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Impedance studies of porous electrolyte with mixed ion conductivity

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In this study mixed ion conductivity of a composite material based on proton conducting $BaCe_{0,85}Y_{0,15}O_{2,925}$ (BCY15) and oxide ion conducting $Ce_{0,85}Y_{0,15}O_{1,925}$ (YDC15) electrolytes has been investigated by Electrochemical Impedance Spectroscopy in relation to its application as a membrane (named central membrane CM) in an innovative design of a high temperature Dual Membrane Fuel Cell (DMFC). One of the most important advantages of the new architecture is the separation of hydrogen, oxygen and exhaust water in three independent chambers. The key-point of the DMFC development is the design and fabrication of the porous CM, which has to combine high mixed ion (proton and oxide ion) conductivity with sufficient porosity necessary for the evacuation of the water produced in this layer. In order to understand and evaluate the processes taking place in the CM, impedance studies were carried out and presented in this work. The obtained results show that a composite central membrane with 50 v % BCY15 and 50 v % YDC15 and porosity about 35-40 % obtained by addition of pore former (graphite) could be used for the fabrication of the first (Proof of the Concept) generation Dual Membrane Fuel Cell.

Keywords**:** Impedance Studies, BCY15, YDC15, Composite Electrolyte, Central Membrane.

INTRODUCTION

The classical solid oxide fuel cell (SOFC) is a high temperature device, that converts the chemical energy of fuel directly in electricity and heat. The oxide ions diffuse through the solid electrolyte toward the anode where they react with the hydrogen and produce water and electricity (Fig.1 a). The basic disadvantage of this concept is that water dilutes the fuel and inhibits the catalytic activity of the electrode.

The second existing concept is that of the proton conducting solid oxide fuel cell (PCFC). Here the reaction takes place on the cathode side (Fig.1 b) and thus the fuel dilutes the oxidizing gas. In addition the produced water is very aggressive and causes severe corrosion problems.

Recently a new concept named Dual Membrane Fuel Cell has been developed [1-4]. It combines the advantages and eliminates the disadvantages of both SOFC and PCFC in respect to the water formation. The main idea consists in joining the anode part of a PCFC with the cathode part of a SOFC by means of a central membrane where the water is produced and evacuated (Fig. 1 c). Thus the cell consists of three independent chambers for hydrogen, oxygen and water which could be separately optimized.

The key factor for the performance of the new concept is the central membrane, which has to ensure high anionic and protonic conductivities in the presence of sufficient porosity. The proper connectivity among the different phases (proton conductor, oxide ion conductor, open porosity for water evacuation), should avoid tortuous and/or resistive paths. Moreover, both solid phases (BCY15 and YDC15) must percolate towards their respective electrolyte, and porosity must percolate towards the outside of the cell for water evacuation. Thus each triple phase boundary (TPB) segment should be connected to both electrolytes.

The aim of this study is impedance characterization and optimization of the CM which has to combine high proton and oxide ion conductivity, thermochemical and mechanical stability and porosity needed for the evacuation of the water.

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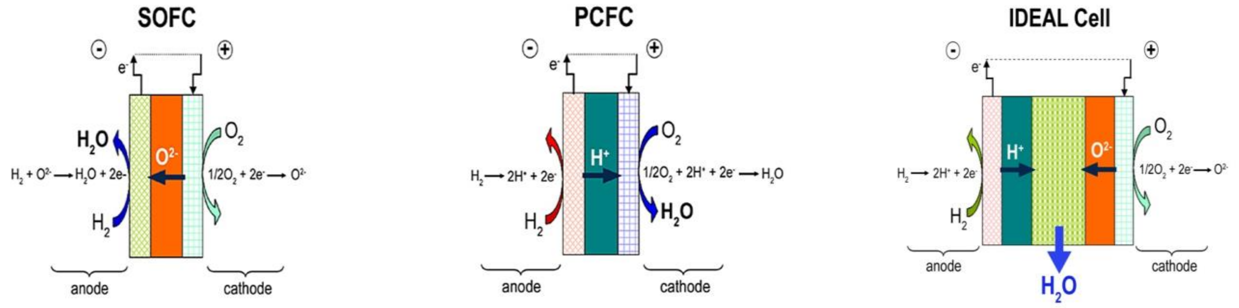


a) **b)** **c)**

Fig. 1. Representation of: **a)** SOFC design, **b)** PCFC design and **c)** IDEAL-Cell concept.

EXPERIMENTAL

The mixed conductivity of the CM has been ensured by the design of a composite based on proton conducting $BaCe_{0,85}Y_{0,15}O_{2,925}$ and oxide ion conducting $Ce_{0,85}Y_{0,15}O_{1,925}$. Preliminary tests determined a composition of 50 % BCY15 and 50 % YDC15. For the performance of impedance studies a new type of electrolyte supported symmetrical half cell with metal electrodes: $Pt/(BCY15+YDC15)_{porous}/Pt$ and $Ag/(BCY15+YDC15)_{porous}/Ag$ was introduced. Graphite and starch (2 - 7 wt %) were used as pore former. The composite electrolytes were sintered at temperatures 1300-1350°C.

The impedance measurements were performed on Solartron 1260 Frequency Response Analyzer in temperature interval 100 - 800°C in a frequency range from 10 MHz down to 0,1 Hz and density of 5 points/decade. They were carried out 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 [4].

An original moment in this study is the performance of the measurements in O_2 and in H_2. A correction of the parasitic inductance and resistance of the measurement rig has been also applied [5, 6]. As it can be seen in Fig. 2, at higher temperatures, the errors coming from the parasitic elements can reach 30 %.

RESULTS AND DISCUSSION

For evaluation of the YDC15 and BCY15 conductivity, measurements of half cells with dense electrolyte support obtained in the absence of pore former and sintering temperatures respectively 1350 and 1450°C were performed. The comparison of the obtained results with data from the literature [7, 8] shows that the conductivity of YDC15 is similar to that of the commonly applied oxide ion conductors (Fig. 3 a). BCY15 enters in the group of the best proton conductors (Fig. 3 b).

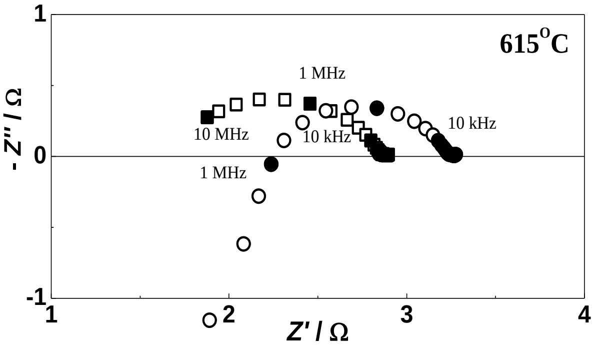
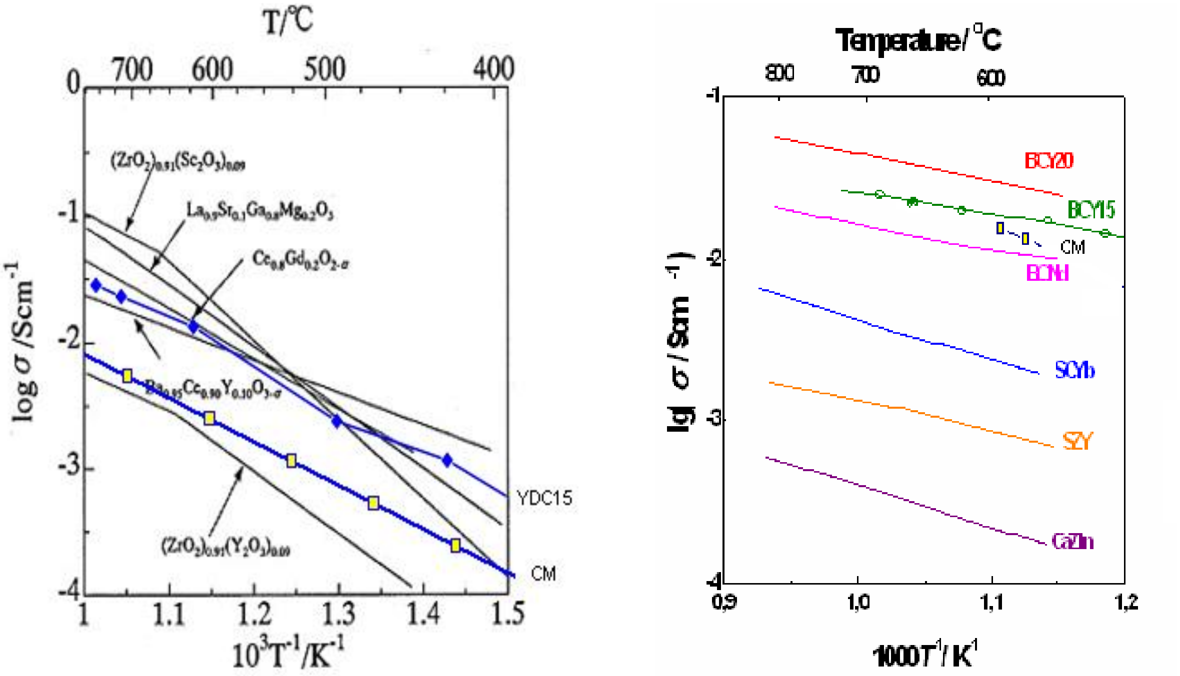


Fig. 2. Complex plane impedance diagrams of Pt/CM/Pt half cell before (●) and after (■) correction of parasitic resistance and inductance.

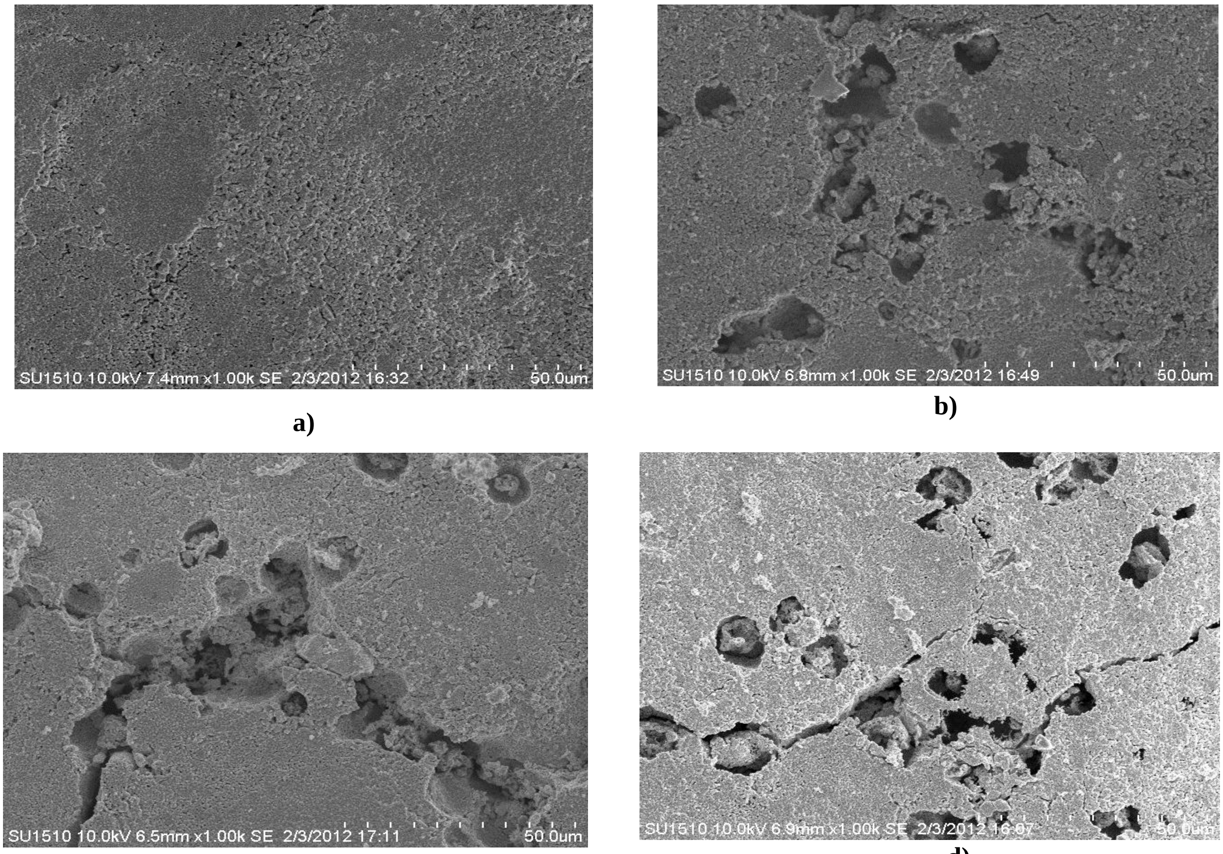
The application of starch and graphite as pore formers influenced the microstructure of the composite CM. The results obtained by Scanning Electron Microscopy (SEM) showed that starch caused big cracks which made the samples mechanically fragile. The addition of 2 - 3 % graphite ensures mechanically stable structures with sufficient porosity (Fig. 4).

As already mentioned the impedance measurements of the CM were performed in O_2 and H_2. The data obtained in oxygen ensure information about the conductivity of the YDC15 phase in the real structure, i.e. in the presence of the proton conducting phase and the pores. Measurements in hydrogen separate the conductivity of the proton conducting BCY15 phase. The Arrhenius plots of the CM with different porosity are presented in Fig. 5. Logically the results show that the increase of the porosity leads to decrease of the conductivity. This effect is more pronounced for the proton



a) **b)**

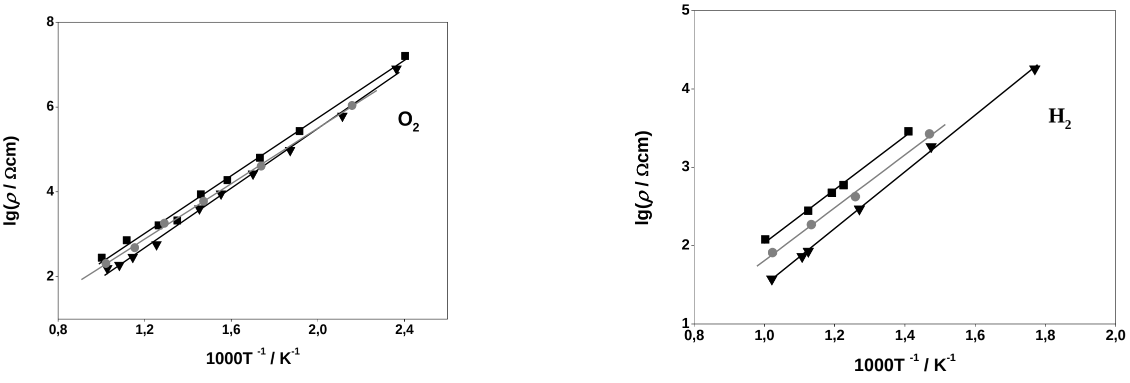
Fig. 3. Comparison of the conductivity of: **a)** dence YDC15 and YDC15 in composite CM with 30% porosity (□) with data from the literature for oxide ion conducting electrolytes [7], **b)** dence BCY15 and BCY15 in composite CM with 30 % porosity (□) with data from the literature for proton conducting electrolytes [8].



a) **b)**

c) **d)**

Fig. 4. SEM micrographs of central membrane with different microstructures: **a)** without pore former, grain size 1-2 μm; **b)** 2 % graphite, grain size 1-5 μm; **c)** 5 % starch, grain size 1-3 μm; **d)** 7 % starch, grain size 1-3 μm.



a) **b)**

Fig. 5. Arrhenius plots for CM with different porosity**:** (■) 42 %, (●) 35 %, (▼) 28 %:**a)** in O_2, **b)** in H_2.

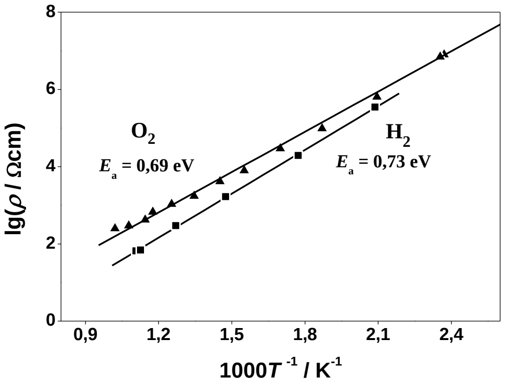


Fig. 6. Arrhenius plots for CM in O_2 and in H_2 atmosphere.

conducting phase which, however, has higher conductivity (Fig. 6), confirmed also by measurements of dense BCY15 and YDC15 samples (Fig. 3 a, b). The comparison of the conductivities for the two ceramic phases in the porous composite CM with data from the literature obtained for dense materials shows that the registered conductivities for samples with 30-40 % porosity are in the frames characteristic for the applied electrolyte materials (Fig. 3 a, b). Thus for composite central membranes with 50 v % BCY15 and 50 v % YDC15 and porosity 30-40 % obtained by graphite pore former good compromise between conductivity and porosity is obtained.

CONCLUSIONS

The impedance studies of the new functional CM layer of the innovative DMFC concept ensured the design and fabrication of appropriate membrane combining sufficient mixed ion conductivity with optimal porosity and good mechanical and thermal stability. It was used for the construction of the first model cell with which the new concept was successfully proved [4, 9].

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ИМПЕДАНСНО ИЗСЛЕДВАНЕ НА ПОРЕСТ ЕЛЕКТРОЛИТ СЪС СМЕСЕНА ПРОВОДИМОСТ

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(Резюме)

В настоящата статия с помощта на Електрохимична импедансна спектроскопия е изследвана смесената проводимост на композитен материал, състоящ се от протон проводящ $BaCe_{0,85}Y_{0,15}O_{2,925}$ (BCY15) електролит и кислород проводящ $Ce_{0,85}Y_{0,15}O_{1,925}$ (YDC15) електролит, с цел използването му като мембрана (т.н. централна мембрана - ЦМ) в нов дизайн на високотемпературна горивна клетка (ДМГК). Едно от най-важните предимства на новия дизайн е разделянето на водорода, кислорода и водата в три отделни, независими една от друга камери. Ключов момент в разработването на ДМГК е създаването на ЦМ, която трябва да комбинира висока смесена (протонна и кислородна) проводимост и оптимална пористост необходима за отвеждането на формираната в мембраната вода.

Представени тук импедансни измервания са извършени с цел да се разберат и оценят процесите които протичат в ЦМ. Получените резултати показват, че композитна ЦМ със състав 50 v % BCY15 и 50 v % YDC15 и пористост 35-40 % (получена с порообразовател графит) може да се използва за получаването на първа генерация ДМГК, което потвърждава валидността на новата концепция.