

Some observations on the synthesis and electrolytic properties of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ -based samples modified with calcium

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In this paper, the impact of partial substitution of calcium for barium in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ on physicochemical properties of the powders and sintered samples was investigated. The powders, with various contents of calcium ($x = 0, 0.02, 0.05, 0.1$), were prepared by means of thermal decomposition of organometallic precursors containing EDTA. All of the BaCeO_3 -based powders synthesised at 1100 °C were monophasic with a rhombohedral structure, however, completely cubic BaZrO_3 -based solid solutions were obtained at 1200 °C. A study of the sinterability of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ -based pellets was performed under non-isothermal conditions within a temperature range of 25 to 1200 °C. The partial substitution of barium for calcium in the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ solid solution improved the sinterability of the samples in comparison to the initial $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ or $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$. The relative density of calcium-modified $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ -based samples reached approximately 95 to 97 % after sintering at 1500 °C for 2 h in air. The same level of relative density was achieved after sintering calcium-modified $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ at 1600 °C for 2 h. Analysis of the electrical conductivity from both series of investigated materials showed that the highest ionic conductivity, in air and wet 5 % H_2 in Ar, was attained for the compositions of $x = 0.02$ to 0.05 $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Zr}, \text{Ce}$. The oxygen reduction reaction on the interface $\text{Pt}|\text{BaM}_{0.9}\text{Y}_{0.1}\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ was investigated using Pt microelectrodes. Selected samples of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Zr}, \text{Ce}$ were tested as ceramic electrolytes in hydrogen-oxygen solid oxide fuel cells operating at temperatures of 700 to 850 °C.

Keywords: ceramics; electrochemical measurements; ionic conductivity; IT-SOFC – intermediate temperature solid oxide fuel cell

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1. Introduction

High-temperature ceramic proton conductors appear to be valuable components for developing cost-effective solid oxide fuel cells operating within an intermediate temperature range of 400 to 800 °C. The application of a ceramic proton-conducting membrane, instead of an oxide ionic conductor as an electrolyte in SOFCs, may lead to simplification of the construction of SOFC stacks. In SOFCs with a ceramic proton-conducting membrane, water evolves on the cathode, thus avoiding fuel dilution on the anode side and reduction of cell

voltage [1–3]. At present, high protonic conduction has been reported for several perovskite-type oxides, such as doped BaCeO_3 , SrCeO_3 , BaZrO_3 and SrZrO_3 [4–7]. Proton conduction can be thermally activated at comparatively low temperatures (400 to 700 °C) due to the low activation energy (0.3 to 0.6 eV) required by this process. In general, $\text{BaCe}_{1-x}\text{M}_x\text{O}_3$, $\text{M} = \text{Y}, \text{Gd}, \text{Sm}$ solid solutions exhibit higher protonic conductivity compared to $\text{BaZr}_{1-x}\text{M}_x\text{O}_3$. The greatest drawback of BaCeO_3 -based ionic conductors is their limited chemical stability in atmospheres containing CO_2/SO_2 gases [8–10].

Doped BaZrO_3 was found to be chemically more stable and was characterized by better

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mechanical properties. However, the poor sinterability of barium zirconate led to the presence of a large grain boundary surface, resulting in lower electrical conductivity than in doped barium cerate [11, 12]. The main challenge for researchers has been to develop new proton conductor materials with higher ionic conductivity and chemical stability over a wide range of IT-SOFCs. One approach is to modify the physicochemical properties of BaCeO₃-based ionic conductors. It has been found that Ba(Ce_{0.3}Zr_{0.5})Y_{0.2}O_{3-δ} is characterized by improved chemical stability and ionic conductivity [13, 14]. Alternatively, Fabbri *et al.* [15] deposited a thin film of Y-doped BaZrO₃ (BZY) on a Y-doped BaCeO₃ pellet, using pulsed laser deposition (PLD) to form a bilayer electrolyte structure. The thin BaZrO₃ film protected the BaCeO₃ pellet with only a slight loss in electrochemical performance.

Bi and Traversa [16] elaborated composite, chemically stable, electrolytes consisting of two layers of stable BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-δ} used to sandwich a highly conductive but unstable BaCe_{0.8}Y_{0.2}O_{3-δ} electrolyte layer. Fuel cell prototypes with the sandwiched electrolyte structure achieved a relatively high performance, above 180 mW·cm⁻², at 700 °C [17].

The proton transport properties of ABO₃ compounds were strictly connected with differences between the radii of the host and dopant ions, their electric charges and the amount of respective dopants. There have been many studies on the proton conductivity of BaMO₃, M = Zr, Ce solid solutions in which the B side was modified by the introduction of M³⁺ cations with various radii, such as M³⁺ = Y³⁺, Sm³⁺, Gd³⁺, La³⁺ and others, whereas there have been very few investigations concerning modification of the A side [18, 19]. It was found that the partial substitution of calcium or strontium for barium in Ba_{1-x}M_x(Zr_{0.9}Y_{0.1})O₃, M = Ca, Sr, 0 < x < 0.1 resulted in an improvement in protonic conductivity compared to Ba(Zr_{0.9}Y_{0.1})O₃ [20, 21].

The aim of this paper was to determine the impact of calcium on the physicochemical and electrochemical properties of (Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O₃

and (Ba_{1-x}Ca_x)(Ce_{0.9}Y_{0.1})O₃; these properties are crucial for the application of the compounds as a protonic ceramic membrane in solid oxide fuel cells.

2. Experimental

Modified calcium (Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O₃, M = Ce, Zr, 0 < x < 0.15 powders were prepared using a polymer complex method with versenate acid (ethylenediaminetetraacetic acid, or EDTA). The initial aqueous solutions were prepared by dissolving appropriate amounts of barium, calcium, cerium/zirconium, and yttrium nitrates (Merck, P.A.) in distilled water, whereas versenate acid, whose solubility in water is very poor, was dissolved in a concentrated solution of ammonia. The ammonium versenate solution was introduced drop by drop into a vigorously agitated solution of each of the cation nitrates. During this operation, some increase in turbidity was observed due to hydrolysis of the versenate acid. Fixing the pH values at ca. 8 with ammonia concentrate led to dissipation of this turbidity. The amount of introduced ammonium versenate exceeded the total amount of cation moles by 10 %. After being stored for 24 h at room temperature, the solutions were dried at 250 °C, using a procedure described in the literature [20, 21].

Small amounts of the prepared precursors were calcined at temperatures ranging from 400 to 1200 °C for 1 h in air. The calcination temperature was increased gradually by 50 °C. To determine the progress of (Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O₃, M = Ce, Zr synthesis, after each thermal treatment, the phase composition of BCY-based samples was monitored using the X-ray diffraction method.

The final temperature of the synthesis of the monophase BaCeO₃-based samples was established at 1100 °C, but in the case of BaZrO₃-based precursors the temperature reached 1200 °C. In the next step, the powders were ground in a rotary-vibrational mill for 30 min. The surface areas of both the initial synthesized and post-milling powders were measured using the multipoint BET method. Isostatic pressing at 250 MPa was used

to compact the powders, which were then sintered at a temperature range of 1400 to 1650 °C for 2 h in air.

The procedure described above enabled the authors to prepare $\text{BaM}_{0.9}\text{Y}_{0.1}\text{O}_3$, $\text{M} = \text{Ce}$, Zr-based samples with the chemical compositions $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$, $(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$, $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$, and $(\text{Ba}_{0.90}\text{Ca}_{0.1})(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$, designated subsequently as BCY, C2BCY, C5BCY, and C10BCY, respectively. A similar procedure was applied to a series of samples involving barium zirconate, such as: $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$, $(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ depicted in this paper as BZY, C2BZY, C5BZY and C10BZY.

Studies on thermal decomposition processes of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr dried gels over a temperature range of 25 to 1000 °C, increased at each step by 10°/min, were conducted using thermogravimetric analysis (TG), differential thermal analysis (DTA), and evolved gas analysis (EGA) of volatile products with a quadrupole mass spectrometer. All of the investigations were performed on a thermoanalyser (TA Instruments SDT 2960), which enabled simultaneous detection of mass changes and heat effects occurring during the heating of the samples. Gaseous products of reactions were analysed using a quadrupole mass spectrometer.

The phase compositions of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr powders were studied using X-ray diffraction analysis method. XRD measurements were performed with a Panalytical X'Pert PRO system with monochromatic $\text{CuK}\alpha$ radiation. The lattice parameters of the BaCeO_3 and BaZrO_3 -based solid solutions were determined using the Rietveld refinement method. Specific surface areas were measured by multipoint nitrogen adsorption at -196 °C (Quantachrome Nova 1200). Transmission electron microscopy (Philips AEM CM20) was used to characterize the morphology of all ground powders.

Scanning electron microscopy (SEM), equipped with an energy-dispersive X-ray

analysing system (EDX) was used to observe the microstructure of sintered samples. Fracture toughness and hardness were measured by means of Vickers indentation using Future Tech (Japan) equipment. Loading forces of 4.90 N in the former case and of 9.81 N in the latter, imposed every 10 s, were applied. No cracks occurred while the lower load was used.

The total electrical conductivity of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr-sintered samples was measured by AC four probe method. The measurement results were plotted as a function of temperature (400 to 800 °C) in 5 % H_2 in Ar and air. For measurements in wet atmospheres, water was incorporated into the samples by exposure to a water-saturated (3 % H_2O) test gas flow.

The Pt porous electrode was applied in all electrical measurements. Prior to each measurement, samples were equilibrated for at least 30 min in given conditions (temperature and gas atmosphere).

In this study, we also investigated the oxygen reduction process (OER) at the interface of metal ceramic proton conducting membranes using microelectrodes made from Pt, with the emphasis placed on the effect of prolonged polarization of the electrode. In the present paper as well as in the literature [22–24] the term microelectrode refers to a spherical electrode made from metallic Pt with a diameter of approximately 180 μm . The procedures involved in Pt metallic electrode preparation were described in paper [22]. The $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr sintered samples took the form of discs: 10 mm in diameter and 3 mm thick. The field of the direct contact between the so formed Pt electrode and the electrolyte had a circular shape [24]. In this study the measurements were performed at 700 °C, corresponding to the operational temperature of an IT-SOFC. The experiments were performed in gas atmospheres with varying oxygen content: argon ($p\text{O}_2 = 3.04 \text{ Pa}$), air ($p\text{O}_2 = 21278 \text{ Pa}$) and oxygen ($p\text{O}_2 = 101325 \text{ Pa}$). Both dry and wet gas atmospheres were applied. During the measurements, two microelectrodes were located on opposite sides of the electrolyte disc. The electrodes and

the disc were assembled inside an alumina holder and held together with springs acting with a force of approximately 0.5 N. A counter electrode, in the form of a platinum ring made from a wire, 0.5 mm in diameter, was located in a groove around the side wall of the disc. During the electrochemical experiment, the working microelectrode was polarized several hours with overpotentials from -0.05 to -0.5 V, then the system was cooled down to room temperature within 2 to 3 h. Also, during the cooling, the overpotential of the working electrode was held mainly at -0.5 V for as long as possible time. An Autolab electrochemical station was used for these measurements. The details of the construction of the electrochemical setup as well as the procedure of electrochemical measurements performed during those investigations were described in papers [22, 23]. Before and after the electrochemical experiments, the surfaces of the Pt microelectrodes as well as the BZY and BCY pellets, were examined by means of a scanning electron microscope (SEM/EDX).

BZY, BCY, C5BZY and C5BCY were tested as solid electrolytes in solid oxide fuel cells operating within a temperature range of 600 to 850 °C:



Humidified hydrogen (3% H_2O) was fed into the anode chamber and oxygen was supplied to the cathode chamber. The flow rate of the oxidant and fuel was 100 mL/min. The family of the overpotential curves (ΔE) – current density curves (I) – was tested using linear sweep voltammetry at a scanning rate of $5 \text{ mV}\cdot\text{s}^{-1}$.

3. Results and discussion

Typical DTA/TG curves recorded for the BCY precursor are shown in Fig. 1a. The EGA gas composition analysis recorded during thermal analysis of the BCY sample is presented in Fig. 1b.

The first feature seen on the DTA curve, in the range of approximately 70 to 120 °C, consisted of

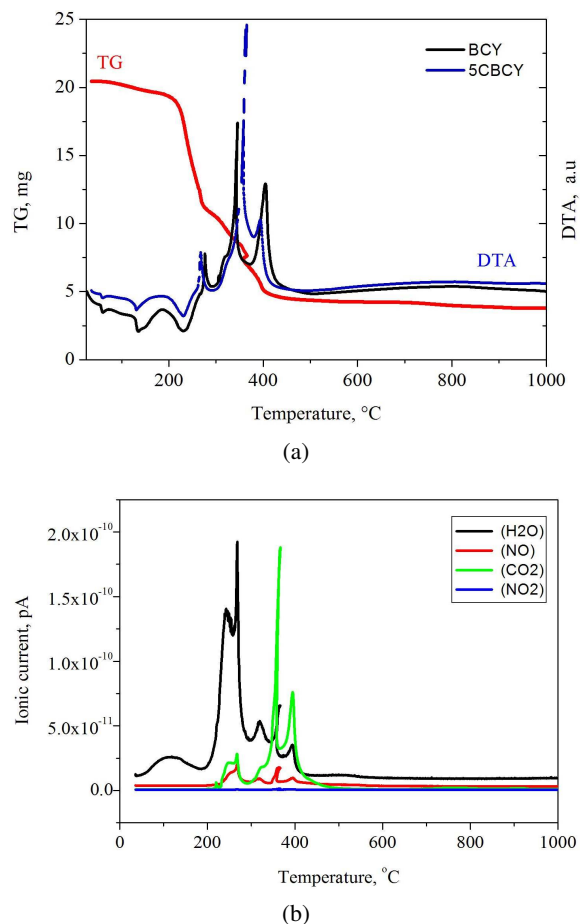


Fig. 1. a) DTA and TG curves recorded for dried $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ precursors; b) EGA gas analysis performed during DTA/TG thermal studies.

small endothermic peaks connected with dehydration. The weight losses began to be visible on the TG curve. The appearance of an H_2O current peak at 100 °C on the EGA curve confirmed these observations. The increase in temperature caused dehydration as well as initiated decomposition of organic matter in the BCY-series precursors. Small peaks, corresponding to exothermic effects over a temperature range of 200 to 300 °C, were observed. These effects could be attributed to the combustion of organic matter in the precursors. The increase in H_2O and CO_2 currents observed on the EGA curve in this temperature range was the same as DTA/TG data.

Some decomposition of nitrate compounds in this temperature range was also observed.

The intense peaks, at temperatures of 300 to 400 °C, corresponded to exothermal effects connected with the combustion reaction, and probably were connected with crystallization of CeO_2 – BaO solid solutions. The observations were confirmed by EGA measurements. Above 500 °C, the sample weight remained unchanged, probably indicating the formation of a stable crystalline BaCeO_3 phase. Similar DTA/TG curves obtained with EGA analysis were recorded for the BZY series of precursors. The comparative analysis of DTA/TG curves recorded for $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ samples indicated that partial substitution of barium with calcium in $0 < x < 0.15$ solid solutions exerted no significant influence either on peaks in crystallization or on the thermal behavior of the samples.

The results obtained via the thermal analysis method agreed with the variation in phase composition determined by the XRD method recorded for BCY-series samples calcined at temperatures of 500 to 1100 °C. Fig. 2 presents the evolution of phase composition for the $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ dried precursor vs. temperature.

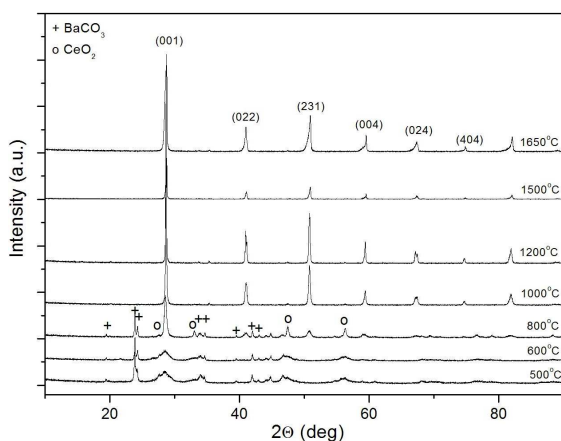


Fig. 2. Evolution of the X-ray diffraction pattern for the $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ dried precursor.

The same BCY sample was calcined at a temperature range between 500 to 1100 °C. The analysis of the evolution of the XRD pattern recorded for this BCY sample, but calcined at a different temperature within the range of 500 to 1100 °C, enabled the authors to determine the phase

composition following each applied heat treatment process. The XRD pattern recorded reflections for the $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ sample heated at 500 °C in the BaCO_3 , cubic CeO_2 – BaO solid solutions and BaCeO_3 phases. The increase in temperature during the calcination of BCY samples from 600 to 800 °C resulted in an increase in the amount of the BaCeO_3 phase; additional reflections of this compound were visible in the recorded XRD pattern. In a temperature range of 1000 to 1100 °C, a fully crystalline BaCeO_3 phase was observed. An increase in temperature from 1500 to 1600 °C only caused the characteristic reflections of BaCeO_3 to become stronger in intensity when compared to the ones obtained in 1100 °C.

Similar investigations were performed for BZY dried precursors. Fully cubic crystalline $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ were obtained at 1200 to 1250 °C. For all investigated compositions of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$, a rhombohedral structure was found. As for the calcium modified barium zirconate series, such as the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ samples, a cubic perovskite structure was detected. The application of the sol-gel method with EDTA as a complexing agent enabled the temperature to be lowered to approximately 100 to 200 °C compared with the Pechini and citrate methods for both the investigated BCY and BZY series [25, 26]. On the basis of X-ray investigations, the cell parameters and cell volume of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr $0 < x < 0.1$ for sintered samples were calculated. In Fig. 3 the variation in cell volume of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}$, Zr $0 < x < 0.1$ samples vs. chemical composition is presented.

In both cases, a decrease in the cell volume was observed. A regular linear decrease in cell volume was observed for prepared samples of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$. This suggested that calcium, partially introduced into barium zirconate, was in a solid solution form. The lattice parameter for 2CBZY, 5CBZY and 10CBZY was significantly smaller than that of BZY. It was consistent with the substitution of the host cation Ba^{2+} by Ca^{2+} ions having a smaller ionic radius (1.34 Å) [27].

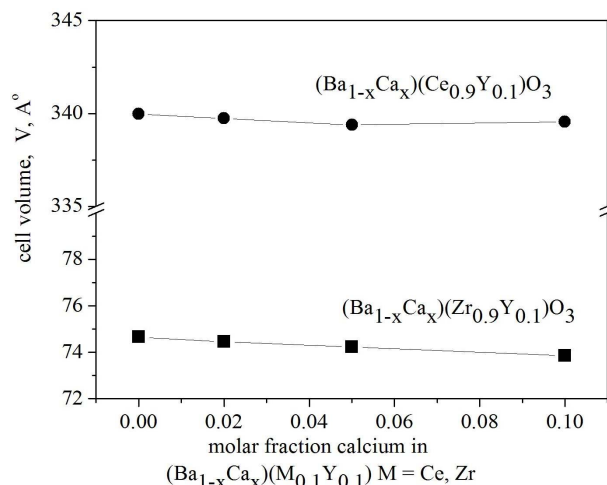


Fig. 3. Variations in cell volume vs. chemical composition of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ sintered samples series.

On the basis of X-ray investigations, it was found that the obtained solid solutions of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ crystallize in rhombohedral structures with the space group R-3c, but the presence of a trace $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ orthorhombic phase cannot be excluded.

Among the main factors determining the potential for using modified $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ based powders for manufacturing gastight sintered samples were the morphology and particle sizes of these powders. The measured surface area of BCY or BZY unground powder ranged from 1.59 to 1.89 m^2/g (BCY) or from 2.1 to 3.6 m^2/g (BZY). An increase in the surface area was observed up to 7 to 8 m^2/g for BCY powders ground in a rotary-vibratory mill. A greater increase was observed for the BZY series, amounting to 12 to 14.1 m^2/g .

Typical microphotographs of BCY and C5BCY synthesised powders are presented in Fig. 4.

All monophasic $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ -series powders were characterized by rather isometric particles with dimensions ranging from 50 to 220 nm although some forms of agglomerates were observed. In the case of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ -series powders, the particles ranged from 40 to 180 nm. No considerable impact of calcium content in the BZY

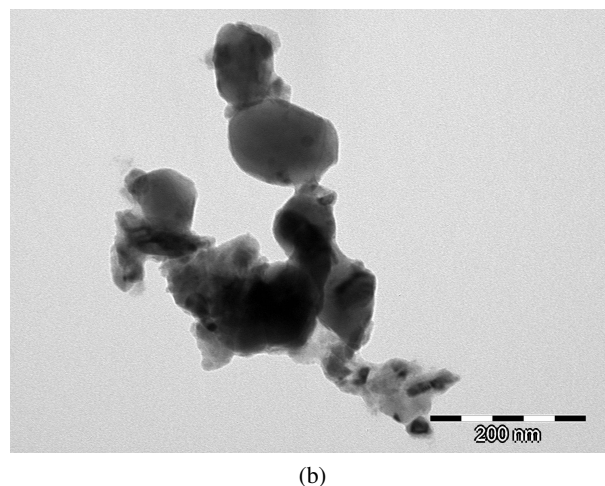
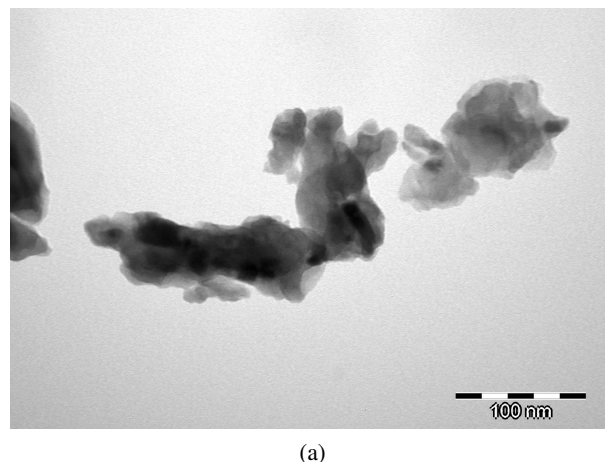


Fig. 4. Representative TEM microscopy images recorded for: $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$ (a) and $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ (b) powders.

or BCY-series solid solution on the morphology and partial size distribution of the particles was observed.

Fig. 5 shows the densification behaviour of compacted $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Zr}, \text{Ce}$ samples under non-isothermal conditions. The samples were heated using a constant rate of 5° per min within a 25 to 1300 °C temperature range.

Detailed analysis of variations in linear dimensions (ΔL) vs. temperature clearly indicated that the partial substitution of calcium with barium in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ caused an improvement in sinterability in both cases in comparison to the starting compositions.

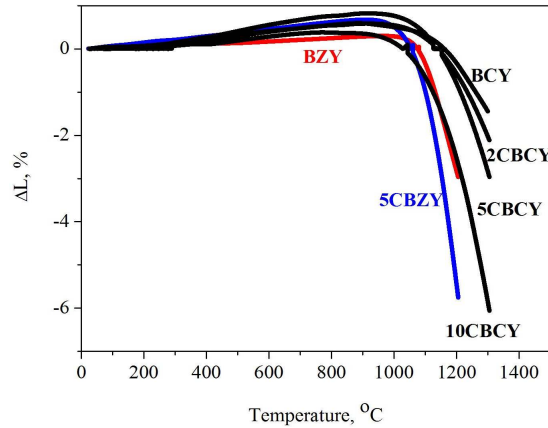
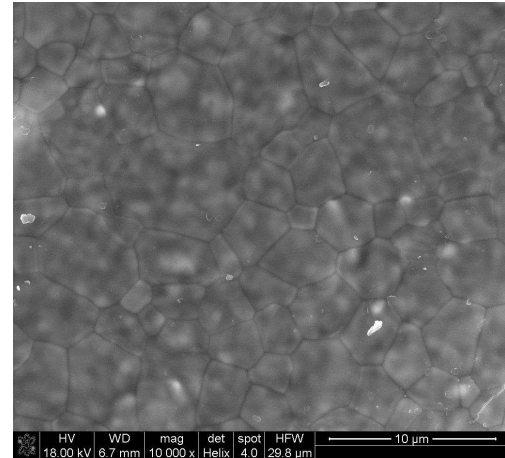


Fig. 5. Dilatometric curves recorded for $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$ pellets during non-isothermal conditions between 25 and 1300 °C.

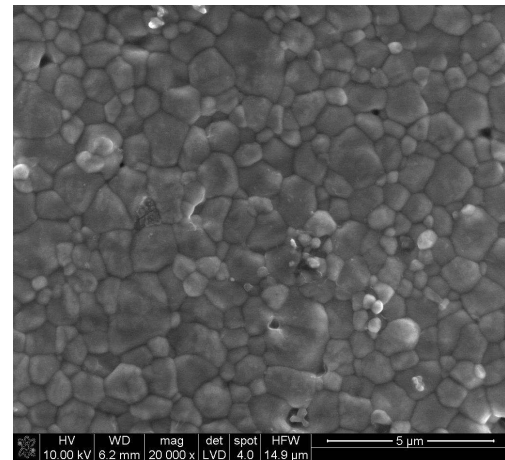
All the samples of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$, after sintering in air at 1500 °C for 2 h, attained more than 96 % of relative density. However, the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ pellets achieved a relative density above 96 % at a higher temperature (1600 °C for 2 h). Both series of sintered samples, $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, were characterized by a uniformly sintered microstructure and a small degree of closed porosity. Fig. 6 shows the microstructure of $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ and $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ sintered samples.

The largest grain sizes were observed for BCY (3 to 7 μm) and BZY (4 to 8 μm) sintered samples. The partial substitution of barium with calcium in the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$ $\text{M} = \text{Ce}, \text{Zr}$ solid solutions appeared to lead to a reduction in grain sizes. Further investigations on the analysis of chemical composition of the grain boundaries using TEM microscopy will be performed, which will be helpful in determining the impact of microstructure on the ionic conductivity of such prepared materials.

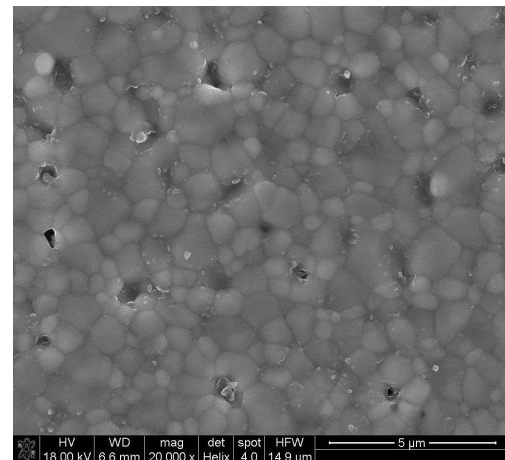
Mechanical properties are also important for $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ or $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ -based materials designed as ceramic proton conducting membranes for solid oxide fuel cells. Determined values of hardness HV or fracture toughness K_{Ic} are listed in Table 1.



(a)



(b)



(c)

Fig. 6. SEM microphotographs of the microstructure of sintered samples: (a) $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$, (b) $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$, and (c) $\text{Ba}_{0.95}\text{Ca}_{0.1}(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$.

Table 1. Hardness HV and fracture toughness K_{IC} of selected $(Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O_3$, $M = Zr, Ce$.

Material	HV, GPa	K_{IC} MPa·m ^{0.5}
$BaZr_{0.9}Y_{0.1}O_3$	8.11±0.21	2.35±0.23
$Ba_{0.95}Ca_{0.05}Zr_{0.9}Y_{0.1}O_3$	8.36±0.19	2.42±0.17
$Ba_{0.9}Ca_{0.1}Zr_{0.9}Y_{0.1}O_3$	8.16±0.27	2.28±0.18
$BaCe_{0.9}Y_{0.1}O_3$	7.01±0.18	1.66±0.24
$Ba_{0.95}Ca_{0.05}Ce_{0.9}Y_{0.1}O_3$	7.19±0.11	1.74±0.22
$Ba_{0.9}Ca_{0.1}Ce_{0.9}Y_{0.1}O_3$	7.24±0.20	1.88±0.28

These values indicate that all the investigated $(Ba_{1-x}Ca_x)(Ce_{0.9}Y_{0.1})O_3$ -based samples had relatively slightly lower values of hardness and toughness compared to ceria-based electrolytes. Observations of crack propagation for ceria-based samples and $(Ba_{1-x}Ca_x)(Ce_{0.9}Y_{0.1})O_3$ -based samples indicated that cracks developed along the grain boundaries and across the grains in the investigated materials. A similar analysis was performed for $(Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O_3$ -based samples, which exhibited mechanical properties (comparable to cubic-zirconia-based solid solutions) superior to those of $(Ba_{1-x}Ca_x)(Ce_{0.9}Y_{0.1})O_3$ -based samples.

One of the crucial parameters used to decide upon the possibility of utilizing ceramic proton conductors in electrochemical devices is ionic conductivity. The ABO_3 -based perovskite materials generally exhibit mixed oxide-electronic conductivity at high oxygen partial pressure, but almost pure hydrogen conductivity in the region of lower oxygen partial pressure in hydrogen-rich atmospheres [28, 29].

Fig. 7 shows the relationship between total electrical conductivity σ vs. temperature measured for $(Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O_3$, $M = Ce, Zr$ in dry air.

As can be seen, the partial substitution of calcium for barium in $(Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O_3$, $M = Ce, Zr$, where x is no higher than 0.05, caused an increase in total electrical conductivity compared to the initial $BaZr_{0.9}Y_{0.1}O_3$ or $BaCe_{0.9}Y_{0.1}O_3$ samples. There are some possible reasons for the variations of ionic conductivity vs. chemical composition in the $(Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O_3$ sintered samples. From

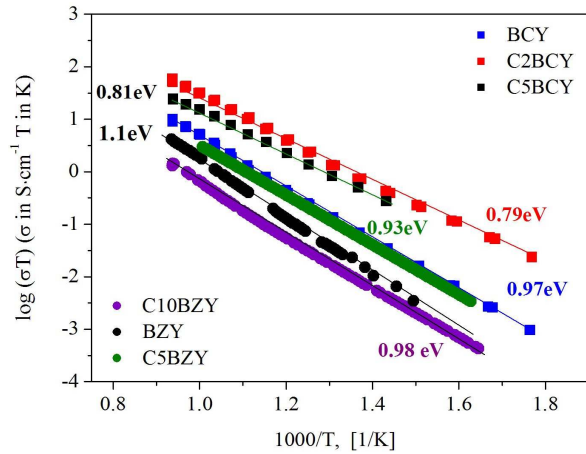


Fig. 7. The temperature dependence of total electrical conductivity of $(Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O_3$ $M = Ce, Zr$ sintered samples measured in dry air.

the crystallographic point of view the analysis of variation in oxide conductivity and, indirectly, proton conductivity of ABO_3 -based compounds is complicated. Some authors [30, 31] have indicated that the main structural parameters, such as tolerance factor, specific free volume and oxygen deficiency are the main factors which have a considerable impact on the variation of electrical conductivity in ABO_3 -based compounds.

The partial substitution of cation Ca^{2+} , which is smaller than Ba^{2+} , into $(Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O_3$ led to an increase in specific free volume from 0.482 to 0.4896. According to the analysis performed by H. Hayashi [32] the ABO_3 -based compounds, which generally increase the specific free volume, lead to an improvement in oxide-ionic conduction. The oxide ionic conductivity in ABO_3 -perovskite based materials is also strictly connected with tolerance factor t , which was proposed by Goldschmidt [33]. The perovskite cubic structure is stable for $0.95 < t < 1.05$. The incorporation of calcium from $x = 0.04$ to 0.1 into $(Ca_{1-x}Ba_x)(Zr_{0.9}Y_{0.1})O_3$ solid solution leads to small variations in tolerance factor t from 0.987 to 0.978. This result indicates that the introduction of calcium into $(Ca_{1-x}Ba_x)(Zr_{0.9}Y_{0.1})O_3$ ($0.02 < x < 0.1$) solid solutions does not lead to considerable variations in cubic structure. It was reported that the highest oxide ionic conductivity

can be observed in ABO_3 -based electrolytes, for $0.96 < t < 0.97$ [32].

Based upon the previously described SEM microstructural observations (Fig. 6), it was found that a decrease in grain sizes was observed for $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$ samples. In this situation the possible precipitation of free CaO in the grain boundary region of $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, especially for $x > 0.05$ and its impact on the variation of electric conductivity should also be considered. The problem involving a high electrical resistance in the grain boundary region of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ samples has still not been resolved [34].

The possible presence of precipitation of CaO in the grain boundary region of $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ based samples may lead to an additional increase in grain boundary electric resistance and consequently, a decrease in oxide-ionic conductivity of $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$, where x is higher than 0.05.

The incorporation of a higher amount of $x > 0.05 \text{ Ca}^{2+}$ into the $(\text{Ca}_{1-x}\text{Ba}_x)(\text{Ce}_{0.9}\text{Y}_{0.1})\text{O}_3$ solid solution has also led to a decrease in electrical conductivity, probably due to an increase in the distortion of the crystal structure to restrain the motion of oxide ions. In the case of ABO_3 -based compounds with a lower symmetry, the structural variations have a great impact on the variations of ionic conductivity. Yajima, et al. [35] also found that the incorporation of calcium into $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Nd}_{0.1})\text{O}_3$ where $x > 0.05$ caused a decrease in the oxide ionic conductivity due to an increase in the distortion of the crystal structure. On the other hand it was also found that the introduction of calcium into $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ce}_{0.9}\text{Nd}_{0.1})\text{O}_3$ also slightly improved its protonic conductivity in an H_2 -rich gas atmosphere.

The electrical conductivity measurements were also performed in wet 5 % H_2 in Ar for calcium-doped barium cerate or calcium-doped barium zirconate sintered samples.

The total electrical conductivity values are depicted in Table 2 along with the activation energy for the process in wet 5 % H_2 in Ar.

The data recorded for BCY and BZY, which are known protonic electrolytes, are in good agreement with the data in the existing literature [36, 37]. The values presented in Table 2 clearly indicate that the partial substitution of calcium for barium in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$ -based solid solutions caused an increase in electrical conductivity compared to the initial compositions $\text{Ba}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$. These results indicate that structural modification of site A in perovskite ABO_3 -based conductors could also be an option for the improvement of the protonic conductivity of such materials. In the previous paper [20, 21] it was mentioned that the increase in electrical conductivity in modified barium zirconate samples $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ or $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ where $0 < x < 0.1$, was strictly connected with changes in the $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ structure. It was stated that the presence of protons in the vicinity of the oxygen shared by ZrO_6 octahedra, resulted in a strong but temporary interaction between protons and all surrounding oxygen. Such a structure is stable and not favourable for proton migration unless trivalent cations are substituted for zirconium. In such a case, local distortion of the crystal lattice and the formation of local O–H bonds are possible. This relatively strong bond can be easily moved from one oxygen to another via a ‘hopping’ mechanism. The effect of the dynamically changing O–H bonds resulted in a local ‘softening’ of the crystal structure responsible for the high mobility of protons.

Table 2. The total electrical conductivity σ (S/cm) and activation energy calculated in the temperature range of 300 to 700 °C. Data of measurements in wet 5 % H_2 in Ar.

Material	σ [S/cm] at 600 °C	E_a [eV]
$\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$	8.29×10^{-4}	0.78
$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$	1.24×10^{-3}	0.74
$\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$	9.05×10^{-4}	0.80
$\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$	1.16×10^{-3}	0.64
$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$	8.21×10^{-3}	0.53
$\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$	4.11×10^{-3}	0.57

The oxygen reduction process at the cathode remains the main limiting factor associated with solid oxide fuel cells, thus a detailed understanding of the reaction mechanism is necessary in order to improve the performance of these devices. The problem is of key importance for SOFCs, where apart from the ohmic drop, the slow kinetics of the electrode process is a source of significant energy loss [38, 39]. In many studies concerning investigations of the kinetics of an oxygen reduction process, porous electrode materials were usually applied. To avoid problems associated with difficult-to-determine structure and geometry, some researchers have applied the concept of utilization of microelectrodes [21–24, 40, 41].

In the authors' previous paper [24], the process of oxygen reduction at the interface of metallic microelectrodes (Pt, Au or Ag) and solid oxide electrolyte made from ($\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-8}\text{YSZ}$) or ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9-20}$ GDC) was investigated at 700 °C under various oxygen partial pressures. In those experimental conditions, an increase in the absolute current was observed when electrodes made of Pt, Ag or Au were polarized with negative overpotentials down to -0.3 V. The application of metallic microelectrodes enabled conducting of simplified investigations. The platinum did not react with the surface of the selected oxide electrolytes in the operating conditions. Such unusual behaviour was explained by an increase in the three-phase boundary length due to the deposition and subsequent reduction of metal oxides in the vicinity of the Pt and Ag electrodes.

As opposed to oxide ion conductors based on zirconia or ceria solid solutions, such as 8YSZ, 20GDC, perovskite-based proton conductors at high oxygen partial pressures (conditions existing on the cathode side of a fuel cell) exhibited both ionic as well as hole conductivity. The actual magnitude of electronic partial conductivity depends on oxygen as well as water ($p\text{O}_2$, $p\text{H}_2\text{O}$) partial pressure. The electronic transfer number for $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ can reach 0.2 or even higher value in a dry atmosphere [42, 43].

In this study, the typical dependencies of the currents flowing through the electrode at negative

step polarization ($\Delta E = -0.05$ to -0.5 V) recorded for the 10CBCY sample at 700 °C in air are depicted in Fig. 8.

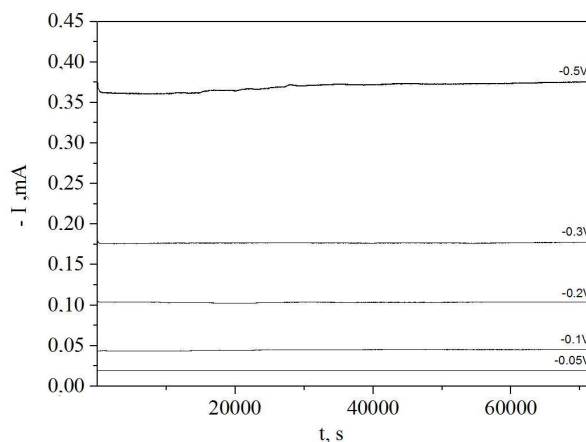


Fig. 8. The family of I-t curves recorded at 700 °C at overpotential (ΔE -0.05 to -0.5 V). The $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ electrolyte was used in this measurement.

Generally, within the overpotential range of -0.05 to -0.5 V, the current had a tendency to increase monotonically over time. Similar results were obtained for classical oxide electrolytes such as 8YSZ and 20GDC in the same conditions. The resulting chronoamperometric curves recorded at 700 °C in air under a load of -0.5 V were compared; on this basis, the relative percentage of current increase during long-term polarization was calculated. Thus, the current results were averaged for the first 20 minutes of measurement, as well as for 20 minutes following 10 hours of the measurement. The estimated values were used to calculate the percentage increase in current after 10 hours of polarization compared to the initial current during long-term polarization. The calculated current increase after prolonged polarization ΔI was 33.6 % for 20GDC, 25.4 % for 8YSZ and 21.68 % for BZY. It is clear from the presented data that the increase in current ranges from 21 to 33 %. In comparison to a 20GDC oxide electrolyte, a 8YSZ on BZY electrolyte exhibits a lower increase than other materials.

The impact of humidity as well as oxygen content in a gas atmosphere on the kinetics

of the oxygen reduction process was also investigated. Current (I)-time (t) (Fig. 9) curves under a load (ΔE) = -0.5 V were recorded for BZY electrolyte at 700°C in dry and wet argon, air and oxygen.

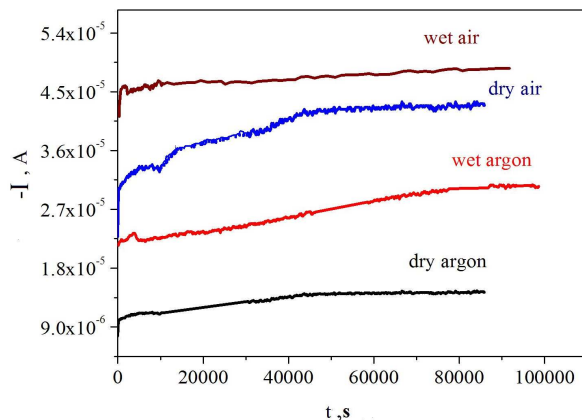


Fig. 9. The family of I-t curves recorded at 700°C under $\Delta E = -0.5$ V in different gas atmospheres. The $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ electrolyte was used in this investigation.

The current values increased along with an increase in oxygen concentration in gas atmospheres. Generally, higher current values were observed in wet rather than dry gas atmospheres.

In Fig. 10 the changes in impedance spectra measured at 700°C before and after polarization of $\Delta E = -0.5$ V for a Pt|BZY system in a wet Ar are presented.

For the Nyquist-plots in the high-frequency region, the decrease in resistance value after polarization to the value before polarization $\Delta E = 0$ is observed. This part of the impedance spectra corresponds to ohmic resistance directly connected with electrolyte resistance. The R_s value before polarization ($R_s = 48.7$ k Ω , 31.7 kHz) is reduced to $R_s = 40$ k Ω after polarization. This result is in good agreement with chronoamperometric measurements in which an increase in current in such conditions was observed. The main reason for such behaviour was the expansion of the reaction zone during polarization.

In an attempt to explain the unusual increase in the absolute value of electric current that occurred

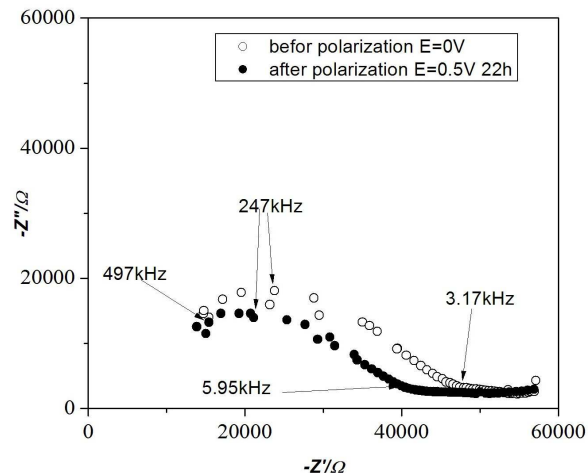


Fig. 10. The Nyquist plots for the Pt|BZY system recorded before and after polarization $\Delta E = -0.5$ V. The measurements were performed at 700°C in a wet argon gas atmosphere.

over time with Pt-electrode polarization, the electrode surface area accessible to the electrolyte was inspected using a scanning electron microscope (SEM). The microscopic observation not only encompassed the electrolyte surface in a direct contact with the electrode, but was extended to include the area around the electrode. The electrolyte surfaces of BZY, BCY were investigated. The test samples were first subjected to long-term polarization (<20 hours) at -0.5 V, sustained with a concurrent sudden decrease in temperature.

The test concerning the above-mentioned electrolytes was carried out in an air atmosphere. As can be seen from the photographic evidence (Fig. 11), Pt deposits formed on the electrode surface which was in a direct contact with the electrolytes.

Based on the analysis of the test results, it can be surmised that the electrode is a source of migrating metal that accumulates along the electrode surface in the form of dendrites. The increase in the absolute value of electric current that occurs with negative electrode polarization can be attributed to the enlargement of the electrode surface resulting from the accumulation of metal.

Preliminary observation of dendrite structures along the Pt-electrode surface suggests

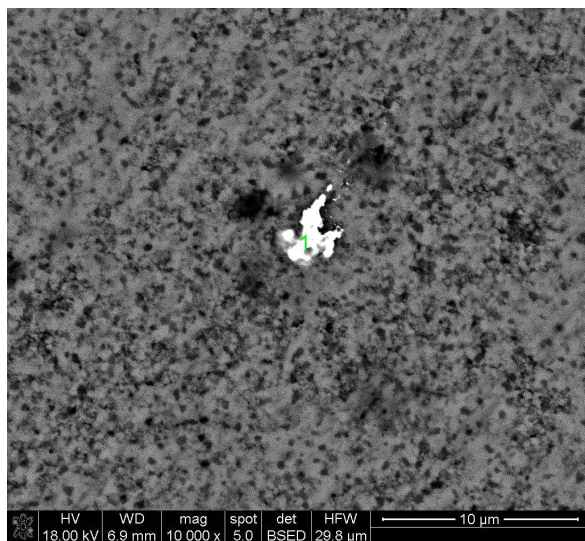


Fig. 11. SEM images of Pt deposit on the surface of the BZY electrolyte recorded after polarization experiments.

the appearance common to both test samples 8YSZ and 20GDC [24].

In the case of proton-conducting electrolytes (BZY and C5BZY), however, the area of the deposit is considerably smaller than that observed in oxygen electrolytes. Furthermore, the measurements taken in gas atmospheres of lower partial pressure (e.g. the argon atmosphere) showed a much smaller area of Pt dendrites on the surface of the BZY electrolyte.

BZY, C5BZY, BCY and C5BCY were tested as protonic conducting materials in solid oxide fuel cells. The first tests of the potential utilization of the modified barium cerate as well as that of barium zirconate samples as proton-conducting membranes in an IT-SOFC consisted of measurements of open circuit voltage (OCV) vs. temperature. Fig. 12 depicts the temperature dependence of the OCV of the BCY and 5CBCY samples. The values recorded for both samples were similar: close to 1. A small increase in OCV values was observed vs. the rising temperatures of the IT-SOFC operation.

Fig. 13 depicts the family of voltage (U)-current density (I) curves recorded for an SOFC with BZY and C5BZY samples as electrolytes at a temperature of 850 °C. Both

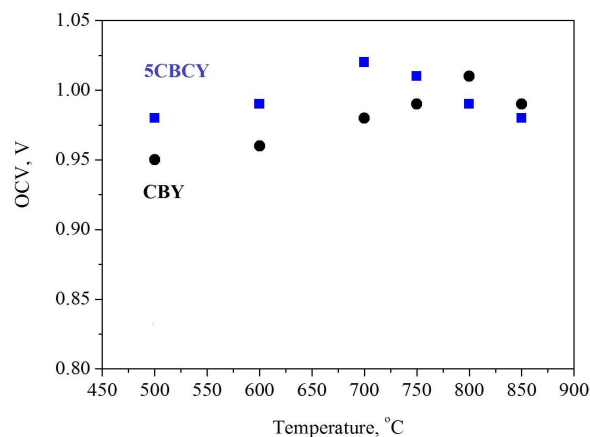


Fig. 12. The temperature dependence of OCV on the cells: $O_2|Pt|BCY$ and $5CBCY|Pt|H_2$ recorded between 500 to 850 °C.

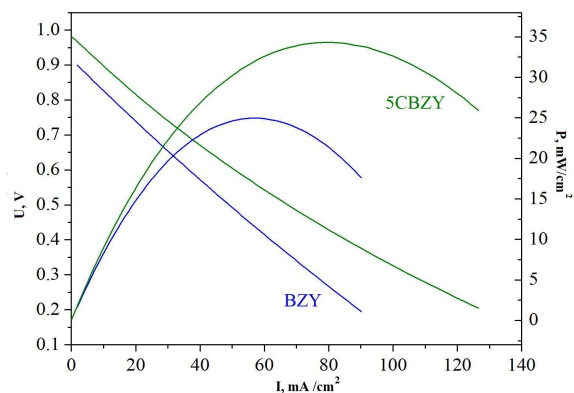


Fig. 13. The family curves U-I and P-I recorded for the cell: $H_2|Pt|BZY$ and $5CBZY|Pt|O_2$ at 850 °C.

the power (P) density and current (I) density of an SOFC with a $Ba_{0.95}Ca_{0.05}Zr_{0.9}Y_{0.1}O_3$ (C5BZY) electrolyte attained higher values than those for the same SOFC with a $BaZr_{0.9}Y_{0.1}O_3$ (BZY) ceramic electrolyte. This could be attributed to a decrease in the resistance of the cell. As can be seen, the utilization of a solid oxide electrolyte with higher ionic conductivity led to a reduction in ohmic losses during IT-SOFC performance.

4. Conclusions

The application of the sol-gel method with EDTA as a complexing agent enabled

the acquisition of monophase $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$ $\text{M} = \text{Ce}, \text{Zr}$ powders. $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$ or $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ modified calcium pellets, sintered at temperatures of 1500 to 1600 °C, exhibited more than 97 % of theoretical density. The partial substitution of barium with calcium in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$ $\text{M} = \text{Ce}, \text{Zr}$ led to an increase in electrical conductivity in air and gas atmospheres involving 2 to 5 % H_2 in Ar. The highest electrical conductivity was found for the composition $(\text{Ba}_{1-x}\text{Ca}_x)(\text{M}_{0.9}\text{Y}_{0.1})\text{O}_3$, $\text{M} = \text{Ce}, \text{Zr}$, where x ranged between 0.02 and 0.05. The determined values of fracture toughness K_{Ic} for the prepared barium cerate and barium zirconate samples indicated that their mechanical properties were similar to those of oxide electrolytes applied or considered for utilization in solid oxide fuel cells. The open circuit voltage (OCV) measurements performed for cell (1), were recorded within a temperature range of 700 to 850 °C, and reached values between 0.95 and 1.04 V. This indicated that the elaborated modified $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$ seem to be suitable for application in SOFC constructions. Preliminary comparative tests of a hydrogen-oxygen fuel cell with $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ or $\text{BaCa}_{0.05}\text{Zr}_{0.9}\text{Y}_{0.1}\text{O}_3$ showed that the application of modified calcium barium zirconate material led to an increase in fuel cell power output due to lower ohmic resistance. The increase in absolute values of current under negative potential $\Delta E = -0.2$ to -0.5 V was observed for microelectrode Pt in barium cerate- or barium zirconate-based electrolytes.

Acknowledgements

The present work was carried out under the Contract No. 11.11.210.217 (AGH University of Science and Technology, Faculty of Fuels and Energy, Cracow, Poland).

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Received 2015-07-07

Accepted 2015-12-11