

Ceramic electrolytes based on $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ solid solution

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Abstract The aim of this work was to study the electrical and electrochemical properties of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.9}\text{Y}_{0.1})\text{O}_3$ solid solutions. The powders of different calcium content ($x=0, 0.05, 0.1, \text{ and } 1$) were prepared by a thermal decomposition of organo-metallic precursors containing ethylenediaminetetraacetate acid. X-ray diffraction analysis showed that a small substitution of calcium for barium caused formation of cubic solid solutions with the decreasing cell parameters. Electrical conductivity measurements were performed by the d.c. four-probe method in controlled gas atmospheres containing Ar, air, H_2 , and/or H_2O at temperature from 300 to 800 °C. It was found that the conductivity depended on a chemical composition of the samples and the atmosphere. Overall, the electrical conductivity was higher in wet atmospheres that contained oxygen that was in accordance with the model of a proton transport in perovskite structure which assumed the presence of the oxygen vacancies. The solid solution containing 5 mol% of calcium

showed the highest conductivity and the lowest activation energy of conductivity regardless of the atmospheres; this can be attributed to the local changes in the cubic perovskite structure. Test results for $\text{CaZr}_{0.9}\text{Y}_{0.1}\text{O}_3$ used as an electrolyte in solid oxide galvanic cells involving CaCr_2O_4 as a reference electrode are also reported.

Keywords Calcium zirconate · Barium zirconate · Ionic conductor · Protonic conductivity

Introduction

In the early 1980s, Iwahara et al. found several perovskite-type oxides exhibiting a high proton conductivity at elevated temperatures [1]. Among these alkaline zirconates (AZrO_3 , $\text{A}=\text{Ba}, \text{Ca}, \text{Sr}$) doped with some trivalent cations as: Y, La, Gd, In is an interesting group of materials called “high temperature protonic conductors” [2, 3]. Yttrium-doped barium zirconate, whose formula is $\text{BaZr}_{1-x}\text{Y}_x\text{O}_3$, $0 < x < 0.2$, was developed for its high protonic conductivity in hydrogen-containing atmosphere; the chemical stability and good mechanical properties have attracted considerable attention due to its possible application in electrochemical reactors, steam electrolyzers, hydrogen sensors, or pumps [4–6]. Doped CaZrO_3 also exhibited a sufficient level of the protonic conductivity where, combined with their high chemical stability, thermal shock resistance and good mechanical properties allowed to utilize these materials as components of electrochemical probes to determine a hydrogen activity in the molten metals as aluminum or copper [7–9]. On the other hand, it was revealed that CaZrO_3 with calcia or zirconia excess practically showed a pure oxygen ionic conduction even at a low oxygen partial pressure and could be used as a probe to control the activity of

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dissolved oxygen in molten metals [10–12]. The application BaZrO₃-based materials as proton-conducting electrolytes for the solid oxide fuel cells (SOFC) was also taken into consideration [13, 14]. In general, the BaZr_{1-x}Y_xO₃-based materials exhibited a lower electrical conductivity compared to BaCe_{1-x}Y_xO₃, where, 0 < x < 0.2. However, the chemical and mechanical stability of ceramic electrolytes involving Y₂O₃-doped BaCeO₃ is limited in gas atmospheres containing CO₂, SO₂, H₂S, and moisture. They could decompose into BaCO₃, BaSO₄, BaS, or Ba(OH)₂ depending on environment and temperature [15–18]. Several studies suggest that a partial substitution of Zr⁴⁺ for Ce⁴⁺ can improve mechanical and chemical stability of Y₂O₃-doped BaCeO₃. In this way, the obtained solid solutions involving Ba(Zr_{1-x}Ce_x)Y_{0.2}O₃, x = 0.1–0.5 exhibited a better ionic conductivity than that of BaZr_{1-x}Y_xO₃ and seemed to have more adequate electrolytes for the application in solid oxide fuel cells [19–21].

Another way of improving an ionic conductivity is also a structural modification of the ionic conductor. A model of proton migration in the perovskite structure assumed the existing two equivalent sites for proton between adjacent oxygens in the B sites, one of which can be occupied by the proton. It reveals the hopping mechanism of proton changing O—H bond, one after another, where distortion of the two neighboring BO₆ octahedrons is necessary to enable this process. The effect of the dynamically changed O—H bonds led to a local “softening” of the crystal structure that was responsible for the high mobility of protons. Proton transport properties of the structure are strictly connected to the differences between radii of the host and dopant ions and their electric charges and the amount of respective dopants [22–24]. There are many studies on the proton conductivity of barium zirconate solid solutions in which B site is modified, whereas studies on the modification of A site are still limited.

The aim of the present paper is to investigate the electrical and electrochemical properties of the (Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O₃ solid solutions.

Experimental

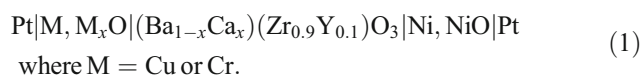
All powders were prepared by a polymer complex method with the usage of versenate acid (ethylenediaminetetraacetate acid—EDTA). The starting aqueous solutions were prepared by dissolving appropriate amounts of barium, calcium, zirconyl, and yttrium nitrates (Merck, p.a.) in distilled water. However, as versenate acid's solubility in water is very poor, it was dissolved in a concentrate solution of ammonia. The ammonium versenate solution was added dropwise into a vigorously agitated solution of the respective cation nitrates. During this operation, some increase of turbidity was

observed due to hydrolysis of the versenate acid. By fixing pH values at about 8 with concentrated ammonia, it led to the dissipation of this turbidity. The amount (in moles) of introduced ammonium versenate exceeded by 10% of the total amount of cation moles. The solutions, after being stored for 24 h at room temperature, were dried at 250 °C. The solutions changed their tint while drying, from colorless through yellow to dark-brown, and at this stage dense, viscous liquid was obtained (resin). By further drying it, this led to a disintegration of this resin, releasing significant amounts of gases and finally setting into a very porous and black solid body. The total drying time extended 12 h. The prepared precursors were initially calcined at 600 °C for 2 h in order to completely remove carbon and/or the rest of organic phases, and then at 1,100 °C for 2 h. The powders were ground in rotary-vibratory mill in dry isopropyl alcohol for 2 h using zirconia grinding media. Isostatic pressing at 250 MPa was used to compact the powders which were then sintered at 1,600 °C for 2 h. The procedure described above allowed us to prepare samples with chemical composition as follows: Ca(Y_{0.1}Zr_{0.9})O₃, (Ca_{0.05}Ba_{0.95})(Y_{0.1}Zr_{0.9})O₃, (Ca_{0.10}Ba_{0.90})(Y_{0.1}Zr_{0.9})O₃, and Ba(Y_{0.1}Zr_{0.9})O₃ which are mentioned in the further text as CYZ, C05BYZ, C10BYZ, and BYZ, respectively.

The phase composition of all powders and sintered bodies was identified by X-ray diffraction analysis based on ICDD data base. XRD measurements were done using Panalytical X'Pert Pro system with monochromatic Cu K_α radiation. Lattice parameters of the identified phases were determined using the Rietveld refinement method. The Archimedeian method was used to determine the relative density of the studied samples.

The total electrical conductivity was measured by the d.c. four-probe method in the temperature range 300–800 °C in different gas atmospheres as: oxygen, synthetic air, Ar, and Ar/H₂ (2 to 5 vol.%) mixtures. The oxygen partial pressure (pO₂) in these mixtures was ranging from 10⁻¹⁰ to 1 atm. Prior to electrical measurements, Pt electrodes (Heraeus) were applied at respective places of the rectangular samples. The thermoelectric power was also measured at 700–800 °C in the pO₂ ranging from 10⁻⁵ to 1 atm. The procedure was similar to the one previously described in the paper [25].

The oxygen ion transference numbers of all samples were estimated from electromotive force (emf) measurements of solid oxide galvanic cell:



The two-phase mixtures (M, M_xO) and (Ni, NiO) with the known equilibrium oxygen partial pressures were used to provide fixed oxygen potentials at the electrodes. The

procedure was practically the same as of that presented in the work of Kiukola and Wagner concerning solid oxide galvanic cells involving the cubic phase of the CaO–ZrO₂ solid solution [26]. The ionic transference numbers (*t*_{ion}) of the samples were determined basing on the emf values (*E*_m) measured for the cell (1) and on the emf values (*E*_t) obtained for the same cell with a pure oxygen ion conductor, Ca_{0.13}Zr_{0.87}O₂ (13CSZ), as an electrolyte:

$$t_{ion} = E_m / E_t \tag{2}$$

The CaZr_{0.9}Y_{0.1}O₃ sample with the known transference number was tested in solid galvanic cell:



to investigate an application of CZY electrolyte with a reference electrode containing CaCr₂O₄ at temperatures 800–1,200 °C. It was earlier found that MCr₂O₄ (M=Ca, Mg) or Y₂Cr₂O₆ materials, due to its low equilibrium of pO₂ close to activity of oxygen dissolved in steel, seemed to be promising electrode materials for construction of electrochemical probes operating on-line in control metal processing [27].

Results and discussion

Decomposition of the organo-metallic precursors followed by milling process leads to preparation of good sinterable powders. Generally, all samples sintered at 1,600 °C for 4 h achieved a relative density exceeding 96% of theoretical density. X-ray diffraction analysis reveals that all sintered samples are composed of one phase only. The structure of CYZ sample was identified as an orthorhombic CaZrO₃ perovskite, whereas the rest of them as a cubic BaZrO₃ one. The XRD measurements show also that substitution of calcium for barium caused a decrease in the cubic perovskite cell volume of the (Ba_{1-x}Ca_x)(Zr_{0.9}Y_{0.1})O₃ samples. The linear compositional dependence of the lattice parameters complied with the Vegard’s rule confirms the formation of solid solutions.

Figure 1 shows the dependence of the total electrical conductivity on oxygen partial pressure that was measured at 700 °C for the CZY and C05BZY samples. Two different pO₂ regions can be distinguished that corresponded to a different conduction mechanism. At a lower oxygen partial pressure, the total electrical conductivity is stable whereas at the oxygen partial pressure above 10⁻⁵ atm, the considerable increase of the total electrical conductivity is observed for both samples. This effect can be attributed to formation of electronic holes and a presence of electronic conductivity. These results are in good agreement with the data present in literature for example: the yttrium-doped barium or strontium zirconates as well as indium-doped

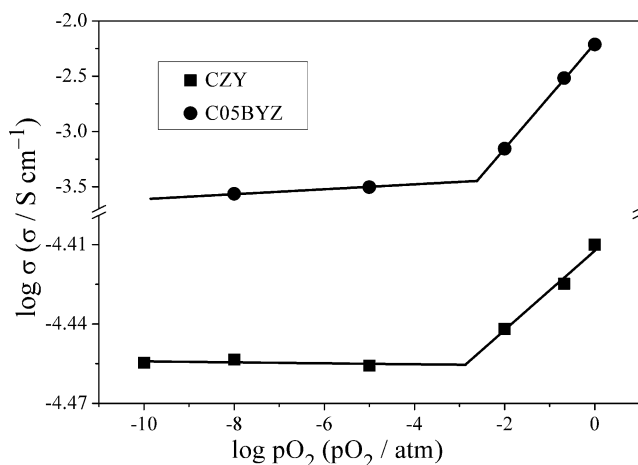
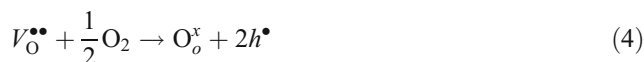


Fig. 1 Dependence of the total electrical conductivity on pO₂ measured for CZY and C05BZY samples at 700 °C

calcium zirconate [28, 29]. In all these materials at respective high oxygen partial pressure, electron holes can be formed via the following reaction:



The measurements of thermoelectric power of the same samples at 700 °C can confirm this statement. Figure 2 shows decrease of positive values of the thermoelectric power, with increase of oxygen partial pressure (from 10⁻⁵ to 1 atm) which corresponds to the dominance of positive electric charge carriers (electron holes or oxygen vacancies). Comparison of the absolute values of the measured thermoelectric power with the literature data [25] suggests that holes are predominate defects in the region of high pO₂.

The oxygen transference numbers were measured using galvanic cell (1) in which the CZY and C05BZY were solid

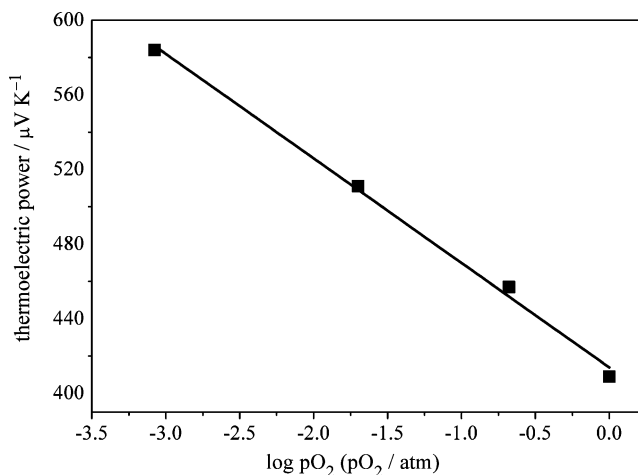


Fig. 2 Thermoelectric power measured at 700 °C as a function of pO₂ for CZY samples

electrolytes as well as Cu, Cu₂O and Ni, NiO mixtures were reversible electrodes [30]. The linear dependences of the measured emf values vs. temperature for both samples are shown in Fig. 3. The emf values measured in the temperature range of 600–1,000 °C are compared with the respective emf values (E_t) measured with the cell (1) containing 13CSZ. The calculated values of the oxygen transference numbers for both samples are about 0.97–0.99, which indicates that the oxygen ion conduction may be predominant at low pO₂ in dry atmospheres.

The temperature dependences of the total electrical conductivity measured in different atmospheres for all samples are linear in Arrhenius coordinates. Figure 4 shows these dependences measured for the sample (Ca_{0.05}Ba_{0.95})(Zr_{0.9}Y_{0.1})O₃ in different atmospheres whereas Fig. 5 reveals the ones for the all samples measured in dry air. In general, the solid solutions based on BaZrO₃ exhibited the higher total conductivity than the CaZrO₃ regardless of the atmosphere (Fig. 6). Among these, the solid solution of barium zirconate with 5 mol% of calcium, the C05BYZ sample, showed the highest total conductivity. This effect can be attributed to the local changes in the cubic perovskite structure. It was confirmed that the presence of proton in the vicinity of the oxygen shared by ZrO₆ octahedra results arrived strong, temporary interaction between proton and all surrounding its oxygens. Such structure is stable and not favorable towards proton migration unless the trivalent cations are substituted for the zirconium ones. In such case, a local distortion of the crystal lattice and formation of located O—H bond are possible. This relatively strong bond can be easily moved from one oxygen to another by hopping mechanism. The effect of the dynamically changed O—H bonds led to a local “softening” of the crystal structure responsible for high mobility of protons [22–24]. The compositional changes of the total conductivity measured at 500 °C

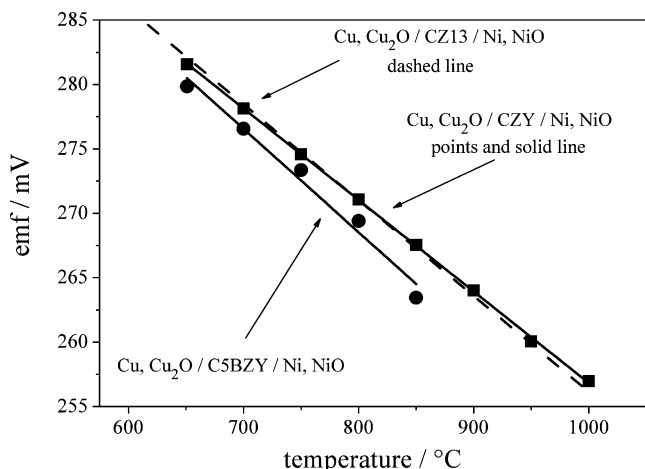


Fig. 3 Electromotive force of the cell (1) with the 13CSZ, CYZ, and C05BYZ samples as electrolytes

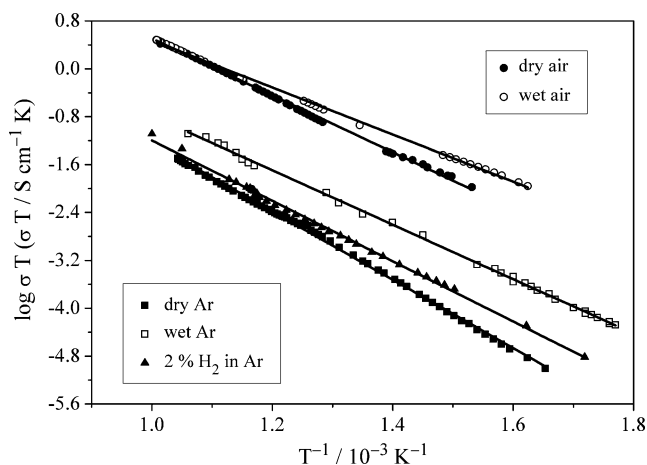


Fig. 4 Arrhenius plots for C05BYZ sample in different atmospheres

(Fig. 6) suggest that a substitution of the smaller cation (Ca) for the bigger one (Ba) in the A site intensifies the structural changes. Such influence is limited—the barium zirconate solid solution with 10 mol% of calcium showed the total conductivity yet worsened than that of the BYZ sample.

It can be also stated that the lowest total conductivities for all samples were measured in dry argon. The presence of 2 vol.% of hydrogen in dry argon increased the total conductivity irrespective of the chemical composition of the samples which confirmed ability of the investigated materials to proton conduction. An increase of the steam partial pressure in wet argon, which also meant an increase of the oxygen partial pressure due to the chemical reaction of water decomposition, causes an increase in total conductivity. This effect can be related to the model of proton transport in perovskite structure which assumed presence of the oxygen vacancies having a lower mobility than that of protonic defects [31, 32]. Further increase of the total conductivity measured in atmospheres with the

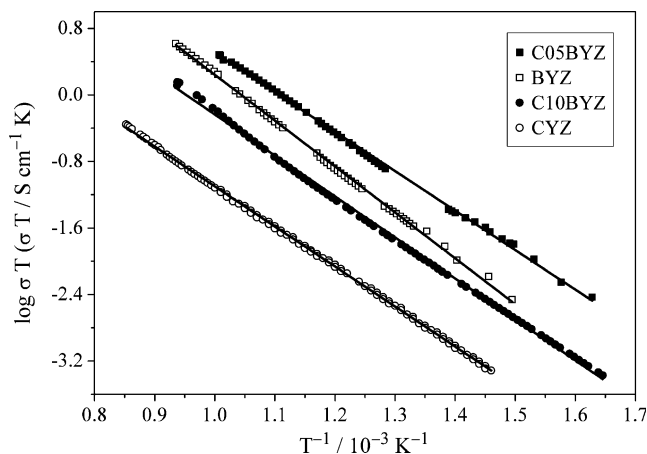


Fig. 5 Arrhenius plots for all samples. Measurements in dry air

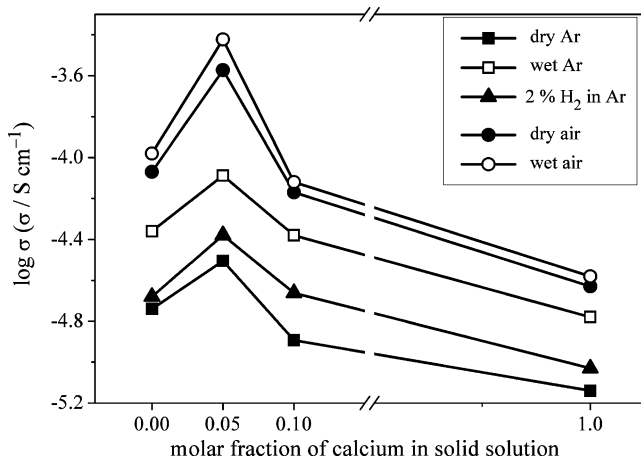


Fig. 6 Compositional dependence of the total conductivity measured at 500 °C in different atmospheres

higher partial pressure of oxygen (dry air) and steam (wet air) corroborates these statements. On the other hand, increase in the oxygen partial pressure causes formation of electron holes as was shown in Eq. (4) which had to increase the total conductivity.

The described changes of the total conductivity result from respective values of activation energies of conductivity, E_a , and pre-exponential factors, σ_0 . Figure 7 presents compositional changes of the E_a determined from the Arrhenius plots. All samples show the highest activation energy of the conductivity in dry argon irrespective of their chemical composition and increase in the steam and/or oxygen partial pressure causes a decrease in E_a values. The solid solutions based on $BaZrO_3$ reveal lower activation energy of conductivity than $CaZrO_3$ while the conductivity is measured in the oxygen-deficient atmospheres—dry and wet argon. At higher oxygen partial pressure (dry and wet air), the activation energy of conductivity of calcium zirconate doped with yttria is also slightly higher than that of barium

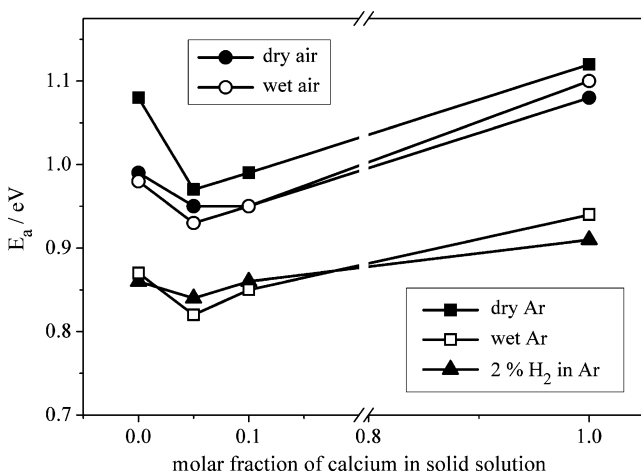


Fig. 7 Compositional dependence of the activation energy of conductivity for all samples

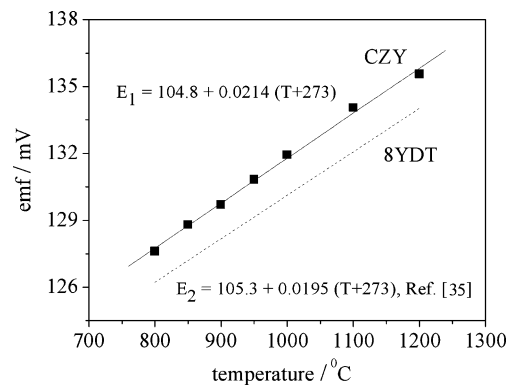


Fig. 8 Temperature dependence of the emf of the cell (3) with CZY and 8YDT as electrolytes

zirconate solid solutions. The values of the activation energy of the total conductivity are correlated with the respective values of the pre-exponential factor—the lower E_a values the lower σ_0 ones. Such effect complies with the Meyer–Neldel compensation rule [33].

The $CaZr_{0.9}Y_{0.1}O_3$ sample was tested in the solid galvanic cell (3) with the reference electrode containing $CaCr_2O_4$ as a potential electrochemical probe for controlling the activity of oxygen dissolved in molten metals [27].

The typical temperature dependence of emf of cell (3) with CZY as an electrolyte is presented in Fig. 8. The measured emf values are compared with the emf values of the same cell containing 8 mol% Y_2O_3 – ThO_2 (8YDT) as an electrolyte [28, 35], which is commonly used in solid oxide galvanic cells to measure oxygen activity at low partial pressure. In each case, the linear increase of the emf values with temperature is observed. The investigations presented in this paper showed that the main advantage of CZY solid oxide electrolyte compared to non-stoichiometric $CaZrO_3$

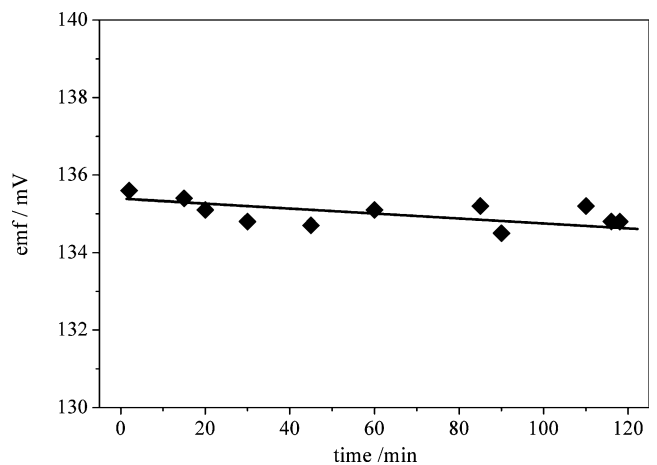


Fig. 9 The time dependence of the emf of the cell (3) containing $CaZr_{0.9}Y_{0.1}O_3$ as an electrolyte measured at 1,200 °C

(51 mol% CaO–CZC) [34, 10–12] was a chemical stability under wet and hydrogen gas-containing atmospheres. Long-lasting heat treatment of CZC-based solid electrolytes in such atmospheres led to the decomposition of non-stoichiometric calcium zirconate with formation of CaO. The presented results show that CYZ appeared to be also suitable for the application as a component of solid galvanic cells designed to measure low oxygen activity in long-term operations.

The time dependence of the emf value measured on the galvanic cell (3) at 1,200 °C is presented in Fig. 9. It was worth noting that the decrease in the emf value during measurement period (120 min) was essentially small; the slope of the correlation line is as low as -0.01 mV. This result also revealed that the CYZ material seemed to be an interesting electrolyte for electrochemical devices designed for on-line control metal processing.

Conclusions

The $(\text{Ca}_x\text{Ba}_{1-x})(\text{Y}_{0.1}\text{Zr}_{0.9})\text{O}_3$ dense samples were successfully prepared by starting from powders synthesized by thermal decomposition of organo-metallic precursors containing EDTA. The results presented in the paper proved that the introduction of 5 mol% of calcium into barium zirconate solid solution led to an improvement of the electrical conductivity in all investigated atmospheres compared to $\text{Ba}(\text{Y}_{0.1}\text{Zr}_{0.9})\text{O}_3$ sample. This material seemed to be a promising solid electrolyte for electrochemical devices operating in an intermediate temperature range (600–700 °C). $\text{Ca}(\text{Y}_{0.1}\text{Zr}_{0.9})\text{O}_3$ solid solution due to its sufficiently high oxide ionic conductivity at low oxygen partial pressure in dry atmospheres could be used as an electrolyte for the probes monitoring oxygen activity dissolved in molten metals.

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