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Differential impedance analysis of the cathode compartment in dual membrane fuel cell

G. Raikova*, D. Vladikova, Z. Stoynov

Institute of Electrochemistry and Energy Sources, Bulgarian Academy of Sciences, Acad. G. Bonchev St, building.10, 1113 Sofia, Bulgaria

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The cathode/electrolyte LSCF48/YDC15 couple is a building block of a new innovative and competitive design of a high temperature fuel cell, operating in the range between 600 and 700°C. It is based on the idea for a junction between a proton conducting SOFC (PCFC) anode/electrolyte part and a SOFC cathode/electrolyte part through a mixed H^+ and O^{2-} conducting porous ceramic membrane. Thus, in this concept, hydrogen, oxygen and water are located in three independent chambers, which allows for avoidance of gases dilution with water. The applicability of different technologies (tape casting and plasma spraying) for the cathode deposition is analyzed in this paper using the Differential Impedance Analysis (DIA). A two step reaction mechanism of oxygen reduction is recognized. The rate-limiting step is the transport of oxygen ions in the volume of the electrode towards the electrolyte. A higher degree of frequency dependence is registered for the plasma spraying deposition technology.

Key words: dual membrane fuel cell, symmetrical electrolyte supported half cell, Differential Impedance Analysis, tape casting, plasma spraying

1. INTRODUCTION

The electrochemical impedance spectroscopy (EIS) is an important tool for solid oxide fuel cell (SOFCs) studies since it is sensitive to sample configuration and fabrication quality, including adhesion between layers and mechanical stability. Therefore, it was chosen for testing of materials and components in an innovative and competitive design of high temperature fuel cell, named „IDEAL-Cell“ after the acronym of the FP7 European project „Innovative Dual mEmbrAne fueL-Cell“[1,2]. The new concept is based on the idea for isolating the formation of the exhaust water in a separate chamber. For this purpose a junction of mixed conducting porous layer between a proton-conducting anode/electrolyte part (hydrogen compartment) and an oxygen-conducting electrolyte/cathode part (oxygen compartment) is introduced. Protons, created at the anode, progress towards the central membrane, where they meet the oxygen ions, created at the cathode. The produced water is evacuated through the pores of the central membrane and thus it does not dilute the two gases as it is in the conventional SOFC and PCFC [1, 2].

This work presents conductivity studies of the oxygen compartment LSCF48/YDC15 couple, applying different technologies for deposition of the electrodes: tape casting and plasma spray. The measured impedance data are analyzed by the technique of the Differential Impedance Analysis (DIA) - an advanced method, which increases the information potential of the impedance data analysis, since it extracts the impedance model structure directly from the experimental data without a preliminary working hypothesis [3-5].

2. EXPERIMENTAL

The investigations were performed on symmetrical electrolyte supported half cells LSCF48/YDC15/LSCF48 [$La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}/Ce_{0,85}Y_{0,15}O_{2-\delta}/La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$]. The electrolyte pellet was prepared by cold pressing and sintering. Electrodes with thickness of 15 to 50 µm were deposited by tape-casting (TC) and plasma spraying (PS).

The impedance measurements were performed on Solartron 1260 FRA over frequency range of 1MHz – 0.1Hz with density of 5 points per decade in a temperature interval of 100-800°C. The wide temperature range ensures impedance characterization of both, the electrolyte and the electrode. For improved data quality potentiostatic and galvanostatic regimes with different amplitudes were applied, depending on the cell impedance [6]. A procedure for correction of the parasitic errors

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* To whom all correspondence should be sent:
E-mail: graikova@bas.bg

coming from the testing cell rig was used for more accurate estimations [3, 7].

3. RESULTS AND DISCUSSION

3.1. Analysis of the electrolyte behavior

The performed DIA analysis of the electrolyte behavior recognizes Voigt's model structure with 2 time-constants, i.e. with 2 meshes with R and C in parallel connection which correspond to the bulk and grain boundary behavior (Fig.1).

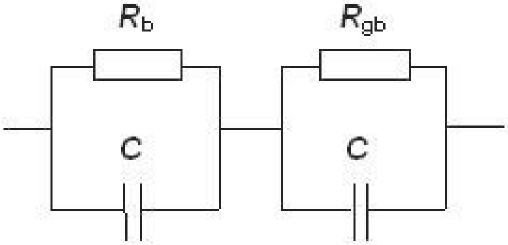
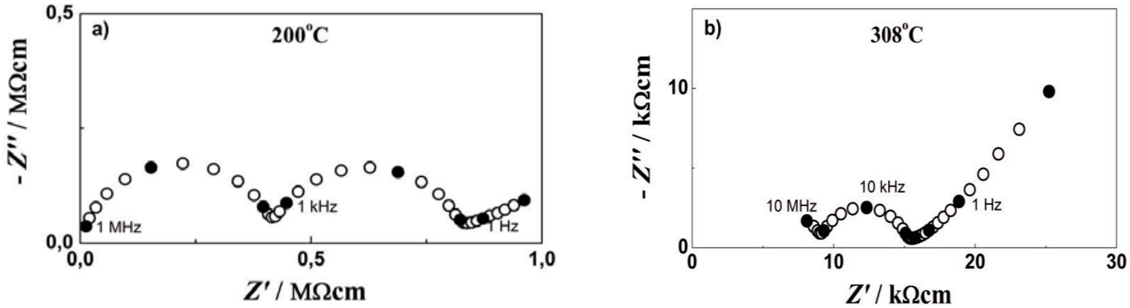


Fig.1. Voigt's model description of the electrolyte behavior extracted from the experimental data by DIA.

The application of the procedure for correction of the measurement rig parasitic inductance and resistance in combination with DIA ensured their separation to up to 500°C, precise structural and parametric identification, and calculation of the corresponding activation energies (Figs. 2,3). It was found that YDC15 has resistivity similar to that of the electrolyte materials, developed for application at intermediate temperatures (Fig. 4).

Both bulk and grain boundary conductivities have similar activation energy, which confirms the formation of clean grain boundaries and good contacts. Their resistivity is also in the same range which is an evidence for the high quality of the shaping technology (Fig. 3). The TC procedure for LSCF deposition does not influence the electrolyte behavior



(a) (b)

Fig.2. Complex plane impedance diagrams of symmetrical half cell with electrodes deposited by TC at different temperatures.

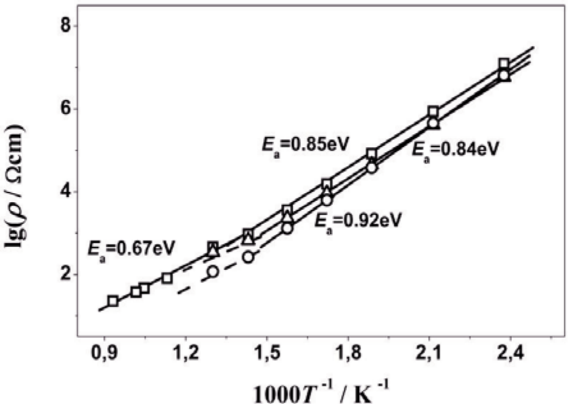


Fig. 3. Arrhenius plots for the bulk (Δ), grain boundary (○) and total (□) resistivity of YDC15 electrolyte.

The TC samples show good performance, stability, reproducibility and easy fabrication. The impedance of the half cell with electrodes, deposited by TC, has been chosen as an internal standard for evaluation of the oxygen compartment.

After PS deposition of the electrodes, DIA registered the appearance of strong frequency dependent behavior for the electrolyte grain

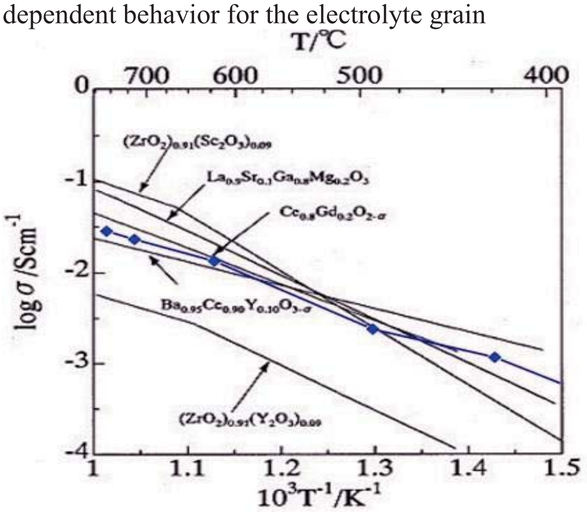


Fig. 4. Comparison of the YDC15 conductivity (Λ) with data from the literature [8].

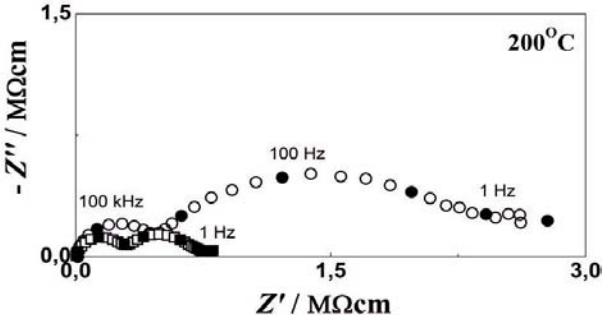


Fig. 5. Complex plane impedance diagrams of symmetrical half cells with LSCF48 electrodes deposited by PS on sand blasted YDC substrate: (○) without cleaning after sandblasting and (□) with cleaning after sandblasting.

boundaries, i.e. grain boundaries resistance with CPE character (Fig. 5). This impedance behavior is an indicator for increased inhomogeneity, caused by the PS deposition. It could be related to the sandblasting pretreatment which produces additional surface roughness and could introduce some impurities at the interface. After a deep cleaning with acetone followed by ultrasonic treatment for removing the possible impurities, this phenomenon disappeared. As it can be noticed in Fig. 5 that the grain boundary resistance becomes comparable with that of the same substrate, measured in a cell with TC deposited electrodes (Fig. 2a).

3.2. Analysis of the cathode reaction mechanism

As to the cathode reaction, the following steps were identified for both, the TC and the PS deposition (Fig.6): charge transfer step at high frequencies, followed by a step corresponding to transport limitations. The charge transfer step is very fast for the TC sample, and its value is negligible. The contribution of the charge transfer is bigger for the PS deposited electrodes - about 30–40% of the total resistance.

The transport limitations, which are the rate-limiting step in both cases, are presented with bounded constant phase element (BCP). It describes the impedance of a bounded homogeneous layer with CPE behaviour of the conductivity in the elementary volume and a finite conductivity at d.c [3 – 4, 9]:

$$Z_{\mathrm{BCP}}(\mathrm{i}\omega) = A^{-1}(\mathrm{i}\omega)^{-n}\,\mathrm{th}R_0A(\mathrm{i}\omega)^n \tag{1}$$

where A, n and R_0 are the structural parameters of the element.

For the TC samples the coefficient n is close to 0.5, i.e. the transport is close to diffusion, while for the PS samples it decreases to 0.2. The physical meaning of the low exponential coefficient corresponds to transport of species (oxygen ions) with restrictions in the host matrix. The bigger depression of the impedance arcs is usually connected with the bigger system inhomogeneity. This tendency is confirmed by the SEM images that show 2 types of structure in the PS deposited electrode layers (Fig. 7) - melted splats (Fig. 7a) and non-molten granulates (Fig. 7c).

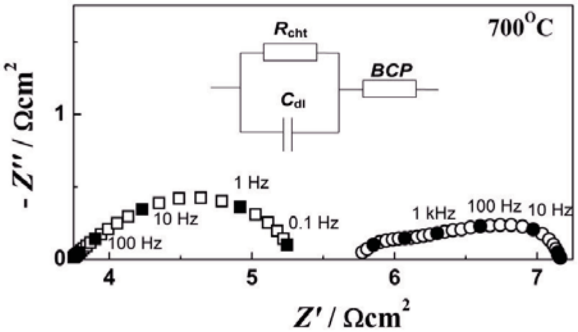


Fig. 6. Complex plane impedance diagrams of symmetric half cells LSCF48/YDC15/LSCF48 with electrodes deposited by TC (□) and PS (○) and corresponding equivalent circuit.

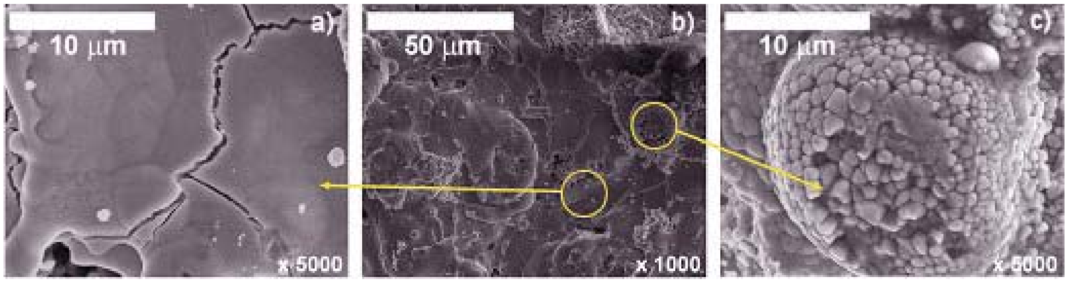


Fig.7. SEM images of plasma sprayed electrodes.

Table 1. ASR of LSCF48 electrodes deposited by tape casting and plasma spraying compared with data from the literature

Electrode Material	ASR at about 600 °C Ωcm^2	ASR at about 70 °C Ωcm^2
LSCF48 (Tape casting)	3.80 (623 °C)	0.360-0.400(725°C)
LSCF48 (Plasma spraying)	4.90 (615 °C)	0.800 (715 °C)
BSZF ($Ba_{0.50}Sr_{0.50}Zn_{0.20}Fe_{0.80}O_{3-\delta}$) [9]	4.87	0.716
BSZF-GDC [9]	3.29	0.373
BSZF-GDC-Ag [9]	2.47	0.278
LSCN [10]	-	0.132 (750 °C)
($Sm_{0.60}Sr_{0.20}$)CoO_3-CYO-Ag [11]	7.10	0.900
($La_{0.60}Sr_{0.20}$)CoO_3-CGO-Ag [11]	0.830	0.190

The obtained results for the ASR of LSCF electrodes deposited by both techniques are competitive with the results from the literature (Table 1).

4. CONCLUSIONS

The DIA analysis ensured deeper insight into the electrochemical behavior of the applied materials and deposition technologies for the oxygen compartment of the dual membrane fuel cell. The YDC15 electrolyte has good conductivity, stability and reproducibility, which makes it appropriate for further application. The applied LSCF electrode materials ensure cathode layers with good electrical properties.

The conductivity of the cathodes, deposited by the investigated techniques, shows that they are competitive, with slightly better performance and good reproducibility for the tape casting.

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ДИФЕРЕНЦИАЛЕН ИМПЕДАНСЕН АНАЛИЗ НА КАТОДНИЯ ЕЛЕМЕНТ НА ДВОЙНО-МЕМБРАННА ГОРИВНА КЛЕТКА

Г. Райкова*, Д. Владикова, З. Стойнов

Институт по електрохимия и енергийни системи, Българска академия на науките,
ул. „Акад. Г. Бончев” бл. 10, 1113 София

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(Резюме)

Комбинацията катод/кислород проводящ електролит на базата LSCF48/YDC15 е използвана като градивен елемент на нов, иновативен и конкурентен дизайн на високо-температурна горивна клетка, работеща в интервала 600-700 °C. В основата на идеята е свързването на анод/електролитната част на протон проводяща твърдоокисна горивна клетка (PCFC) с катод/ електролитната част на класическа клетка (SOFC) чрез пореста керамична мембрана със смесена H^+ и O^{2-} проводимост. По този начин водородът, кислородът и водата са разположени в три самостоятелни камери, което дава възможност да се избегне разреждането на двата газа с водата. В настоящата статия с помощта на диференциалния импедансен анализ (ДИА) са изследвани възможностите за отлагане на катода чрез различни технологии (лентово отливане и плазма-спрей). Установено е, че кислородната редукция протича като двустъпков процес. Скоросто-определящата стъпка е транспортирането на кислородни йони в обема на електрода. При плазма-спрей отлагането е регистрирана по-висока степен на честотна зависимост.