, 1500 °C, and 1600 °C, respectively. The BCN18 pellet was still rather porous after sintering at 1400 °C, preventing its use as electrolyte for SOFCs. The porosity decreased with increasing the sintering temperature, as shown in Fig. 1. The pellet sintered at 1500 °C showed the presence of small closed pores, which were eliminated by further increasing the sintering temperature up to 1600 °C. At the last sintering temperature, the BCN18 pellet was almost fully dense, and therefore the BCN18 pellet sintered at 1600 °C was selected for the electrochemical impedance spectroscopy measurements.

Figure 1. SEM micrographs of the fracture surface of BCN18 pellets after sintering for 10 h at 1400 °C (a), 1500 °C (b), and 1600 °C (c).

Figure 2 shows the XRD pattern of the BCN18 pellet after sintering at 1600 °C for 10 h. Only the BCN18 phase can be observed, without evidence of the presence of other impurity phases. The XRD findings for our samples match well the XRD data reported for the BCN18 material in the literature (13). The insert SEM micrograph shows the surface of the BCN18 pellet after sintering at 1600 °C for 10 h at high magnifications.

One can observe that the pellet is quite dense with large grain size from around 2 up to 8 μm).

Figure 2. XRD pattern for the BCN18 pellet sintered at 1600 °C. The inserted SEM micrograph shows the surface of the BCN18 sintered pellet.

Electrochemical measurements for the BCN18 pellets

The BCN18 pellets sintered at 1600 °C were selected for the electrochemical tests due to its high density and composition phase purity. The samples were tested in dry and wet ($\sim 3\%$ H_2O) air atmospheres. The “wet” testing conditions were achieved by sweeping the BCN18 samples with humidified air ($\sim 3\%$ H_2O) at 200 °C, holding the samples overnight in these conditions. After completing the tests in wet atmosphere, the “dry” testing condition was achieved by holding the sample at 700 °C overnight under dry air flow.

Figure 3 shows the total conductivity of the sintered BCN18 pellets in wet and dry air atmospheres. The conductivity in wet atmosphere was significantly larger than that in dry air. The difference in conductivity in wet and dry atmospheres is a typical behavior for proton-conducting oxides, due to the formation of the proton within the material lattice in wet atmosphere. The total conductivity of the BCN18 sample in the present study reached $10^{-3} \text{ S cm}^{-1}$ at 600 °C in wet air atmosphere. This conductivity value is smaller than that reported by Du and Nowick (8), $10^{-2} \text{ S cm}^{-1}$ at 600 °C, but larger than that reported by Viana and Irvine (14), which was only $7 \times 10^{-4} \text{ S cm}^{-1}$ at 900 °C. The difference in the conductivity results for nominally the same BCN18 material suggests that a detailed electrochemical analysis is necessary to find the factors influencing the conductivity. It is well known that the total conductivity of a polycrystalline sample may include the contribution from both bulk and grain boundaries. The separation of the bulk and grain boundary conductivity contributions was carried out in this study to get a deeper insight on the electrical properties of the BCN18 sample.

Figure 3. Total conductivity of the BCN18 pellets in wet and dry air atmospheres.

Figure 4 shows the electrochemical impedance spectroscopy (EIS) plots of the BCN18 sample measured at 500 °C in dry (Fig. 4a) and wet air (Fig. 4b) atmospheres. The plots showed semi-circles in the intermediate frequency region with a capacitance in the order of 10^{-7} F, which is reported as a typical capacitance value of grain boundary for BCN18 (11). The bulk resistance can be obtained from the intercept of the high frequency part of the grain boundary semi-circle with the real axis. The analysis of the EIS data showed that the bulk resistance value in wet air atmosphere was distinctly smaller than that in the dry atmosphere, while there was no obvious difference in the grain boundary resistance value in both dry and wet atmospheres.

Figure 4. Complex-impedance plane plots for the BCN18 pellet measured at 500 °C in dry (a) and wet air (b) atmospheres.

Figure 5 shows the Arrhenius plots of the bulk and grain boundary conductivity values for the BCN18 pellet, obtained from the EIS measurements. The bulk conductivity in the wet air atmosphere was significantly larger than that in the dry air atmosphere (Fig. 5a), suggesting the occurrence of proton conductivity in the bulk, for the sample in the wet air environment. The activation energy for the bulk conductivity in the wet condition was 0.52 eV, in good agreement with the reported bulk activation energy values for BCN18 (0.52 to 0.55 eV) (11, 12). In dry air, proton cannot be formed in the lattice due to the lack of hydrogen source, being oxygen-ions and electron holes the main charge carriers in dry atmosphere (15, 16). The activation energy for the sample in dry air was 0.63 eV, which is close to the activation energy reported for other proton-conducting oxides in a similar atmosphere (3, 17, 18). The larger bulk conductivity in wet air suggests the occurrence of proton conductivity in the BCN18 bulk, in agreement with the literature that reports protons as the dominant charge carriers in the bulk for BCN18 in wet atmospheres (11, 12).

Figure 5b shows that the grain boundary conductivity was almost the same in wet and dry atmospheres, suggesting that other species rather than protons are the main charge carriers at the grain boundary. The grain boundary activation energy for the BCN18 sample in the wet air condition is 1.26 eV which is much larger than that for the proton-conduction and also imply that the proton is not the main charge carrier at the grain boundary. This finding seems to contradict that reported for BCN18 prepared by sol-gel, for which the grain boundary conductivity in wet atmosphere was reported to be significantly larger than that in dry air (11, 13), but agrees with that for the BCN18 prepared by solid-state reaction, for which the main charge carriers at the grain boundary were not protons (11, 19). The BCN18 materials prepared by the combustion method in our study show an electrical behavior similar to that for the BCN18 material prepared by solid-state reaction. It should be noted that the pellets prepared using the sol-gel BCN18 powders were sintered at 1400 °C, which is much lower than the sintering temperature used in our study. The BCN18 pellets after sintering at 1400 °C were still porous, despite the BCN18 powders were synthesized using a wet chemical route. The sintering temperature of 1600 °C was used also for the BCN18 samples prepared from the solid-state reaction materials. Therefore, the sintering temperature might be also another important parameter influencing the electrical properties of the BCN18 material.

Figure 5. Bulk conductivity (a) and grain boundary conductivity (b) of the BCN18 sample in wet and dry air conditions.

Conclusions

We successfully synthesized BCN18 powders using a combustion method. The prepared BCN18 powders were sintered into pellets at 1600 °C to reach almost full density, which was almost the same temperature needed for sintering BCN18 powders prepared by solid-state reaction. The dense BCN18 pellets were tested in wet and dry air atmosphere, showing in the wet air atmosphere a total conductivity larger than that in dry air, which suggested the proton conduction behavior for the BCN18 material. A detailed EIS analysis was performed to separate the contributions of bulk and grain boundary from the total conductivity, revealing that the bulk conductivity of the BCN18 material presented a proton conduction behavior while the main charge carriers at grain boundaries were not proton.

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