



# CARACTERIZĂRI STRUCTURALE ȘI MICROSTRUCTURALE LA INTERFAȚA CATOD/ELECTROLIT/ANOD ÎN CELULA DE COMBUSTIE CU ELECTROLIT SOLID<sup>▲</sup>

## STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION AT THE CATHOD / ELECTROLYTE / ANODE INTERFACE IN SOLID ELECTROLYTE FUEL CELL

GEORGETA VELCIU<sup>1,2\*</sup>, CRISTIAN ȘEITAN<sup>1</sup>, ALINA DUMITRU<sup>1</sup>, VIRGIL MARINESCU<sup>1,3</sup>, MARIA PEDA<sup>2</sup>,  
ALINA MELINESCU<sup>2</sup>

<sup>1</sup>Institutul Național de Cercetare-Dezvoltare pentru Inginerie Electrică ICPE-CA, Splaiul Unirii nr.313, sector 3, 030138, București, România

<sup>2</sup>Universitatea POLITEHNICA București, Splaiul Independenței nr. 313, sector 6, 060042, București, România

<sup>3</sup>Universitatea din București, Bd. M. Kogălniceanu nr.36-46, sector 5, 050107, București, România

*Solid electrolyte fuel cells (SOFC), the cleanest sources of electricity generation, are formed of three main components: solid electrolyte, cathode and anode. The cathode and anode (electrodes) are activation support of electrochemical reactions and transporting charge carriers, electrons and partly or totally ions. With electrolyte forms a triple interface "gas - electronic solid - solid ionic" that changes abruptly the conduction mechanism from electronic (TPB - Triple Phase Boundary) to ionic. The study of processes taking place in the TPB in a solid electrolyte fuel cell is important for optimization of electrochemical reactions. This paper presents the structural and microstructural characteristics of interfaces cathode / electrolyte / anode in a fuel cell with solid electrolyte with following ceramic components: solid electrolyte on CeO<sub>2</sub> based with addition of calcium oxide and yttrium oxide, cathode of perovskite type based on lanthanum manganite doped (LSM) with strontium and anode a cermet from cerium oxide doped with gadolinium (Ni-CeGd). Mineralogical composition of components used for the fuel cell was performed by X-ray diffraction. Its microstructure was determined by electron microscopy, and the distribution of chemical elements at interfaces cathode / electrolyte and anode / electrolyte was examined by EDX. Cathode and anode surface condition was examined by AFM. The results show a good adhesion of the layers used as electrodes on solid electrolyte support.*

*Celulele de combustie cu electrolit solid (SOFC), cele mai curate surse de generare a energiei electrice, sunt constituite din trei componente principale: electrolitul solid, catodul și anodul. Catodul și anodul (electrozii) reprezintă suportul activării reacțiilor electrochimice și asigură transportul purtătorilor de sarcini, total pentru electroni și parțial pentru ioni. Împreună cu electrolitul formează o interfață triplă „gaz – solid electronic – solid ionic”, la nivelul căreia mecanismul de conducție se schimbă brusc de la ionic la electronic (TPB – Triple Phase Boundary). Studiul proceselor care au loc la nivelul TPB într-o celulă de combustie cu electrolit solid este important în vederea optimizării reacțiilor electrochimice. În lucrare sunt prezentate caracteristicile structurale și microstructurale ale interfețelor catod/electrolit/anod realizate într-o celulă de combustie cu electrolit solid cu următoarele componente ceramice: electrolitul solid pe bază de CeO<sub>2</sub> cu adaosuri de oxid de calciu și de oxid de ytriu, catodul de tip perovskit pe bază de manganit de lantan impurificat cu stronțiu (LSM), iar anodul un cermet pe bază de Ni și oxid de ceriu impurificat cu gadolinium (Ni-CeGd). Prin difracție de raze X s-a determinat compoziția mineralogică a componentelor utilizate pentru realizarea celulei de combustie. Textura acestora s-a determinat prin microscopie electronică, iar distribuția elementelor chimice la interfațele catod/electrolit și anod/electrolit s-a examinat prin EDX. Starea suprafețelor catodului și anodului s-a examinat prin AFM. Rezultatele arată o aderență bună a straturilor de electrozi la electrolitul solid folosit ca suport.*

**Keywords:** SOFC, cathode, electrolyte, anode, microstructure

### 1. Introduction

Solid electrolyte fuel cells (SOFC) are electrochemical systems for direct conversion of chemical energy of a fuel into electrical energy at high temperature. They consist of a solid electrolyte, two electrodes anode and respectively cathode and interconnect. The SOFC have all the

ceramic components operating at high temperatures, generally around 900-1000°C. Current trends aimed at reducing operating temperature of the fuel cell and the cells are made of ceramic and metal components (interconnect) and works in the 500-800°C (IT-SOFC). A decisive factor for these cells is to increase activity of electrodes and especially of cathode [1-3].

\* Autor corespondent/Corresponding author,  
Tel.: +4 0213467231,3467235, e-mail: gvelciu@icpe-ca.ro

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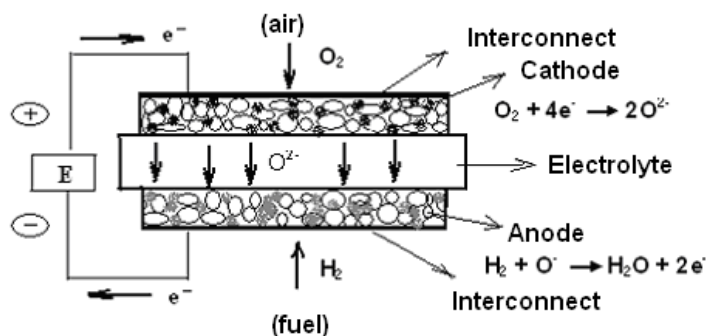


Fig. 1 - The reactions that occur in the operation of a fuel cell.  
Reacțiile care au loc la funcționarea unei celule de combustie.

Solid electrolyte is a dense ceramics with selective conductivity by oxygen ions and free of electronic conductivity. It can be used as support of electrodes to obtain a fuel cell. The cathode and anode respectively should be mixed conductivity, both ionic and electronic. Also to manifest as a catalyst for electrochemical reactions of reduction and oxidation that develops at functioning cell as shown in Figure 1. Fuel cells operate with a wide variety of fuels (hydrogen, methane, natural gas, etc.) with an energy efficiency of up to 70% and can be considered clean power sources [4-5].

At cathode the oxygen's reacts with electrons and oxygen ion became which then moves through solid electrolyte towards the anode. It's displacement is favored by the presence of oxygen vacancies in solid electrolyte that moving in the opposite direction.

Electrochemical oxidation of fuel occurs at the anode with releasing electrons entering the external circuit. In order to achieve fuel cell operating to low temperature are used as solid electrolyte, ceramics based on solid solutions of cerium dioxide with divalent or trivalent oxides. In order to be conductive by oxygen ions, cerium dioxide is doped with the elements valence  $2^+$  or  $3^+$ , in particular rare metal ions, which substitute  $Ce^{4+}$  ion in network. Due to the difference in valence between cerium ions and used doping oxides in the network appear oxygen vacancies, which should compensate the absence of positive charge, which lead to increased mobility of oxygen ions. Oxides usually used for doping are  $CaO$ ,  $Y_2O_3$ ,  $Gd_2O_3$ ,  $Sm_2O_3$ ,  $Nd_2O_3$ , etc. [6-9]. These materials compared to solid electrolyte  $ZrO_2$ -based, traditionally used for fuel cells, have the electrical conductivity by oxygen ions of the same order of magnitude but at lower temperature.

Ceramic materials used for cathodes are perovskites with the formula  $ABO_3$  being used especially  $LaMnO_3$  and  $LaCoO_3$ . They have good catalytic properties and electrical conductivity appropriate. Material properties can be improved by partial substitution of cations. In  $LaMnO_3$ , the controlled substitution of lanthanum with  $Sr^{2+}$  or  $Ca^{2+}$  lead to formation of electronic defects localized in manganese [10-11]. A typical material with electronic conductivity is composition of perovskite type. A typical material with electronic

conductive is composition  $La_{1-x}Sr_xMnO_3$  perovskite type, which is non-stoichiometric and induce defects in the crystal lattice. These defects are compensated by changing the valence of manganese and where the anions are in excess  $Mn^{4+}$  occurs. Simultaneous presence of ions  $Mn^{4+}$  and  $Mn^{3+}$  in the network of manganites lead to complex electronic transitions, which depend on the partial pressure of oxygen, heat treatment, and the homogeneity of composition [12-13].

Anode or fuel electrode must have mixed conductivity, mainly electronic and is generally a cermet consist of nickel and yttrium-stabilized zirconia (YSZ) [14-16].

An important role they have solid electrolyte interfaces/electrodes because they must ensure a adequate mechanical adhesion of layers and good chemical stability that does not lead to changes in mechanical or electrical properties during cell operation [17-21].

In this paper we have studied the structure and microstructure of interfaces cathode/electrolyte and anode/electrolyte for solid electrolyte fuel cell based on cerium dioxide.

## 2. Experimental

Components electrolyte, cathode and anode for the fuel cell used were obtained by solid phase reactions starting by high purity oxides and carbonates. It was used for the electrolyte a composition of the ternary system  $CaO-Y_2O_3-CeO_2$  proportions of calcium oxide and yttrium trioxide being equal to 5%. After homogenization we were obtained from powder pellets with a diameter of 20 mm and a height of 2 mm at 200 daN/cm<sup>2</sup> pressure. The samples were heat treated at 1350 and 1400°C with a plateau of two hours at maximum temperature. Details about how to obtain electrolyte are presented in [9].

Ceramic powder for the cathode  $La_{0.45}Sr_{0.55}MnO_3$  (LSM) was obtained starting from the composition  $LaMnO_3$ , when lanthanum with the strontium was replaced. The raw materials used were  $La_2O_3$ ,  $SrCO_3$ ,  $MnCO_3$  and homogenization of mixtures was made by wet route for 6 hours. After drying at 105°C, the powder was granulated, lighters and then calcined at 1000°C with a plateau of two hours. After calcination the material was

milled for 16 hours in a moist ball mill. The obtained powder was used to prepare the slurry for the cathode. Ceramic powder for obtain CeGd Ni-type anode was prepared by the method presented in [16] and was used to achieve the anode slurry. Recipe used to deposit of electrodes (anode and cathode) is presented in Table 1.

Table 1

Recipe of slurry used for deposit of electrodes <i>Reteta suspensiei utilizată pentru depunerea electrozilor</i>	
Components <i>Componente</i>	%grv
Ceramic powder <i>Pulbere ceramică</i>	55.40
Binder / <i>Liant</i>	16.60
Plasticizer / <i>Plastifiant</i>	4.90
Dispersant / <i>Dispersant</i>	23.10

Slurry used for deposition was prepared by mixing of ceramic powder with solvents (toluene and isopropyl alcohol) in the ratio 1:1. Homogenization was done together with a binder (polyvinyl alcohol molecular weight 60000), plasticizers (Triolein, Triton X) and a dispersant (Dibutyl phtalat 99% p.a. molecular weight 278.34). After complete homogenization, the suspension was used to achieve thin electrodes (cathode and anode). Suspension for obtaining of cathode was sprayed with a pistol airbrush on the support which is electrolyte. After drying in an oven at 220°C for 4 hours samples were sintered at 1070°C with a heating speed of 3°C/min and a plateau 2 hours. On the opposite side of the electrolyte was deposited powder of anode. After drying in an oven at 220°C for 4 hours, the samples were sintered with a speed heating of 3°C/min to 970°C with a plateau 2 hours.

Structural characterization of the samples was performed by X-ray diffraction using a diffractometer Bruker-AXS X-ray type D8 ADVANCE with radiation with  $\text{Cu}_{K\alpha}$ . Microstructure of interfaces cathode/electrolyte and anode/electrolyte was analyzed by electron microscopy (SEM) with a FESEM-FIB device, Auriga Workstation. Distribution of elements in the structure of components and at interfaces were analyzed using semiquantitative technique with a probe INCA Energy 250 EDX detector Si (Li) 30 mm cooled with liquid nitrogen. Surface topography of cathode and anode layers deposited on electrolyte was performed using atomic force microscopy (AFM type Veeco) analysis was made without contact-Tapping Mode).

### 3. Results and discussion

#### 3.1. Mineralogical composition

Identification of specific phases for components of studied cell thermal treated in their specific conditions was performed by X-ray diffraction. In Figure 2 are presented the XRD

spectra of solid electrolyte that was thermal treated at 1350 and 1400°C. It was found regardless of the firing temperature the presence of lines of solid solutions with fluorite structure type specific of cerium dioxide. This shows that calcium and yttrium oxides have penetrated into its network and the two cations have substitute  $\text{Ce}^{4+}$  ion.

In Figure 3 presented the X-ray spectrum of LSM cathode deposited on the electrolyte, and are observed the lines of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  solid solutions and a smaller proportion  $\text{MnO}_2$ . Diffraction lines for Ni-CeGd anode deposited on the electrolyte are shown in Figure 4 and found specific lines of solid solution  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.85}$  with a cubic network specific of anode and nickel metal.

#### 3.2. Study of cell interfaces

Cross-sections cathode/electrolyte and respectively anode/electrolyte were studied by electron microscopy SEM. In Figure 5 are electronic micrographs of interface cathode/electrolyte.

The SEM analysis (Fig.5,a.) found that solid electrolyte has a uniform and dense microstructure and LSM cathode layer adheres well to the electrolyte. Figure 5b showed characteristic microstructure of LSM cathode and

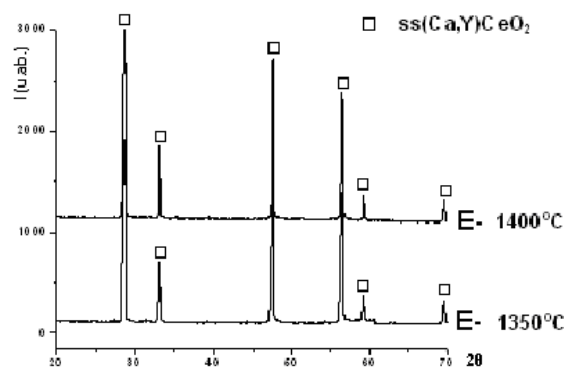


Fig.2 - Diffraction spectra for solid electrolyte of ternary system  $\text{CaO-Y}_2\text{O}_3\text{-CeO}_2$  depending on the sintering temperature / Spectrele de difracție pentru electrolitul solid situat în sistemul ternar  $\text{CaO-Y}_2\text{O}_3\text{-CeO}_2$  în funcție de temperatura de sinterizare.

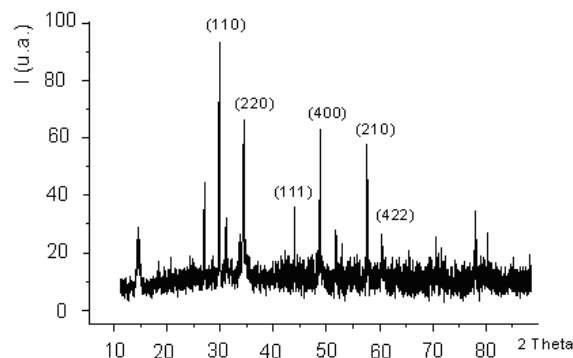


Fig. 3 - X-ray diffraction lines for cathode - LSM / Liniile de difracție de raze X pentru catodul - LSM.

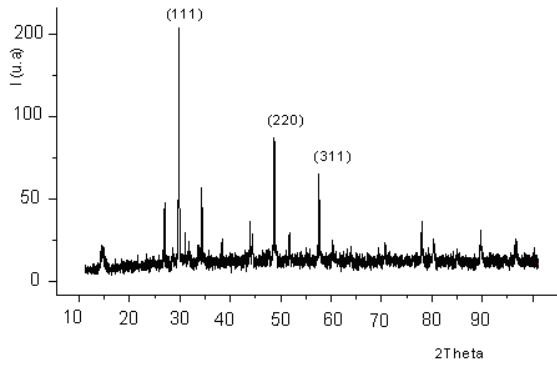
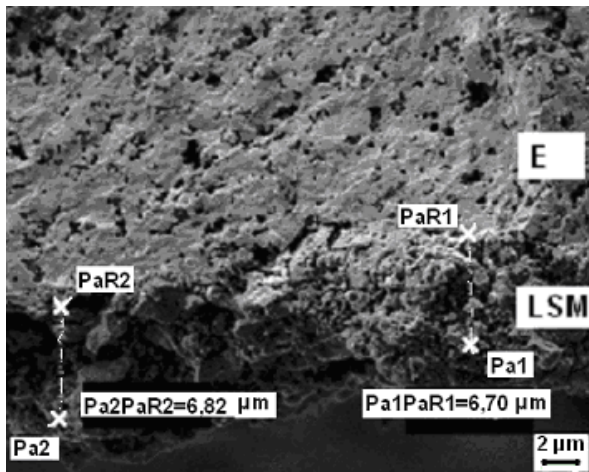


Fig. 4 - X-ray diffraction lines for the anode Ni-CeGd deposited on solid electrolyte / *Linii de difracție XRD pentru anodul Ni-CeGd depus pe electrolitul solid.*

noticing a grain size about 1µm. It also noted the presence of pore evenly distributed.

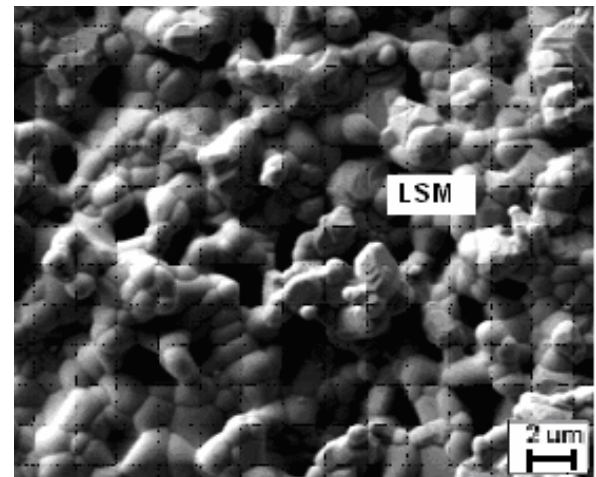
EDX quantitative analysis (fig.5.c, d) shows the variation of chemical elements at limit LSM



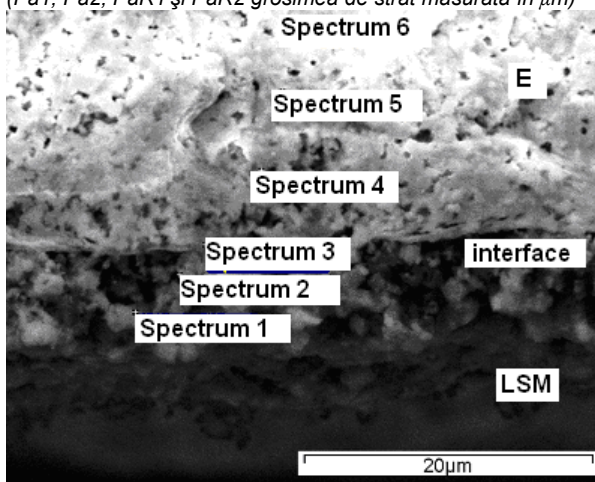
a. Cross section image (Pa1, Pa2, PaR1 and PaR2 is layer thickness measured in µm) /  *imaginea secțiunii transversale (Pa1, Pa2, PaR1 și PaR2 grosimea de strat măsurată în µm)*

cathode/electrolyte solid in sections indicated. Thus, it is seen from Fig. 5.d. that in sections 1 and 2 elements Sr, La and Mn from cathode are present and their proportion has decreased at Section 3. The third section is the boundary between electrolyte and cathode and is observed appearance of two elements cerium and calcium by diffusion from the electrolyte. Beyond this increases the proportion of cerium, which reaches the limit from solid electrolyte and also yttrium that is content in this component.

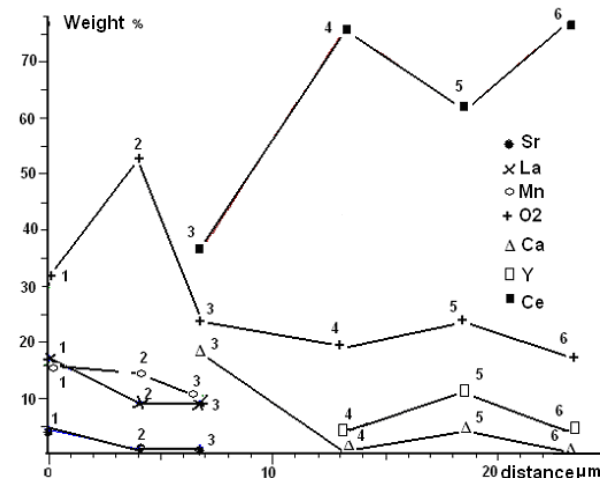
Electron microscopy performed on anode layer deposited on the solid electrolyte (Fig. 6.a.) heat treated at 1150°C, with two hours at maximum temperature, shows a porous texture and grains of different sizes (Fig.6.b). At the interface anode-electrolyte (Fig. 6.a.) it observed a layer of uniform thickness less variable comparative with cathode. There is no crack at the interface which means that there is mechanical compatibility between fuel cell components.



b. Characteristic microstructure of deposited cathode layer / *textură caracteristică stratului de catod depus*

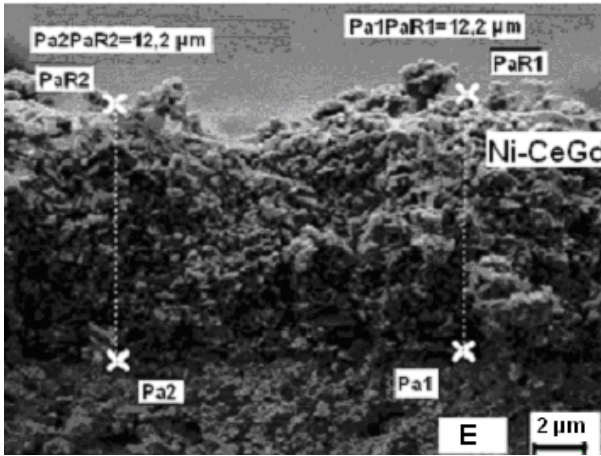


c. Sections for the study of the chemical composition / *secțiuni pentru studiul compoziției chimice*

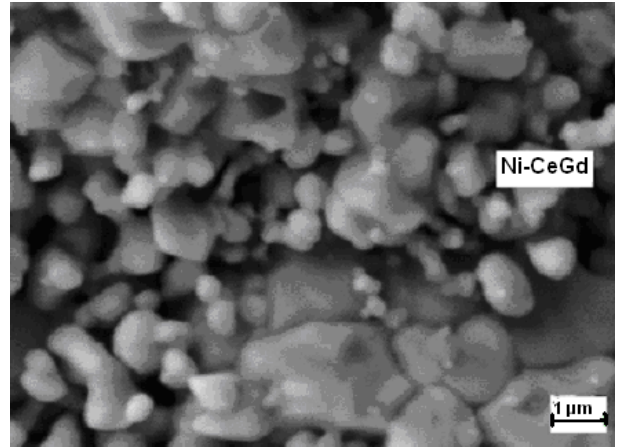


d. Variation of chemical elements at the cathode /  *variația elementelor chimice la interfața catod/electrolit*

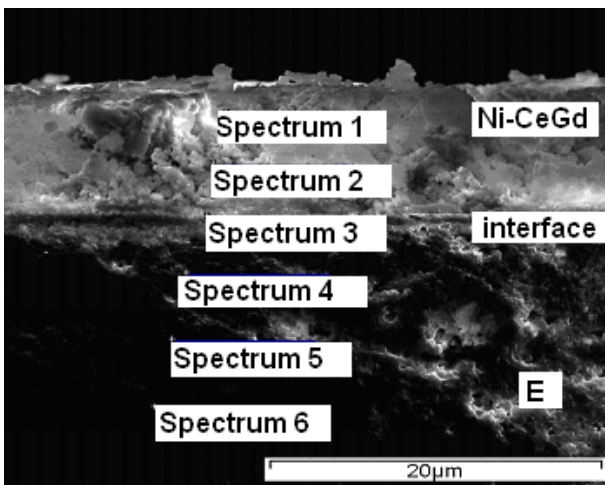
Fig. 5. Electronic micrograph of interface LSM cathode/electrolyte / *Micrografia electronică a interfeței catod LSM/electrolit/*



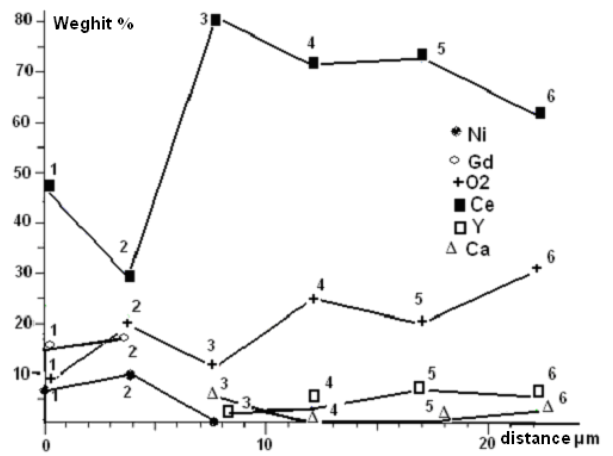
a. Section through the layer deposited (Pa1, Pa2, PaR1 and PaR2 are thickness of layers measured in μm) / secțiune prin stratul depus (Pa1, Pa2, PaR1 și PaR2 grosimea de strat măsurată în μm)



b. The characteristic microstructure of anode layer deposited / textură caracteristică stratului de anod depus

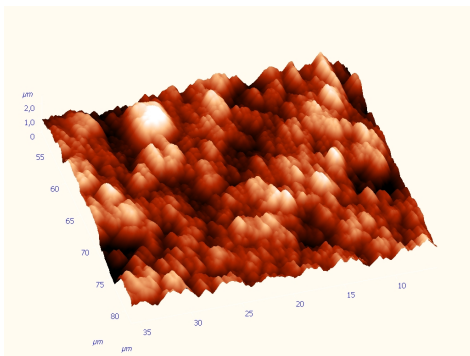


c. Sections for the study of the chemical composition / secțiuni pentru studiul compoziției chimice

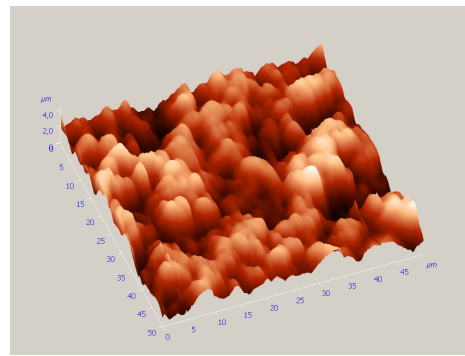


d. Electrolyt/ variation of chemical elements at the interface anode / electrolyte / variația elementelor chimice la interfața anod/

Fig.6 - Electronic micrograph of the interface anod/electrolyte / Micrografia electronică a interfeței anod/electrolit.



a. 3D topographic image of LSM cathode deposited on electrolyte / imagine topografică 3D a catodului LSM depus pe electrolit



b. 3D topographic image of Ni- CeGd anode deposited on electrolyte / imagine topografică 3D a anodului Ni- CeGd depus pe electrolit

Fig.7 - AFM images for interfaces cathode / electrolyte (a) and anode / electrolyte (b) / Micrografie AFM pentru interfațele catod/electrolit (a) și anod/ electrolit (b).

Analyze EDX (fig.6.c, d) in sections 1 and 2 show the presence of specific elements of anode and a diffusion of nickel in the solid electrolyte. Starting from section 3 to other sections was observed characteristic elements of solid electrolyte.

Morphology of surface of cathode and anode by AFM microscopy was characterized. Roughness average at cathode is 586.47 nm and at anode is 280.43 nm (Fig. 7).

#### 4. Conclusions

In this paper were examined structure and microstructure of interfaces cathode/ electrolyte / anode in a solid electrolyte fuel cell. The cathode is lanthanum manganites doped with strontium which was deposited on an electrolyte with a composition based on  $\text{CeO}_2$  with addition of calcium oxide and yttrium oxide. Interface anode/electrolyte, was analyzed, the anode being a Ni-based cermet and cerium oxide doped with gadolinium (Ni-CeGd). Deposits of electrodes, cathode and anode were obtained by spray and the results are similar to those obtained by other authors on materials comparable to those used by us [17,18]. XRD patterns of the two components confirm the formation of phase orthorhombic perovskite LSM type and specific phases of the cubic structure of Ni-cermet CeGd. Microstructural analysis shows degree of porosity of the cathode and anode and their chemical interaction with the electrolyte, which allows the use of these components to obtain fuel cell operating at intermediate temperature.

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