Selected aspects of the design and diagnostics of solid oxide fuel cells

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Abstract. An increased growth in demand for energy accompanied by efforts to limit its negative impact on the environment is forcing society to seek new, more efficient energy sources. Fuel cells are one of the most promising solutions among the widely developed new generation of electrical generators. Fuel cells directly convert chemical fuel into electricity. Water and waste heat are by-products of fuel cell operation. Solid oxide fuel cells (SOFCs) have proven to be one of the most interesting solutions among the five types of technologically advanced fuel cells, for their ability to operate at temperatures above 800°C. Furthermore, SOFCs are characterized by other advantages in comparison to PEMFCs, including: (1) no need to use expensive catalysts (e.g. platinum, the price of which is high, and its resources limited), (2) the possibility of direct, internal conversion of hydrocarbon fuels, (3) lower sensitivity to contaminants (in particular, hydrogen fuel containing CO, which is useful for SOFCs instead of the platinum catalyst poisoners), and (4) the possibility of using waste heat in a gas turbine, or for heating or other industrial purposes. The paper discusses selected issues regarding the construction and characteristics of planar solid oxide fuel cells. Selected results of the following electrochemical investigations: $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3-x}$ -based proton electrolyte as possible components of SOFCs operating at intermediate temperature range (500–700°C).

1 Introduction

A fuel cell (FC) is a type of a galvanic cell, along with primary cells, electrochemical accumulator batteries, and flow-through accumulators. As in any galvanic cells, what occurs in an FC is a direct (single-stage) conversion of chemical fuel energy into electricity (and waste heat). A characteristic feature of FCs is that the electroactive substances, i.e. the oxidiser and the fuel, are delivered to them from outside, and the reaction product is removed from the fuel cell [1–7].

Currently, the most rapid technological development can be observed for proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs). Small units with fuel cells (with power ranging from several up to a dozen watts, mainly PEMFCs) have already appeared on the commercial market; they can be used, for example, to power portable electronics or mobile phones. Slightly larger stacks of fuel cells (approximately 250–1000 W) can serve as power sources for electric motors for unmanned aerial vehicles (drones). Even larger fuel cells (1–200 kW) are being built for application in cars and small planes. Stationary units, with power in megawatts [8–13], have been commercialised for phosphoric acid fuel cells (PAFCs) and molten carbonate fuel cells (MCFCs), whereas the development of PEMFCs and SOFCs remains consistently at the level of advanced prototype units.

Among five types of technologically advanced fuel cells special attention should be given to solid oxide fuel

cells (SOFCs). Solid oxide fuel cells which currently utilise $\text{ZrO}_2\text{-Y}_2\text{O}_3$ as solid electrolytes operate at temperatures of 850–1000°C and require the use of components (i.e. electrodes and interconnectors) made from materials characterised by high thermal and chemical stability as well as high corrosion resistance in an oxidation-reduction environment. This vastly increases the cost of producing fuel cells, due to the high cost of suitable materials, and limits their use [14].

The reduction of operation temperature to 550–700°C seems to be most important strategic goal of SOFC technology. There are two main approaches to solve this problem. The application of some oxygen ionic conductors as well as proton conducting ceramics, which exhibited higher ionic conductivity than 8YSZ at intermediate temperature range seem to be most often considered solution. Ceria-based solid electrolytes still seem to be the most attractive oxide conducting ceramic membranes at intermediate temperature ranges (600–800°C) [15–17]. The utilization of ceramic proton conducting membrane instead to oxygen ionic conductor as an electrolyte in SOFCs can lead to simplification of the SOFC stacks construction. In SOFCs with a ceramic proton conducting membrane, the water evolves on the cathode, avoiding the fuel dilatation on the anode side, as well as reduction of cell voltage.

At present, high protonic conduction is reported for several perovskite-type oxides, such as doped BaCeO_3 , SrCeO_3 , BaZrO_3 , and SrZrO_3 . Proton conduction can be

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thermally activated at comparatively low temperatures (400–700°C) due to the low activation energy (0.3–0.6 eV) required by this process [18,19].

Currently, research and development for SOFCs are conducted in order to improve the efficiency of conversion of chemical energy of fuels into electrical energy in these devices. These efforts are also aimed at improving the reliability of fuel cells, prolonging their life, and reducing the costs of single cells and their stacks. The results of this work are modifications in the already produced SOFC stack systems, and the construction of a new type of a SOFC [20].

The latter requires confirmation of the effectiveness of its performance. Due to the cost of SOFC components, as well as the cost production of SOFCs, electrochemical tests are usually performed for SOFCs of small sizes. For this reason, the most often applied systems are button solid oxide fuel cells. The basic element of this measurement station is a button solid oxide fuel cell with electrodes with a maximum geometric surface area of 2 cm². Standardising procedures can be easily introduced for this kind of SOFC construction, as they will take into account, among other factors, the size of the active surface of the electrode material, the impact of the ohmic polarisation, and the area of the surface changes in the electrode material, or the electrolyte after long-term testing for all single SOFC performances.

The aim of this study is to determine the possibility of designing a SOFC operating in the temperature range of 600–800°C using a BaCeO₃-based ceramic proton conductor.

2 Experimental

A solid-state proton-conducting electrolyte (Ba_{0.9}Ca_{0.1}Ce_{0.9}Y_{0.1}O_{3-d}, 10CBCY) was fabricated via the sol-gel method. Stoichiometric amounts of BaCO₃, CaCO₃, and Y₂O₃ were dissolved in nitric acid and mixed with a Ce(NO₃)₃ solution. In a separate beaker, EDTA was dissolved in an ammonia solution diluted with distilled water. The two solutions were mixed and heated to 80°C. The ratio of total metal cations to EDTA was maintained at 1:1.1. As a result of continuous heating and stirring, excess water was evaporated and a viscous gel was formed. The gel was placed in a furnace and heated to 900°C. White ash was collected and milled in an agate mortar in the presence of isopropanol. Subsequently, the powder was heated to 1000°C for 2 h.

The powder was grounded in an agate mortar and uniaxially pressed in a 28mm pressing die under 9 tonnes of force. Then the sample was sintered at 1500°C for 2 h. The sintered sample was cut into the shape of a circle with a diameter of 20 mm. Both sides of the samples were grounded and polished. Platinum paste electrodes were screen-printed on both sides of the cylindrical cell. In order to sinter the electrodes with the cell surfaces, the sample was heat-treated in air at 815°C for 15 min. The anode and cathode surfaces of the commercial cell were screen-printed with a platinum honeycomb network current collector (Fig.1a-b). The prepared powder and sintered electrolyte were examined using the X-ray diffraction method.

Solid oxide button fuel cells (proton- and oxide-conducting) were tested using an elaborated setup (Fig.1c-d). Single SOFCs cells were placed inside a ceramic socket and pressed with another alumina tube in order to obtain a gastight configuration, gold gaskets were placed on both sides of the cell.

Hydrogen was supplied from a bench-scale PEM electrolyser using a liquid-gas water separator. In the case of the solid oxide button cell, 20% oxygen in an argon mixture was fed to the cathode. A Solartron electrochemical interface (SI1287) with a frequency response analyser (FRA 1255B) was used for electrochemical measurement. Impedance spectroscopy measurements were also performed to identify the sources of electrochemical losses during SOFC performance.

Figure 1. Photographies of tested electrolyte –supported solid oxide fuel cells. A) The cathode side of the solid button oxide fuel cell, B) The 10CBCY electrolyte with printed Pt electrodes. C) The scheme of electrochemical testing setup, D) The electrochemical testing setup inside opened furnace.

3 Results and discussions

The details of structural and physicochemical investigations of Ba_{1-x}Ca_xCe_{0.9}Y_{0.1}O_{3-d}-based solid solutions were presented in the previous paper [21]. Analysis of the electrical conductivity of both series of investigated materials showed that the highest ionic conductivity, in air and wet 5–10 % H₂ in Ar, was attained by compositions of x = 0.02–0.05 (Ba_{1-x}Ca_x)(M_{0.9}Y_{0.1})O₃, M=Zr, Ce.

Figure 2 presents the XRD diffraction pattern obtained for BaCe_{0.9}Y_{0.1}O_{3-d} (BCY) as well as Ba_{0.9}Ca_{0.1}Ce_{0.9}Y_{0.1}O_{3-d} (10CBCY) sintered samples. The introduction of 10 % calcium cations in place of barium in the solid solution Ba_{0.9}Ca_{0.1}Ce_{0.9}Y_{0.1}O_{3-d} left the perovskite structure unchanged. Button solid oxide fuel cells incorporating electrode material with an active surface area of about 1.3–2 cm² are very often used in solid oxide fuel cell technology as standardised

ceramic elements for preliminary electrochemical tests. Ceramic shaped parts in these sizes are very often offered by well-known fuel cell manufacturers as a reference for tests of single SOFCs [22,23].

Figure 2. The X-ray diffraction pattern recorded for BCY (a) and 10CBCY (b) sintered samples.

In this study efforts were aimed at the manufacture of gastight $\text{Ba}_{0.9}\text{Ca}_{0.1}\text{Ce}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ sintered samples with diameters about 2 cm and the performance tests of hydrogen-oxygen solid oxide fuel cells. Figure 3a-b presents a photo of commercial 8 %mol Y_2O_3 in ZrO_2 8YSZ ceramic foil (Fuel Cell Material, USA) used as a reference electrolytic material and a newly manufactured ceramic 10CBCY proton-conducting electrolyte. Based on this comparison, plane-parallel ceramic discs based on 10CBCY were obtained.

Figure 3. a) Photo of commercial 8YSZ ceramic electrolyte foil (supplier Fuel Cell Material, USA) b) Photo of a newly manufactured ceramic 10CBCY proton conducting electrolyte

The microscopic investigations performed on 10CBCY, using confocal, atomic force microscopy as well as scanning electron microscopy (Figure 4 a, b), showed no open porosity in the sintered sample.

The image of surface of the elaborated cell was compared with surface of commercial electrolyte presented on figure 4 (c,d). No significant differences in roughness was observed.

Electrochemical tests of a single SOFC were performed for reference solid button oxide fuel cells (Fuel Cell Materials, USA). The aim of these investigations was the verification of correct performance and the reproducibility measurements.

The characteristic U-I and P-I curves was presented in Figure 5.

Figure 4a. Scanning electron microscopy image of the microstructure of a 10CBCY sample sintered at 1500°C for 2h.

Figure 4b. Image of the surface of a 10CBCY sample sintered at 1500°C for 2h. The observations were carried out under optical confocal microscopy.

The data obtained for a commercial E-SOFC (Fuel Cell Material) was compared with the parameter declaration provided by the manufacturer [22].

As can be seen, current density (I) and power density (P) increase with rising temperature. The obtained power outputs $P_{\max}$ are very close to data provided by the supplier of the components of this SOFC. Figure 6 presents the family of voltage (U)-current (I) and of power (P)-current (I) curves recorded for an $\text{H}_2/\text{Pt}|10\text{CBCY}|\text{Pt}/\text{O}_2$ fuel cell over a range of 550–750°C. An increase was reported in the current density (I) as well as power density (P) in an SOFC involving a 10CBCY solid electrolyte. These results were compared with data in the literature. Matsumoto et al. [12] investigated an IT-SOFC in which a $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ electrolyte with a thickness of 0.5 mm was tested. In the case of $\text{H}_2/\text{Ni-BCY}|\text{BCY}|\text{LSCF}/\text{O}_2$, he obtained a power output of 60 mW/cm² at 700°C. The main difference between the lower power output (15 mW/cm²) obtained for a SOFC involving 10CBCY as an electrolyte and the SOFC investigated by Matsumoto can be directly attributed to the difference in the thickness

of the electrolyte and the different cathode and anode materials applied in the cited paper. The results obtained by the author in this study appear to be valuable for further electrochemical investigations.

C

D

Figure 4.c,d Image of the surface of commercial 8YSZ ceramic electrolyte foil (supplier Fuel Cell Material, USA) obtained by atomic force microscope (AFM).

Figure. 5 The U-I curves recorded for an E-SOFC (Fuel Cell Material, SOFCs)

Figure 6. Voltage - Current density and Power density characteristics recorded for an $H_2Pt|10CBCY|PtO_2$ fuel cell over a temperature range of 550–750°C

The electrochemical impedance spectroscopy (Figure 7) method was used to determine the impact of ohmic resistance (R_s) and (R_p) on the performance of the tested SOFC with a 10CBCY electrolyte. The data are collected in Table 1.

Table 1. The values of ohmic resistance (R_s) and polarisation resistance (R_p) determined for a $H_2Pt|10CBCY|PtO_2$ fuel cell within a temperature range of 600–650°C

Temperature [°C]	R_s [Ω]	R_p [Ω]
600	14.9	18.1
650	11.1	5.9

Figure 7. Electrochemical impedance spectra recorded for a $H_2Pt|10CBCY|PtO_2$ fuel cell at various temperatures.

Based on data presented in Table 1, it was found that the values of R_s and R_p decrease with increasing temperatures of SOFC operation. This phenomenon is typical for SOFCs which are constructed correctly. The values of both R_s and R_p obtained by EIS method,

are in good agreement with data obtained from U-I measurements.

Electrochemical impedance spectroscopy measurements were also performed in an oxygen-rich and a hydrogen-rich gas atmosphere. The recorded impedance plots in the Z'' - Z' coordination are presented in Figure 8a - b. The values of R_p and R_s are collected in Table 2.

Figure 8. Electrochemical impedance spectroscopy of a symmetrical Pt|10BCBY|Pt cell in various gas atmospheres at 550°C: a) air, b) humidified oxygen (20%) with argon, c) fuel cell conditions; d) humidified hydrogen.

Table 2. Values of R_s and R_p recorded for Pt|BC10CY|Pt in different gas atmospheres

Gas atmospheres	R_s [Ω]	R_p [Ω]
H ₂ (humidified)	19.9	1.7
Fuel cell condition, H ₂ (humidified) + 20% O ₂ in Ar (humidified)	2.3	24.8
20% O ₂ in Ar (humidified)	26.0	26.0
Air	52.0	65.0

Analysis of data collected in Table 2 indicated that values of R_s and R_p decrease with increasing H₂ content in gas atmospheres. The highest values of ohmic resistance R_s and polarisation resistance R_p were found in an oxygen-rich atmosphere. In a highly rich oxygen gas atmosphere, BaCe_{0.9}Y_{0.1}O₃-based electrolytes exhibited rather mixed electronic conductivity. This caused an increase in values of polarisation resistance, especially in the cathode reduction process. On the other hand, in the case of a hydrogen-rich gas atmosphere, the BCY-based electrolytes exhibited practically pure proton conductivity. These results clearly indicated that cathode polarisation has a considerable impact on the performance of a SOFC with a BCY electrolyte.

Conclusions

Ba_{0.9}Ca_{0.1}Ce_{0.9}Y_{0.1}O₃-d (10BCBY) proton-conducting disc-shaped ceramic electrolytes were

obtained. Based upon confocal and scanning microscopy observation, no cracks or other surface defects were found for sintered samples of 10BCBY; only low closed-porosity content was observed in the case of 10BCBY sintered samples. The obtained 10BCBY proton-conducting ceramic was applied as an electrolyte for IT-SOFC operating within a temperature range of 550–750°C. An increase was observed in the performance of H₂/Pt|10BCBY|Pt/O₂ in this range. The results of these initial electrochemical tests appear to justify further investigations of an SOFC utilising 10BCBY with reduced thickness.

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