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ELECTRICAL PROPERTIES OF INDIUM AND YTTRIUM-DOPED BARIUM CERATE-BASED COMPOUNDS FOR USE AS CERAMIC FUEL CELL ELECTROLYTES

WŁAŚCIWOŚCI ELEKTRYCZNE ZWIĄZKÓW NA BAZIE CERANU BARU DOMIESZKOWANYCH INDEMI I ITREM DO ZASTOSOWANIA JAKO ELEKTROLITY W CERAMICZNYCH OGNIWACH PALIWOWYCH

The aim of this work is to compare the electrical properties of $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCY15), $\text{BaCe}_{0.70}\text{In}_{0.30}\text{O}_{3-\delta}$ (BCI30) and a composite material consisting of 30%vol. BCY15 and 70%vol. $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{2-\delta}$ (YDC15). BCY15 and YDC15 were synthesized by co-precipitation, whereas BCI30 was obtained using the solid-state reaction method. Pellets were initially formed from powders at 5 MPa, after which they were isostatically pressed at 250 MPa and sintered at 1500°C. Electrochemical impedance spectroscopy (EIS) was used to determine the electrical properties of the samples in both air ($p_{\text{O}_2} = 0.021$ MPa) and Ar-5% H_2 atmospheres. In the temperature range 200-400°C in air atmosphere the highest conductivity values were determined for BCY15 ($5,22 \cdot 10^{-5} - 2,74 \cdot 10^{-3}$ S/cm). On the other hand, the electrical conductivity values obtained for Y70B30 in both atmospheres between 200 and 550°C are in the order of magnitude of $10^{-7} - 10^{-3}$ S/cm. Consequently, it can be concluded that the compounds exhibit significant H^+ and O^{2-} electrical conductivity at temperatures above 500°C, which indicates the possibility for their potential use as ceramic fuel cell electrolytes.

Keywords: perovskites, solid oxide fuel cell electrolytes, electrical conductivity, composite materials

Celem niniejszej pracy jest porównanie właściwości elektrycznych związków $\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCY15), $\text{BaCe}_{0.70}\text{In}_{0.30}\text{O}_{3-\delta}$ (BCI30) oraz materiału kompozytowego złożonego z mieszaniny 30%obj. BCY15 i 70%obj. $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{2-\delta}$ (YDC15). Proszki BCY15 i YDC15 były syntezowane metodą współstrącania, natomiast proszek BCI30 otrzymano metodą reakcji w fazie stałej. Z proszków formowano wstępnie pastylki pod ciśnieniem 5 MPa, a następnie prasowano izostatycznie pod ciśnieniem 250 MPa i spiekano w temperaturze 1500°C. W celu określenia właściwości elektrycznych próbek posłużono się metodą elektrochemicznej spektroskopii impedancyjnej (EIS). Badania wykonano w atmosferze powietrza ($p_{\text{O}_2} = 0.021$ MPa) oraz w mieszaninie gazów Ar-5% H_2 . W zakresie temperatur 200-400°C w atmosferze powietrza najwyższe wartości przewodnictwa uzyskano w przypadku BCY15 ($5,22 \cdot 10^{-5} - 2,74 \cdot 10^{-3}$ S/cm). Natomiast wartości przewodnictwa dla Y70B30 mierzone w obu atmosferach w zakresie 200-550°C są rzędu $10^{-7} - 10^{-3}$ S/cm. Z otrzymanych wyników badań wynika, że w/w związki posiadają znaczne przewodnictwo zarówno protonowe (H^+) jak i jonowe (O^{2-}) w temperaturach powyżej 500°C, co wskazuje na możliwość potencjalnego zastosowania tych materiałów jako elektrolity w ceramicznych ogniwach paliwowych.

1. Introduction

Solid oxide fuel cells (SOFC) and protonic ceramic fuel cells (PCFC) have been considered as promising alternative energy devices due to their relatively high efficiency (50-60%) amongst fuel cells. Unfortunately, both fuel cells have a fundamental disadvantage, i.e. the production of water vapour (H_2O) at one of the electrodes, which lowers the electrical efficiency of the system. A solution to this problem was proposed by the “Innovative Dual mEmbrAne fuEL Cell” (IDEAL-Cell) project. The idea behind this project is to connect a PCFC anode/electrolyte (anode compartment) with a SOFC electrolyte/cathode (cathode compartment) via a porous membrane, from which H_2O is evacuated through open porosity, as schematically shown in [1].

$\text{BaCe}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ (BCY15) was chosen as the PCFC electrolyte material due to the relatively high protonic conductivity of yttrium doped barium cerate (BCY) among other perovskite-based compounds [2-8]. Furthermore, it has been determined that the optimal amount of yttrium doping is 15%at. [6]. However, these materials have poor resistance against corrosion in CO_2 -containing atmospheres [9-11]. It has been determined that barium cerate doped with 30%at. indium (BCI30) exhibit better stability against CO_2 [12,13].

On the other hand, CeO_2 doped with Gd_2O_3 , Sm_2O_3 or Y_2O_3 have shown significant oxide ion conductivity [14-16]. Among these potential electrolytes, $\text{Ce}_{0.85}\text{Y}_{0.15}\text{O}_{2-\delta}$ (YDC15) was selected for use as the SOFC electrolyte in the dual PCFC-SOFC fuel cell. This is because BCY15 and YDC15 are chemically compatible with one another, which can be

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explained by the following decomposition reaction of BCY15 at high sintering temperatures:

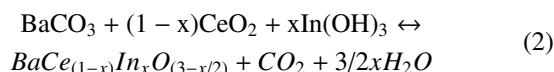


This reaction shows that YDC15 is a decomposition product of BCY15. Therefore, it is also possible to obtain composite materials by mixing BCY15 and YDC15 together. It was assumed that such materials will have the necessary properties for application as the central membrane material, such as high H^+ and O^{2-} conductivity. According to eq. (1), a BCY15-YDC15 composite material should also be more resistant against decomposition due to the Le Chatelier-Braun principle and therefore more stable than pure BCY15. It has also been determined that composite materials have better chemical stability in $\text{CO}_2/\text{H}_2\text{O}$ atmosphere than BCY15 [17,18].

The objective of this work is to study the electrical properties of a BCY15-YDC15 composite bulk sample in both Ar-5\%H_2 and air atmosphere, as well as compare these properties with those of non-composite BCY15 and BCI30 samples.

2. Experimental procedure

BCY15 and YDC15 powders were synthesized via oxalate co-precipitation using barium, cerium and yttrium dissolved salts. The composite powder was obtained by mixing 30%vol. BCY15 with 70%vol. YDC15 via 24 hr. ball milling (120-150 rpm) of the two powders in a PET bottle in presence of zirconia balls and isopropanol (~20 ml). Afterwards, the mixtures were freeze dried (the bottles were frozen in liquid nitrogen) and finally the mixtures were separated from the ZrO_2 -balls by sieving (53 μm mesh). On the other hand, BCI30 powder was synthesized by the following solid state reaction:



Each of the obtained powders was annealed at 1100°C for 2 1/2 hrs (heating/cooling rate: 10°C/min) in flowing synthetic air. Afterwards, these powders (~ 0.7 g of each) were pressed into pellets with 1 cm diameter. The BCY15 and BCI30 pellets were sintered first at 1300°C for 2 hrs, then at 1500°C for another 2 hrs, whereas Y70B30 was sintered at 1500°C for 4 hrs (heating/cooling rate: 3°/min).

Analysis of the microstructure and chemical composition of the powders and bulk samples was provided using Scanning Electron Microscopy combined with Energy Dispersive Spectroscopy (SEM-EDS). The phase composition of the samples was determined by X-ray Diffraction (XRD).

Electrochemical Impedance Spectroscopy (EIS) was used to determine the electrical resistance of the materials in both Ar-5\%H_2 and air atmosphere. Measurements were carried out at temperatures from 200 to 800°C for the frequency range 1 mHz – 1 MHz. By interpreting the obtained data, activation energy values (E_a) for ionic diffusion through the samples were determined, assuming that ionic transport numbers of H^+ and O^{2-} are approximately equal to 1.00 in BCY15 and YDC15, respectively.

3. Results

XRD analysis of the initial BCY15, YDC15, BCI30 and Y70B30 are presented in Fig. 1. Figures 1a-1c show that BCY15, YDC15 and BCI30 consist of one phase with minor amounts of impurities leftover from the respective synthesis procedure and manipulation of the samples in air. However, the Y70B30 powder consists of two phases from the initial BCY15 and YDC15 samples used to obtain the composite sample.

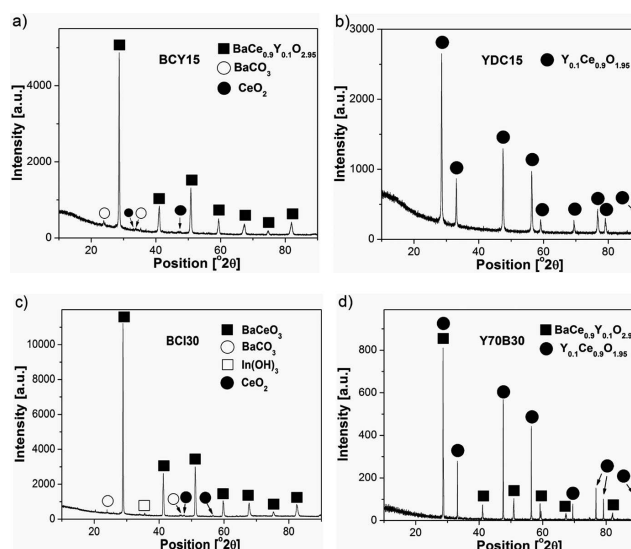


Fig. 1. XRD analyses of a) BCY15, b) YDC15, c) BCI30 and d) Y70B30 initial powders

SEM microphotographs of the sintered BCY15, BCI30 and Y70B30 samples are given in Fig. 2. From Fig. 2 it follows that the largest grains were obtained in the case of BCY15 (Fig. 2a). The observations also show that the BCI30 sample (Fig. 2b) has high porosity. Furthermore, despite the longer sintering time at 1500°C, the grains of the Y70B30 bulk sample (Fig. 2c and Fig. 2d) are smaller than those of BCY15.

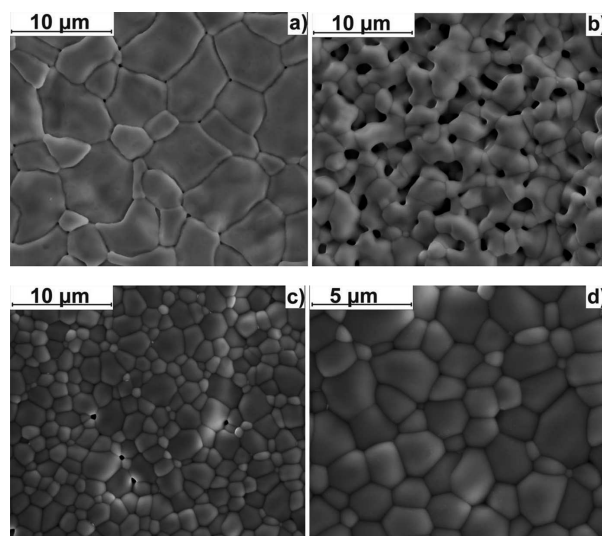


Fig. 2. SEM microphotographs of a) BCY15, b) BCI30, c) Y70B30, d) Y70B30 (greater magnification) bulk samples obtained by sintering at 1500°C

Figure 3 presents the dependence between temperature and total electrical conductivity of the BCY15 and BCI30 samples in air atmosphere. From Fig. 3a it follows that the conductivity values determined for BCY15 in the temperature range 200–400°C are comparable to those obtained in the case of BCI30 between 500 and 800°C. Conductivity values of BCY15 are not presented for higher temperatures, as at these temperatures the electrical conductivity of the studied sample is so high that the resistance of the material becomes similar to the resistance of the apparatus. Consequently, the impedance spectra at these temperatures show the effects of parasitic inductance instead of an arc pertaining to the afore-mentioned conductivity in the material. Significant conductivity values in hydrogen-containing atmospheres have also been determined for BCY15 [6–8].

The high resistance values determined for BCI30 (Fig. 3b) can be explained by the porous morphology of the sample. Research on BCI30 with more compact morphology has yielded more promising electrical conductivity results [12,13]. Nevertheless, higher conductivity values at the respective temperatures have been determined for BaCeO₃ samples doped with yttrium [2–8,12].

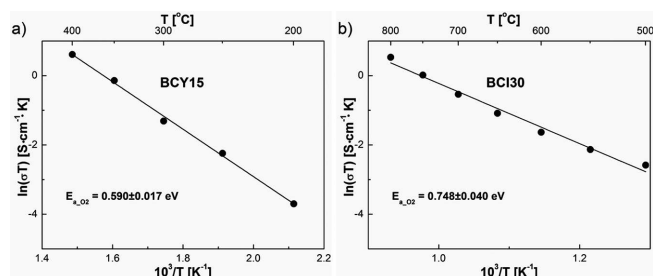


Fig. 3. Arrhenius correlation between electrical conductivity and temperature obtained from EIS measurements in air for: a) BCY15 in the temperature range 200–400°C and b) BCI30 in the temperature range 500–800°C

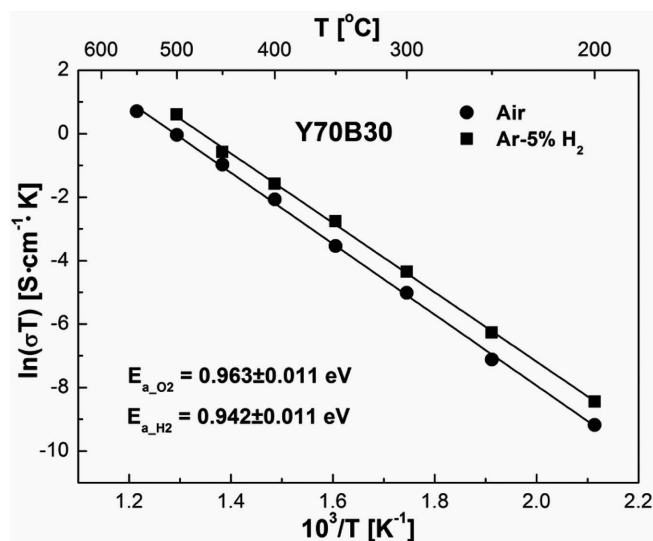


Fig. 4. Arrhenius correlation between electrical conductivity and temperature obtained from EIS measurements in air and Ar-5%H₂ atmospheres for Y70B30 in the temperature range 200–550°C

The Arrhenius correlation between temperature and the conductivity of Y70B30 in both Ar-5%H₂ and air atmosphere is presented in Fig. 4. From this figure it follows that pro-

ton conductivity is slightly higher than oxide ion conductivity in the temperature range 200–500°C. However, seeing as the activation energy for conductivity in Ar-5%H₂ atmosphere ($E_{a,H_2} = 0.942 \pm 0.011$ eV) is somewhat lower than in the case of conductivity in air ($E_{a,O_2} = 0.963 \pm 0.011$ eV), it can be assumed that above a certain temperature oxide ion conductivity will become the dominant mechanism.

The Arrhenius plots of the non-composite bulk samples studies (Fig. 3) show that BCI30 has higher activation energy for oxide ion conductivity ($E_{a,O_2} = 0.748 \pm 0.040$ eV) than that determined for BCY15 ($E_{a,O_2} = 0.590 \pm 0.017$ eV). However, Y70B30 (Fig. 4) possesses higher activation energy than both non-composite samples. The activation energy value for Y70B30 obtained from EIS measurements in Ar-5%H₂ atmosphere is also higher than those determined for BCY15 and BCI30 in hydrogen-containing atmospheres [8,12].

4. Conclusions

From the impedance measurements at different temperatures, it can be concluded that BaCe_{0.85}Y_{0.15}O_{3-δ} (BCY15) exhibits higher electrical conductivity than Y70B30 (70%vol. YDC15 + 30%vol. BCY15). Furthermore, the addition of Ce_{0.85}Y_{0.15}O_{2-δ} (YDC15) in the BCY15 sample increases the activation energy of ionic transport through the material. The influence of morphology on ionic transport is also apparent. Both BaCe_{0.70}In_{0.30}O_{3-δ} (BCI30) and Y70B30 have proven more difficult to sinter than BCY15. Nevertheless, both the H⁺ and O²⁻ conductivity of Y70B30 is significant at temperatures above 500°C and therefore the material shows promise as a potential ceramic membrane of a dual PCFC-SOFC fuel cell.

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