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Differential impedance analysis of $BaCe_{0,85}Y_{0,15}O_{2,925}$

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In this study the technique of the Differential Impedance Analysis (DIA) is applied for characterization of the proton conducting material $BaCe_{0,85}Y_{0,15}O_{2,925}$ (BCY15), which will be used in a new dual membrane fuel cell design. The BCY15 was investigated in symmetrical electrolyte supported half cell with Ag electrodes. The impedance measurements were performed in a temperature interval of 200 – 700ºC. The combination of DIA and correction of the measurement rig parasitic inductance and resistance (L-correction) ensured a good separation of the bulk and grain boundaries contribution. The comparison of the results, obtained for the BCY15 proton conductivity, with the literature data demonstrates the good quality of the developed material.

Keywords: Impedance Spectroscopy, Differential Impedance Analysis, Yttrium Doped Barium Cerate ($BaCe_{0,85}Y_{0,15}O_{2,925}$)

INTRODUCTION

The attempts for turning fuel cells into commercially successful alternative energy sources concern improvements towards lower cost, better stability of the performance, and higher fuel efficiency [1]. The main pathway for achievement of those objectives in solid oxide fuel cells (SOFCs) is the reduction of the operating temperature down to 600 – 700ºC [2, 3], since those conditions will increase the cell stability, improve the compatibility of the materials, and ensure replacement of the ceramic interconnects with the cheaper metallic alloys. However, dilution of the fuel with water by-product is a principle construction disadvantage of the classical SOFCs, which is closely related to their lower efficiency. A new concept for overcoming this problem, known as the IDEAL-Cell after the acronym of the FP7 European project, is under development [4, 5]. It is based on a cell design with three independent chambers for hydrogen, oxygen, and water (Fig. 1a). In addition the efficiency of the system could be enhanced by an easy and independent application of pressure on the water-free hydrogen and oxygen electrodes. The proof of the proposed concept is the first stage in the development of the new design, for which a 3-chambered testing cell has to be produced with routine raw materials.

The aim of this study is the impedance characterization of the proton conducting yttrium doped barium cerate ($BaCe_{0,85}Y_{0,15}O_{2,925}$) for application in the new dual membrane fuel cell design as electrolyte in the hydrogen chamber and in the porous mixed conducting central membrane chamber (CM), where the water is produced and evacuated.

EXPERIMENTAL

The BCY15 electrolyte material was investigated in symmetrical electrolyte supported half cell with Ag electrodes (Fig. 1b). Since the central membrane consists of three phases - BCY15, oxygen conducting electrolyte $Ce_{0,85}Y_{0,15}O_{1,925}$ (YDC15), and pores, it is important to study the behaviour of the hydrogen conducting phase in the presence of both, the YDC15 and the pores. The investigations were performed on central membrane supported half cell $Ag/YDC15_{porous}+BCY15_{porous}/Ag$ (Fig. 1c) which ensured direct measurement of the BCY resistivity in the central membrane.

The impedance measurements were performed with a Solartron 1260 Frequency Response Analyser in a temperature interval of 200 – 700ºC, at scanning range from 10 MHz down to 0.1 Hz, and density of 5 points/decade. They were done in two modes: potentiostatic and galvanostatic. The change of mode and amplitude, which depends on the sample resistance, ensures higher quality of the measured data. Wet hydrogen (3% H_2O), diluted

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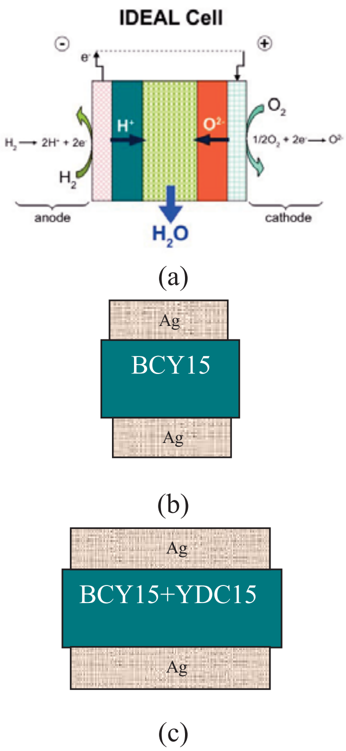

Fig.1. IDEAL Cell: a) concept; b) symmetrical electrolyte supported half cell Ag/BCY15/Ag; c) symmetrical CM supported half cell $Ag/YDC15_{porous}+BCY15_{porous}/Ag$

with nitrogen or argon and air/oxygen for evaluation of the CM oxygen conductivity, were applied. The experiments at lower temperatures ensure information about the electrolyte behaviour, including separation of the bulk from the grain boundaries contribution, while at higher temperatures the electrode reaction behaviour is well pronounced. For more precise determination of the BCY15 resistivity and activation energy, a correction of the measurement rig parasitic inductance and resistance was performed following a well developed specialized procedure (Fig. 2) [6, 7].

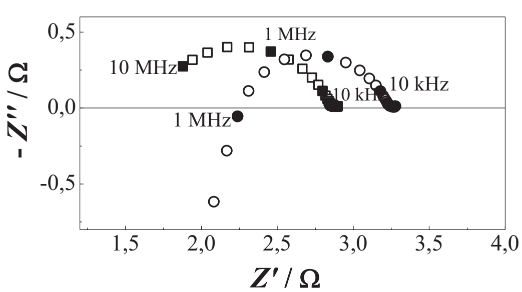

Fig. 2. Complex plane impedance diagrams of Ag/CM/Ag half cell before (●) and after (■) correction for parasitic resistance and inductance.

For a deeper insight into the investigated processes (recognition and separation of different steps and characterization of the rate-limiting one), the data were analysed by the technique of the Differential Impedance Analysis (DIA) [6–9]. DIA works with no preliminary working hypotheses, because the information about the model structure is extracted directly from the experimental data. After a specialized mathematical procedure, the initial data set (frequency ω, real and imaginary components of the impedance) is presented in new coordinates, which give the frequency dependence ($\nu = \lg \omega^{-1}$) of the effective parameters ($\hat{P}$), additive effective resistance $\hat{r}_{ad}$, effective resistance $\hat{R}$, effective capacitance $\hat{C}$, and effective time-constant $\hat{T} = \hat{R}\,\hat{C}$. The approach is deterministic. The new form of presentation, called temporal analysis, recognizes well sub-models with lumped parameters. It also identifies frequency dependent behavior, which can be additionally analyzed by secondary analysis. More information about the secondary DIA can be found in [6–8]. In addition, the method has high selectivity and good noise immunity. The application of DIA is demonstrated in the example, shown in Fig. 3. It represents a two step reaction (i.e. a process described with 2 time-constants). The two plateaus, observed in the temporal plots, exhibit the presence of two time constants (Fig. 3b). They are separated by a region of frequency dispersion, which corresponds to the transition between the two reaction steps.

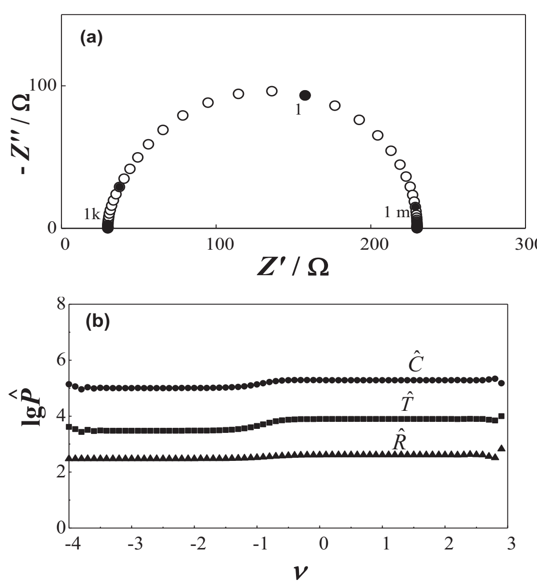

Fig. 3. DIA of simulated Faradaic reaction involving one adsorbed species: a) complex plane impedance diagram; b) temporal plots.

Thus the presence of plateaus ensures the recognition of the model, while their position enables the parametric identification. This example demonstrates also the good DIA selectivity, which can distinguish two time-constants with high degree of mixing.

RESULTS AND DISCUSSION

The impedance measurements of testing cell with dense electrolyte, the Ag/BCY15/Ag (Fig. 4a), were performed in a single gas flow (wet hydrogen). The data were analyzed by DIA. The grain boundaries contribution can be estimated by the corresponding plateau in the $\hat{R}$ - plot (Fig. 4b).

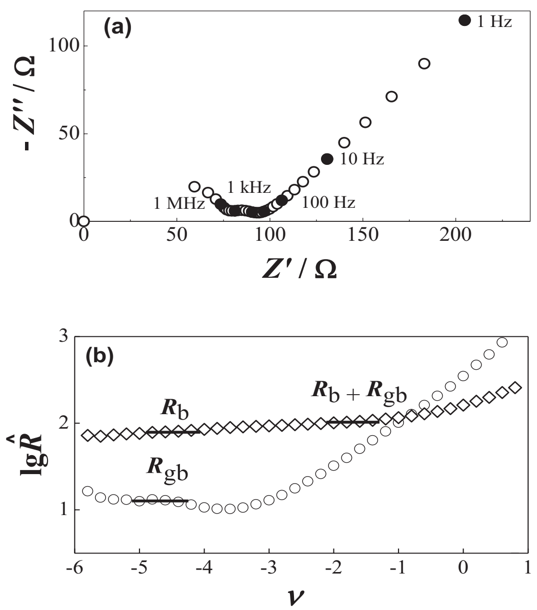

Fig. 4. Complex plane impedance diagram of symmetric half cell Ag/BCY15/Ag at 200 °C: a) Z-plot; b) $\hat{r}_{ad}$ (◊) and $\hat{R}$ (○) temporal plots.

The contribution of the bulk is insufficient for identification. However, the first plateau in the $\hat{r}_{ad}$ -plot recognizes this parameter, which is an additive term in respect to the grain boundaries performance. The combination of L-correction and information, extracted from $\hat{R}$ and $\hat{r}_{ad}$ temporal plots, enables a good separation of the bulk and grain boundaries contribution for the hydrogen conducting electrolyte in a wide temperature range [10]. The Arrhenius plot of dense BCY15 is presented in Fig. 5. To be noticed here is the faster decrease of the grain boundaries resistivity with the temperature. Thus, at operating temperatures (600–700ºC), the bulk contribution is dominating.

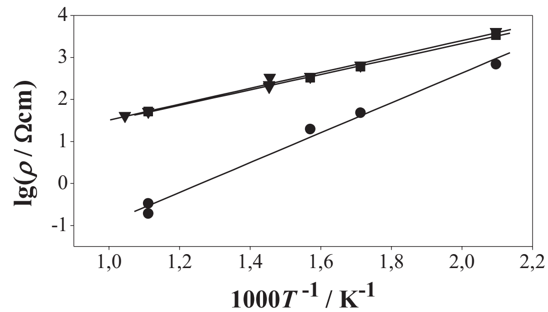

Fig. 5. Arrhenius plots for dense BCY15: (●) grain boundaries (E_a=0.71eV); (■) bulk (E_a=0.36eV) and (▼) total (E_a=0.37eV).

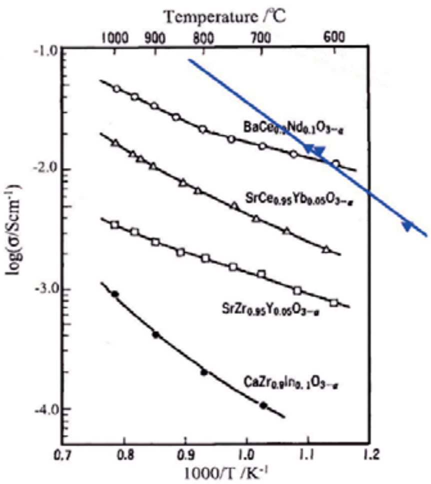

Fig. 6. Comparison of the BCY15 proton conductivity (▼) with data from the literature.

The comparison of the results, obtained for the BCY15 proton conductivity using the literature data, demonstrates the good quality of the developed material [11–13] (Fig. 6).

The results obtained on CM half cells in a single gas atmosphere were used for quantitative estimation of the effect of the pores and the presence of the second phase on the resistivity of every electrolyte phase. This estimation does not take into account the influence of the water vapor formation and evacuation. The DIA procedure was successfully applied for estimation of both, the bulk and the grain boundary resistivity.

The grain boundary contribution was determined from the $\hat{R}$-temporal plot, although the contribution of the bulk is invisible in the Z-plot (Fig. 7 a). The first plateau in the $\hat{r}_{ad}$-plot, which gives the sum of R_b and R_{gb}, ensured its estimation (Fig. 7b).

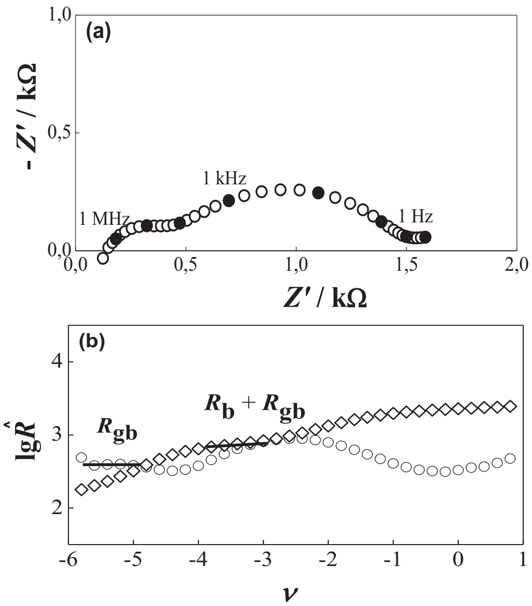

Fig.7. Complex plane impedance diagram and corresponding DIA plots for measurements of symmetric half cell Ag/CM/Ag at 300 ^{O}C in hydrogen: a) Z-plot; b) $\hat{r}_{ad}$ (◊) and $\hat{R}$ (○) temporal plots.

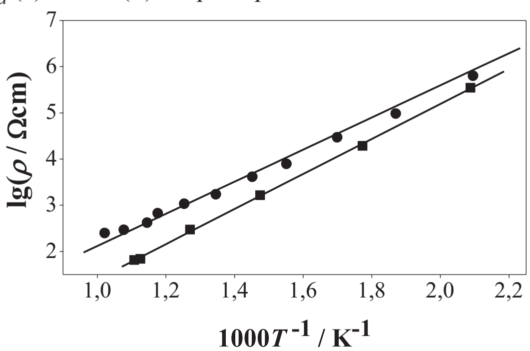

Fig. 8. Arrhenius plots for CM: (■) in H_2: total E_a=0.74 eV; (●) in O_2: total E_a=0.70 eV

The corresponding Arrhenius plots summarize the obtained results (Fig. 8). As it could be expected, the resistivity of the CM is lower in the hydrogen due to the higher proton conductivity of BCY15.

CONCLUSIONS

The performed Differential Impedance Analysis of the proton conducting electrolyte BCY15 proved that it has stable performance in wet hydrogen atmosphere, which makes it desirable material for further application as a proton conductor in the hydrogen compartment and in the central membrane. The obtained results for the central membrane are very promising. They will be used for its further optimization by deeper insight into the effect of composition and microstructure on the electrochemical performance.

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ДИФЕРЕНЦИАЛЕН ИМПЕДАНСЕН АНАЛИЗ НА $BaCe_{0,85}Y_{0,15}O_{2,925}$

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(Резюме)

В това изследване е приложена техниката на диференциалния импедансен анализ (ДИА) за охарактеризиране на протонно проводимия материал $BaCe_{0,\ 85}Y_{0,\ 15}O_{2,\ 925}$ (BCY15), с цел използването му в нова двойно мембранна горивна клетка. Експериментите са проведени в симетрична полу-клетка със Ag-електроди. Импедансните измервания са проведени в температурния интервал 200 - 700°C. Комбинацията от ДИА и корекцията за паразитна индуктивност и съпротивление (*L*-корекция) осигурява добро разделяне на проводимостта дължаща се на обема и границите на зърната. Сравняването на резултатите получени за протонната проводимост на BCY15 с данни от литературата показва доброто качество на разработения материал.