Comparative studies of the electrochemical behaviour of $\text{Me|Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$, $\text{Me|Ce}_{0.8}\text{Gd}_{0.2}\text{O}_1.9$, and $\text{Me|Zr}_{0.84}\text{Y}_{0.16}\text{O}_3$ systems caused by long-term cathode polarisation, where $\text{Me} = \text{Ag}$, Au quasi-point electrodes

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Electrochemical measurements were performed with applied potential of −0.05 to −0.7 V at 700°C. An increase in absolute current was observed in chronoamperometric curves during long-term negative polarisation from −0.3 to −0.7 V for an Ag quasi-point electrode in Ag$|\text{E}$, $\text{E} = \text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$, and Zr$0.84\text{Y}_{0.16}\text{O}_3$ systems. Decreases in ohmic resistance $R_\text{o}$ and polarisation resistance $R_\text{p}$ for Ag$|\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$, Ce$0.8\text{Gd}_{0.2}\text{O}_1.9$, or Zr$0.84\text{Y}_{0.16}\text{O}_3$ systems were determined by means of electrochemical impedance spectroscopy in analogous conditions. Confocal or scanning electron microscopy observation confirmed the migration of silver particles onto ceramic electrolytes under long-term negative polarisation. A silver deposit was found near the site of direct contact of the Ag electrode with the surface of the Ba$0.95\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$ electrolyte. An expansion of the reaction zone in the Ag$|\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$ system is the main reason for the increase in absolute current values. A similar electrochemical response was found in the case of zirconia or ceria-based solid electrolytes with Ag quasi-point electrodes. The effect of the chemical composition and physicochemical properties of ceramic electrolytes and applied negative potential on electrochemical response in Au$|\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$, Au$|\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_1.9$, and Au$|\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_3$ systems was recorded. In the case of Au$|\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$ system, during negative polarisation with an applied potential in the range from −0.05 to −0.3 V, a small increase in absolute current values was observed on the chronoamperometric curves. In the case of Au$|\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3^\ast$ system, decreases in ohmic resistance $R_\text{o}$ and polarisation resistance $R_\text{p}$ were noticed vs applied potential.

Key words: ceramic proton ion conductor, Ba$0.95\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$, point-electrode, intermediate temperature solid oxide electrolyte, oxygen reduction process.

1. INTRODUCTION

The increased demand for efficient and environmentally friendly energy systems and the direct conversion of gaseous fuels into electricity by fuel cells have received tremendous attention during the past decades. A recent classification has distinguished five basic energy systems and the direct conversion of gaseous fuels into electricity by fuel cells have received tremendous attention during the past decades. A recent classification has distinguished five basic energy systems and the direct conversion of gaseous fuels into electricity by fuel cells have received tremendous attention during the past decades. A recent classification has distinguished five basic energy systems and the direct conversion of gaseous fuels into electricity by fuel cells have received tremendous attention during the past decades. 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2. EXPERIMENTAL

2.1 Preparation of solid electrolytes and electrode materials

Ba$_x$Ca$_y$Ce$_{1-x}$Y$_{0.1}$O$_3$ (5CBCY) powder was prepared using a polymer complex method with EDTA. The details of the experimental procedure and physicochemical properties of the resulting 5CBCY samples were described in the cited paper [28]. In this study, 10% mol Gd$_2$O$_3$ in CeO$_2$ (20GDC) and 8% mol Y$_2$O$_3$ in ZrO$_2$ (8YSZ) were also used as reference electrolytes in electrochemical studies. The 20GDC, 8YSZ powders were supplied by Fuel Cell Materials, USA. Pellets of 5CBCY, 20GDC, 8YSZ were isostatically pressed at 250 MPa, then sintered at 1500°C for 2 h in air. The applied sample preparation conditions enabled the acquisition of gastight disc samples from the electrolytic materials, with a relative density above 95 wt %. The disc-shaped (diameter 12 mm, thickness 2 mm) samples obtained from all solid electrolytes were polished to obtain shiny, mirror-like surfaces. Spherical Au and Ag electrodes, approximately 0.5 mm in diameter, were made by melting wires of 4N purity.

2.2 Experimental procedure and method applied in the electrochemical investigations

This study of the kinetics of oxygen reduction at the cathode of a IT-SOFC was carried out using the simplest possible system, a half-cell: O$_2$|Au/CE, O$_2$|Ag/CE, O$_2$|electrolyte: 5CBCY, 20GDC, 8YSZ or 3YSZ. All measurements were performed in dry air at 700°C. In the case of solid oxide fuel cells involving a ceramic proton-conducting membrane, water was secreted as a by-product on the cathode side. Compared to a classic SOFC with an oxide ion-conducting membrane, this may have additionally complicated the cathodic oxygen reduction reaction. In the first stage of this study, all electrochemical investigations with quasi-point electrodes were performed in a dry air atmosphere. Taking measurements in analogous conditions enabled us to carry out a direct comparison of phenomena occurring at interfaces with different physicochemical properties. The prepared Au, Ag wire, including an electrode, was dragged by a single channel bead made of Al$_2$O$_3$, so that the ball was based on its flat side.

Formed Au, Ag quasi-point electrodes were placed along with ceramic electrolytes in a specially designed handmade electrochemical setup [23]. The field of direct contact between the formed noble electrode Au, Ag and all investigated electrolytes was circular in shape. Chronoamperometric (CA) and electrochemical impedance spectroscopy (EIS) techniques were used in this study. Due to the long-term effects of electrode polarisation, the dependencies of current on the time of polarisation were recorded over a period of at least 15 h. In the CA experiments, the microelectrodes were polarised stepwise at potentials from −0.05 to −0.65 V. For additional information, EIS was applied in order to determine and characterise the impedance of the electrode prior to the polarisation at the end of the potential step. The electrochemical measurements described in this paper were carried out mainly at 700°C in air. The samples were measured with the GPES (CA) and FRA (EIS) modules of Autolab PGSTAT30 interfaced with a computer. The impedance spectroscopy measurements were performed within a frequency range of 0.001 Hz–1 MHz using sinusoidal voltage with an amplitude of 10 mV. A program based on a complex non-linear regression least-squares fit, provided by the software developer, was used for data analysis.

2.3 Analytical method of solid electrolytes and electrode materials evaluation before and after electrochemical investigations

The phase composition of 5CBCY, 20GDC and 8YSZ, both initial sintered samples and samples following electrochemical measurements,
was studied using the X-ray diffraction analysis method. XRD measurements were done with a PANalytical X’Pert Pro system with monochromatic CuK$_\alpha$ radiation. The microstructure of all ceramic electrolytes prior to their application in electrochemical studies was also observed using scanning electron microscopy. During the investigated cathode reaction in Au|5CBCY, Ag|5CBCY, as well as in the reference pairs Au|20GDC or Au|8YSZ, Ag|20GDC, the same analytical method was used to obtain more information which might be helpful in explaining the unusual increase in the absolute value of the current over the time of polarisation of the tested electrodes. The application of confocal as well as scanning electron microscopy enabled identification of changes in the chemical composition and surface structure of the 5CBCY, 20GDC, 8YSZ electrolytes. Following electrochemical measurements, the samples were ‘frozen’ following 12 or 56 h of polarisation at –0.5 V; polarisation was maintained during rapid cooling to room temperature.

The purpose of the XPS/ESCA study was to identify changes in the composition and electronic states of the elements at the surfaces of certain investigated ceramic electrolytes. The measurements were performed with XPS/ESCA technique, using the methodology described in the previous papers [25, 26]. For this reason, the tests were carried out both for fresh samples of the electrolytes (polished sections not used previously for any electrical or electrochemical investigations) and for the areas of the electrolyte surfaces near electrodes following electrochemical experiments. In these experiments, quasi-point Au, Ag electrodes were polarised at –0.5 V for 48 hours at 700°C in air.

3. RESULTS

3.1. Characteristics of sintered electrolyte samples

The X-ray diffraction analysis method revealed that all of the sintered samples of 5CBCY, 20GDC, 8YSZ and 3YSZ were composed of a single phase. The analysis of the structure and physicochemical properties of the new modified material Ca$_{0.05}$Ba$_{0.95}$Ce$_{0.9}$Y$_{0.1}$O$_3$, was described in a previous paper [28]. The present study summarises the most important electrolytic properties exerting a direct impact on the kinetics of the oxygen reduction process. The data are listed in Table 1.

All samples exhibited more than 95 wt % theoretical density. In Figure 1, a typical 5CBCY sintered sample is presented. The sintered samples are characterized by a uniform microstructure with a grain size between 0.5 and 4 µm (Feret diameters in X and Y directions).

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure/cell parameter, Å</th>
<th>Electrical conductivity at 700°C σ(S/cm)</th>
<th>Activation energy, $E_a$, eV calculated in the temperature range 300–700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CBCY</td>
<td>perovskite $a = 6.2152$ $b = 8.7767$ $c = 6.2285$</td>
<td>$5.41 \times 10^{-2}$</td>
<td>0.54</td>
</tr>
<tr>
<td>20GDC</td>
<td>cubic $a = 5.4211$ $c = 6.2285$</td>
<td>$3.11 \times 10^{-2}$</td>
<td>0.81</td>
</tr>
<tr>
<td>8YSZ</td>
<td>cubic $a = 5.1361$ $c = 5.168$</td>
<td>$3.6 \times 10^{-3}$</td>
<td>0.90</td>
</tr>
<tr>
<td>3YSZ</td>
<td>tetragonal $a = 3.610$ $c = 5.168$</td>
<td>$1.04 \times 10^{-3}$</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The 20GDC and 8YSZ electrolytes are also characterised by a similar grain size distribution and microstructure.

3.2. Electrochemical investigations of the Au|5CBCY and Ag|5CBCY interfaces

In this study, the typical dependencies of the currents flowing through the Au electrode at negative step polarisation ($E = –0.05$ to –0.65 V) recorded for a 5CBCY sample at 700°C in air are depicted in Figure 2. Generally, within the applied potential range (from –0.05 to –0.3 V), the current had a tendency to increase monotonically over time. An increased potential of –0.5 V caused an initial increase in the current, which then stabilised. Different behaviour was observed at the applied potential of –0.65 V. In this case, the current flowing in the system gradually decreased, but was always greater than the current which flowed with an applied potential of –0.5 V.

Fig. 1. Microstructure of the 5CBCY sintered sample at 1500°C, 2 h

Rys. 1. Mikrostruktura próbki 5CBCY spieczonej w temperaturze 1500°C przez 2 h

Fig. 2. Family of chronoamperometric curves recorded at a Au-pointed electrode in contact with a 5CBCY electrolyte. The measurements were performed at 700°C in air. Applied potentials are given above the respective curves

Rys. 2. Rodzina krzywych chronoamperometrycznych zarejestrowana dla elektrody Au przyłożonej do elektrolitu 5CBCY. Pomiary przeprowadzono w temperaturze 700°C w powietrzu. Wielkości napięć polaryzacji zostały umieszczone nad odpowiadającymi ich krzywymi
In analogous conditions, measurements were performed for the above-mentioned oxide electrolytes, such as 20GDC and 8YSZ. Based upon comparative analysis of the obtained electrochemical data for 20GDC (Fig. 3), two different electrochemical outcomes were recorded, depending on the applied overpotential. In the case of lower values of applied potential (from -0.05 V to -0.3 V), initially a small increase in relative current (ΔI) compared to starting values, from \( E = -0.1 \) to -0.25 V, was observed. In the case of a higher range of applied potential, from -0.3 to -0.6 V, a decrease in relative current (ΔI) was observed. Similar behaviour was observed for the 8YSZ polycrystalline sample. Figure 3 presents the results for 3% mol Y2O3 in ZrO2 (3YSZ) samples, characterised by a different microstructure. The greatest increase was observed for the 3YSZ sample with smaller grain sizes (0.1÷0.3 μm) (sample A) [29] than in case of sample with the same composition but exhibited larger grain sizes distribution from 1 to 6 μm (sample B). This finding clearly indicated that surface physicochemical properties and microstructure characterised by small grain sizes have an additional impact on the electrochemical behaviour of an Au|3YSZ system operating under electrical load. Generally, for all investigated ceramic electrolytes in this study, a decrease was observed in the case of applied potentials more negative than -0.3 V.

Different electrochemical behaviour was observed in the case of the Ag|5CBCY system. Generally, within the applied potential range (from -0.05 to -0.65 V) (Fig. 4), the current had a tendency to increase monotonically over time for the 5CBCY as well as for the 20GDC and 8YSZ electrolytes [22, 24]. To better interpret and demonstrate the considerable difference between Au and Ag electrodes, additional experiments were performed, involving the influence of the time of applied polarisation vs different period times.

Figure 5a, b shows the dependency of current flowing through the tested electrodes at polarisation of -0.2, -0.3, and -0.5 V, respectively, with increasingly longer polarisation times: 1, 2, 4, 8, and 16 h. Polarisations were interrupted with continuous 1-hour electrode relaxation periods. The results indicate variable current responses of the system depending on the applied potential. Interruption of polarisation does not reduce the (absolute) current response values. The results obtained from these measurements are in good agreement with previous data obtained from classical CA measurements. In the case of polarisation/relaxation measurements, two different responses were also observed, depending on the applied potential range. Based on the analysis (Fig. 5c) for \( E = -0.5 \) V, it can be concluded that the absolute current flowing through an Ag electrode increases during the first 7 hours of total polarisation time. Interrupting the polarisation process no significant impact on this tendency. In the third and fourth polarisation cycles, current characteristics following the relaxation period exhibit changes, with the absolute current increasing sharply before falling again over time. This shows the importance of polarisation time (in addition to the applied potential) relative to the direction of current variability, i.e. its increase or decrease.

In the case of a AgGDC (Fig. 6) system, there was a steady increase in the absolute value of the current flowing through the Ag electrode during the applied polarisation over the entire range of applied potentials. The character of the current changes was affected neither by the duration of the polarisation nor the applied relaxation time. It is also notable that the electrode made of Ag tended to return to its original state following relaxation, although the process was not fully reversible.

EIS was also applied to study the electrochemical behaviour of Au electrode. Typical EIS spectra in Nyquist representation consists of a small part of high frequency semicircle and two depressed overlapped semicircles in the medium and low frequency range. The high frequency semicircle can be ascribed to the electrolyte resistance \( R_1 \), whereas the others semicircles to the processes connected with electrode reaction. It means that the polarization resistance \( R_p = R_2 + R_3 \). The assumed equivalent electrical circuit (EEC) consists of resistance \( R_0 \), representing cable connection...
resistance and three (R, C) pairs connected in series. Capacitors are replaced by constant face elements (CPE) which impedance may be expressed by the formula:

$$Z_{\text{CPE}} = \left( \frac{1}{\omega \alpha} \frac{C_0}{j \omega} \right)^\alpha$$  \hspace{1cm} (1)

where:
- $\omega$ is the angular frequency,
- $\omega_0$ is the angular frequency of reference (assumed 2π × 1000 s$^{-1}$),
- $C_0$ is the capacitance at the frequency of reference,
- $\alpha$ is a coefficient which is equal to 1 for an ideal capacitor and $j$ is the imaginary unit. The sample of fitting results is presented in Figure 7.

The impedance spectra recorded for Au|20GDC and Au|8YSZ at 700°C towards the end of the 18 h polarisation period, at –0.1, –0.2, and –0.3 V, are presented in Figures 8, 9.

Figure 8 shows mainly semicircles in the low frequency range, which correspond to the polarisation resistance of the $R_p$ electrode. Included at top right in Figure 8 is a magnified initial section of the impedance spectrum in the highest frequency range. At a measurement temperature of 700°C, this is represented by a section of the semicircle interpreted as total ohmic resistance $R_s$, mostly due to the resistance of the electrolyte.

Figure 7. Example of results of fitting, crosses experimental spectra recorded for Au|8YSZ after 135 min of polarization at –0.5 V at 700°C, circles fitted data, the numbers near filled symbols denote the logarithm of the frequency.

Fig. 5. Dependency of the current flowing through a Au electrode over the duration of a polarisation at: a) –0.2 V, b) –0.3 V, c) –0.5 V. The polarisation (a) and (b) was interrupted for one hour at 1-, 2-, 4-, and 8-hour intervals. Polarization (c) lasting 2 h with breaks of 2, 4, 8 and 16 h. The measurements were performed at 700°C in air.

Rys. 5. Zależność prądu płynącego przez elektrodę Au w funkcji czasu trwania polaryzacji napięciem: a) –0,2 V, b) –0,3 V, c) –0,5 V. Polaryzacją (a) i (b) była przerwana na 1 h po 1, 2, 4 i 8 h. Polaryzacja (c) trwała 2 h z przerwami 2, 4, 8 i 16 h. Dane zarejestrowano dla temperatury 700°C.

Fig. 6. Dependency of the current flowing through a Ag electrode over the duration of a polarisation at –0.5 V. The polarisation was interrupted for one hour at 1, 2, 4, and 8 hour intervals.

Fig. 7. Zależność prądu płynącego przez elektrodę Ag w funkcji czasu trwania polaryzacji napięciem –0,5 V. Polaryzacja była przerwana na 1 h po 1, 2, 4 i 8 h. Dane zarejestrowano dla temperatury 700°C.

The impedance spectra recorded for Au|20GDC and Au|8YSZ at 700°C towards the end of the 18 h polarisation period, at –0.1, –0.2, and –0.3 V, are presented in Figures 8, 9.

Figure 8 shows mainly semicircles in the low frequency range, which correspond to the polarisation resistance of the $R_p$ electrode. Included at top right in Figure 8 is a magnified initial section of the impedance spectrum in the highest frequency range. At a measurement temperature of 700°C, this is represented by a section of the semicircle interpreted as total ohmic resistance $R_s$, mostly due to the resistance of the electrolyte.
to electrolyte resistivity. The magnitude of resistance $R_s$ does not change under polarisation, unlike the $R_p$ polarisation resistance of the electrode, which falls with rising voltage applied to the electrodes. It is this polarisation resistance, caused by kinetic processes in the cathode, which is responsible for large polarisation losses in SOFCs. A similar situation was observed for the Au|8YSZ interface (Fig. 9).

As shown in Figure 10, neither the value of applied overpotential $E$ nor the duration of polarisation has any significant effect on $R_s$. Similar dependence of $R_s$ vs applied potential was found for 8YSZ and 3YSZ electrolytes.

However, a different impedance response was observed for an Au|5CBCY system (Fig. 11) in analogous conditions. It should be noted that in these conditions the material $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_3$, unlike the 20GDC or YSZ electrolytes, includes the significant contribution of $p$-type electronic conductivity [30].

Figure 12 presents the dependence of $R_s$ resistance vs applied overpotential. Based on analysis of this data, it can be shown that the magnitude of $R_s$ resistance decreases with increased applied potential, ranging from 0 to $-0.6$ V. One of the possible reasons for the decrease in $R_s$ resistance is increased electrolyte conductivity $\sigma_s$. In this case, it is likely that one of the underlying causes is an increase in the $n$-type conductivity component in the electrolyte as a result of cathode polarisation. Another possible reason could be occurrence of electrochemical changes on the 5CBCY surfaces occurring during long-term polarisation.

The Nyquist plot of impedance spectra recorded for Ag|8YSZ at 700°C during 56 h polarisation period at $-0.7$ V, is presented in Figure 13. The measurements were taken in air at 700°C based on comparison of the resulting Nyquist plots for the Ag|8YSZ systems, before and after the 56 hour polarisation, it is concluded that the $R_s$ resistance decreases following the polarisation of the Ag electrode with negative potential. In previous studies it was found that an Ag electrode could be a source of migrated metal which proliferates...
Fig. 12. Variation of ohmic resistance $R_s$ vs applied potential, recorded for a Au|5CBCY system. Data were obtained from EIS measurements carried out at 700°C in air

Rys. 12. Zmiany oporności omowej $R_s$ wyznaczone dla spolaryzowanej i niespolaryzowanej elektrody Au umieszczonej na elektrolicie 5CBCY. Dane zostały wyznaczone z pomiarów impedancyjnych w 700°C w powietrzu

Fig. 13. The impedance spectra recorded for Ag|8YSZ at 700°C in air before applying the polarization at −0.7 V after 56 hours

Rys. 13. Diagramy impedancyjne zarejestrowane dla układu Ag|8YSZ w 700°C w powietrzu przed i po polaryzacji napięciem −0.7 V przez 56 h

around the working electrode in the form of a dendrite-like structure. The main reason for the increase in absolute current vs time under load observed on chronoaamperometric curves was the growth of a metallic zone around the Ag electrode placed on the 20GDC or 8YSZ ceramic electrolytes.

The data presented in previous papers [20, 24, 26] referred to electrochemical investigations done for no longer than 60 h. In this study, the electrochemical studies for Ag|20GDC or Ag|8YSZ were completed for longer periods, and they were performed for more than 23 days.

Figure 14 depicts the relationship between $R_s$ ohmic resistance and the applied potential to the Ag|20GDC system over a period of 23 days. The ohmic resistance $R_s$ in the Ag|20GDC system decreased with an increase in the applied potential. These data, completed previously, obtained results for this system, and confirmed the dynamic behaviour of the Ag|20GDC system under long-term polarization with negative potentials.

This phenomenon was not reported in the literature for an Ag point electrode in contact with BaCe$_{0.9}$Y$_{0.1}$O$_3$-based electrolytes. Figure 15 presents the Nyquist plots recorded for an Ag|5CBCY system, before and after polarisation at −0.5 V and 700°C. The quantitative analysis of an Ag|5CBCY system before and after polarisation indicated the reduction of the $R_s$ and $R_p$ values during the applied polarisation.

Figure 16 presents the variation of ohmic resistance $R_s$ vs the applied potential. A decrease in the value of $R_s$ vs applied polarisation ranging from −0.1 to −0.6 V was observed. The observed phenomena indicate a possible expansion of the reaction zone in the Ag|5CBCY system due to migration of silver onto the 5CBCY surface and the presence of a dendrite-like structure. A silver deposit was also found (Fig. 17) near the Ag electrode placed on the 5CBCY electrolyte. This indicated that the Ag electrode is a source of migrated metal, which proliferates in the form of a dendrite-like structure on the 5CBCY electrolyte.

Fig. 14. Variation of ohmic resistance $R_s$ vs applied potential, recorded for a Ag|20GDC system

Rys. 14. Zmiany oporności szeregowej $R_s$ wyznaczone układu Ag|20GDC. Dane dla temperatury 700°C

Fig. 15. Nyquist plots recorded for a Ag|5CBCY system before and after polarisation at −0.5 V

Rys. 15. Wykresy Nyquista zarejestrowane dla układu Ag|5CBCY przed i po polaryzacji potencjałem −0.5 V
The XPS/ESCA studies performed for 5CBCY before and after polarization of Ag electrode with negative –0.5 V confirmed presence of silver at the surface of 5CBCY (Tab. 1). The analysis showed very low amount of Ag leading to Ag/O ratio of 5 \times 10^{-6}. The surface analysis showed decrease in Ba content at the surface layer after polarization and increase of Ce, Ca and Y amount (Tab. 2). The high resolution spectra acquired in three different places around the electrode sticking area (Fig. 18a) revealed presence of silver. Moreover, the value of electron binding energy (BE) at maximum of Ag 3d_{5/2} core excitation at 369.0 eV indicated nanosized silver clusters. According to the works by Luo et al. [31, 32], their nominal size was lower than half monolayer of silver.

On the other hand, in case of Au|E, where E = 5CBCY, 20GDC, 8YSZ investigated electrolytes the deposition of nanocrystalline gold metal particles (1÷10 nm in size) was observed (Fig. 20). In case of 8YSZ system, the XPS analysis (Tab. 2) of the surface after polarization with Au electrode showed presence of small amount of Au at the level of Au/O ratio of 2 \times 10^{-4}. The ratios of other elements at the surface to oxygen were lower indicating oxidation of the surface layer. The Au 4f high resolution spectrum (Fig. 18b) showed maximum of Au 4f_{7/2} core excitation at 84.3 eV indicated again the nanosized particles [33, 34]. According to Boyen et al. [33], the size of Au particles was in the range of 1÷2 nm that agreed with the work by Kitsudo et al. [34] indicating particle size of around 1 nm.

| Table 2. Metal/oxygen ratios at the surfaces analysed by XPS metod Tabela 2. Udział metalu do tlenu na powierzchniach analizowany metodą XPS |
|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                | Ba/O          | Ca/O          | Ce/O          | Y/O           | Zr/O          | Zn/O          | Ag/O          | Au/O          |
| 5CBCY          | 0.22          | 0.06          | 0.03          | 0.02          | —             | —             | —             | —             |
| Ag 5CBCY       | 0.15          | 0.09          | 0.06          | 0.04          | —             | —             | 5 \times 10^{-6} | —             |
| YSZ            | —             | —             | —             | —             | 0.03          | 0.57          | 0.02          | —             |
| Au YSZ         | —             | —             | —             | —             | 0.02          | 0.49          | —             | 2 \times 10^{-4} |

Fig. 16. Variation of ohmic resistance $R_s$ vs applied potential recorded for a Ag|5CBCY system

Rys. 16. Zmiany oporności omowej $R_s$ dla układu Ag|5CBCY wraz ze zmianą wielkości przyłożonego potencjalu

Fig. 17. Surface image of the site of direct contact of a Ag electrode with a 5CBCY electrolyte, recorded under optical confocal microscopy observation

Rys. 17. Obraz obszaru przyelektrodowego Ag na powierzchni elektrolitu 5CBCY uzyskany za pomocą mikroskopu konfokalnego

Fig. 18. The Ag 3d (a) and Au 4f (b) spectra acquired at the 5CBCY or 8YSZ electrolyte surfaces, respectively. In case of Ag|5CBCY system, three places around the electrode contact area were analysed

Rys. 18. Widmo Ag 3d (a) oraz Au 4f (b) zarejestrowane dla powierzchni elektrolitu 5CBCY lub 8YSZ. W przypadku układu Ag|5CBCY trzy wybrane obszary poddano analizie

Fig. 19. The form of the observed Au deposit on the 5CBCY electrolyte (Fig. 19) is considerably different than in the case of zirconia–yttria or gadolina-doped ceria electrolytes. In the case of 20GDC or 8YSZ electrolytes, the deposition of nanocrystalline gold metal particles (1÷10 nm in size) was observed (Fig. 20).
Nielsen and Jacobsen also conducted research on changes in the structure of the electrolyte occurring because of the electrode polarization at the phase boundary of Au|8YSZ. These experiments were performed at high temperature (1000°C) [20]. In the quoted work, the authors not observed any form of deposition of gold on the surface of the electrolyte. In their next work [21], however, they presented changes taking place on the surface of the electrolyte around the electrode during its polarization, which resulted in the formation of “hills and valleys”. These changes, according to the authors, were responsible for specific properties of current-voltage dependencies observed during long-term polarization in the Au|8YSZ system.

5. CONCLUSIONS

In this paper, investigations of the oxygen reduction process on the surface of Ca0.05Ba0.95Ce0.9Y0.1O1.9 (5CBCY) were performed using quasi-point electrodes made from Au, Ag at 700°C. Comparative measurements were also carried out for well-known oxide electrodes involving 8% mol Y2O3 in ZrO2 (8YSZ) or 10% mol Gd2O3 in CeO2 (20GDC). An increase in absolute current values was observed along with changes in chemical composition in the interfaces Ag|5CBCY, Ag|8YSZ, and Ag|20GDC under cathodic polarisation. This unusual behaviour was explained by an increase in the three-phase boundary length due to the deposition of Ag near the electrode in all ceramic electrolytes. XPS measurements confirmed that this deposit contained Ag/AgO particles. However, in the case of Au|5CBCY, Au|8YSZ, and Au|20GDC, variable electrochemical behaviour was observed, depending on the applied potential and chemical composition of the electrolyte material. In the case of a Au|5CBCY system, a decrease in ohmic resistance R<sub>e</sub> vs applied potential was observed, as opposed to Au|20GDC and Au|8YSZ systems, where no changes in R<sub>e</sub> value vs applied potential were noted. The main reason for this behaviour was the various changes in the electrochemical interface occurring in the 5CBCY electrolyte. The results of the electrochemical investigations showed that some changes in the properties of electrolytic materials can also occur under electrical load.

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Analiza zmian zachodzących pod wpływem długotrwałej polaryzacji katodowej na granicy faz Me|Ba$_{0.95}$Ca$_{0.05}$Ce$_{0.9}$Y$_{0.1}$O$_3$, Me|Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ i Me|Zr$_{0.84}$Y$_{0.16}$O$_{1.9}$, gdzie Me = pseudo-punktowa elektroda wykonana z Ag, Au

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Słowa kluczowe: ceramiczny przewodnik protonowy, BaCe$_{0.9}$Y$_{0.1}$O$_3$, elektroda punktowa, elektrolit tlenkowy pracujący w obniżonym zakresie temperatury, proces redukcji tlenu.

1. CEL PRACY

Celem pracy była analiza możliwych zmian zachodzących pod wpływem długotrwałej polaryzacji katodowej na granicy faz Me|Ba$_{0.95}$Ca$_{0.05}$Ce$_{0.9}$Y$_{0.1}$O$_3$, Me|Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ i Me|Zr$_{0.84}$Y$_{0.16}$O$_{1.9}$, gdzie Me = pseudo-punktowa elektroda wykonana z Ag, Au.

2. MATERIAŁ I METODYKA BADAŃ

Porównawcze badania elektrochemiczne procesu redukcji tlenu wykonano dla obiecz stosowanego w ogniach palliwowych SOFC elektrolit źródeł $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{3}$ oraz materiałów pretendujących do zastosowania w ogniach SOFC pracujących w obniżonym zakresie temperatury (intermediate temperature solid oxide fuel cells, IT-SOFCs), tj. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.2}$, czy $\text{Ca}_{0.05}\text{Ba}_{0.95}\text{Ce}_{0.8}\text{Y}_{0.1}\text{O}_{3}$, oraz $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{3}$, $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, $\text{Ca}_{0.05}\text{Ba}_{0.95}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3}$ metodą skanującej mikroskopii elektronowej lub konfokalnej stwierdzono osadzanie się cząstek srebra wokół elektrody na skutek migracji. Obecność depozytu Ag na powierzchni badanych elektrolitów prowadzi już do mniejszego początkowego przyrostu natężenia prądu, a następnie jego stabilizacji. Pomiary wykonane metodą elektrochemicznej spektroskopii EIS wykazały zmniejszenie oporności szeregowej $R_p$ dla wszystkich badanych układów. Na podstawie prze prowadzonych obserwacji powierzchni elektrolitów ceramicznych $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.2}$, $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, $\text{Ca}_{0.05}\text{Ba}_{0.95}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3}$ metodą skanującej mikroskopii elektronowej lub konfokalnej stwierdzono osadzanie się cząstek srebra wokół elektrody na skutek migracji.

W przypadku badanych układów z pseudo-punktową elektrodą złożą $\text{AuCe}_{0.93}\text{Gd}_{0.07}\text{O}_{3}$, $\text{AuZr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$ czy $\text{AuBa}_{0.05}\text{Ca}_{0.05}\text{Ce}_{0.8}\text{Y}_{0.1}\text{O}_{3}$, charakter zmian natężenia prądu oraz powierzchni elektrolitu zależy od składu chemickiego elektrolitu stałego, jego mikrostruktury, a także wielkości przykładowych potencjałów. Dla układu $\text{AuBa}_{0.05}\text{Ca}_{0.05}\text{Ce}_{0.8}\text{Y}_{0.1}\text{O}_{3}$, w zakresie polaryzacji ujemnymi potencjałami wynoszącymi od –0.05 do –0.3 V można zaobserwować wzrost natężenia prądu w trakcie długotrwałej polaryzacji katodowej. Z kolei zwiększanie natężenia prądu w czasie trwania prądu polaryzacji katodowej na granicy faz $\text{Me}\mid\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3}$, $\text{Me}\mid\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ i $\text{Me}\mid\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, gdzie Me = pseudo-punktowa elektroda wykonana z Ag, Au, do –0.7V następuje wzrost natężenia prądu w czasie trwania polaryzacji. Zastosowanie elektrochemicznej spektroskopii impedancji EIS pozwoliło na wyznaczenie zmian oporności szeregowej $R_p$ oraz oporności polaryzacyjnej $R_s$ w odniesieniu do warunków bez polaryzacji. Zaobserwowano zmniejszenie zarówno rezystancji $R_p$, jak i $R_s$ dla wszystkich badanych układów. Na podstawie przeprowadzonych obserwacji powierzchni elektrolitów ceramicznych $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.2}$, $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, $\text{Ca}_{0.05}\text{Ba}_{0.95}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3}$ metodą skanującej mikroskopii elektronowej lub konfokalnej stwierdzono osadzanie się cząstek srebra wokół elektrody na skutek migracji. Obecność depozytu Ag na powierzchni badanych elektrolitów prowadzi już do mniejszego początkowego przyrostu natężenia prądu, a następnie jego stabilizację.

3. WYNIKI I ICH Dyskusja

Na podstawie pomiarów chronoamperometrycznych wykonanych dla układów $\text{AgBa}_{0.05}\text{Ca}_{0.05}\text{Ce}_{0.8}\text{Y}_{0.1}\text{O}_{3}$, $\text{AgCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3}$ i $\text{AgZr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, stwierdzono, że podczas długotrwałej polaryzacji katodowej w zakresie przykładowych potencjałów od –0.05 do –0.7V następuje wzrost natężenia prądu w czasie trwania polaryzacji. Zastosowanie elektrochemicznej spektroskopii impedancji EIS pozwoliło na wyznaczenie zmian oporności szeregowej $R_p$ oraz oporności polaryzacyjnej $R_s$ w odniesieniu do warunków bez polaryzacji. Zaobserwowano zmniejszenie zarówno rezystancji $R_p$, jak i $R_s$ dla wszystkich badanych układów. Na podstawie przeprowadzonych obserwacji powierzchni elektrolitów ceramicznych $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2.2}$, $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$, $\text{Ca}_{0.05}\text{Ba}_{0.95}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3}$ metodą skanującej mikroskopii elektronowej lub konfokalnej stwierdzono osadzanie się cząstek srebra wokół elektrody na skutek migracji. Obecność depozytu Ag na powierzchni badanych elektrolitów prowadzi już do mniejszego początkowego przyrostu natężenia prądu, a następnie jego stabilizację. Pomiary wykonane metodą elektrochemicznej spektroskopii EIS wykazały zmniejszenie oporności szeregowej $R_p$ podczas polaryzacji dla układu $\text{AuBa}_{0.05}\text{Ca}_{0.05}\text{Ce}_{0.8}\text{Y}_{0.1}\text{O}_{3}$, a w przypadku układów $\text{AgCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3}$ i $\text{AgZr}_{0.84}\text{Y}_{0.16}\text{O}_{1.9}$ parametr ten pozostaje praktycznie niezmienny w czasie. Zastosowanie metod mikroskopowych oraz spektroskopii mikroskopowej XPS pozwoliło na wskazanie czynników odpowiedzialnych za odmienne zachowanie się elektrolitów ceramicznych wobec warunków polaryzacji.