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RF assisted pulsed laser deposition of electrodes for YSZ based SOFCs

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NiO-YSZ anodes and CeO_2-PrO_2 cathodes dedicated to solid oxide fuel cells (SOFCs) based on YSZ electrolyte have been realized by pressing powders synthesized using self assembling method associated with hydrothermal treatment and by RF assisted Pulsed Laser Deposition techniques. The obtained materials have been characterized by XRD, XPS, AFM, SNMS and SEM techniques which revealed their structure, composition and morphology. The anode/electrolyte/cathode assemblies used in SOFC's based on thin films grown by RF-assisted PLD show superior electrocatalytic activity as compared to thick based SOFC in respect with the operating temperature (as low as 450 °C) and the fuel conversion efficiency.

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1. Introduction

The fuel cells technology has been intensively developed in the last years, as a great promise of future energetic economy, since the availability of fossil fuels is decreasing. The fuel cells based on solid oxide electrolyte present certain advantages related to their flexibility in using various fuels and the possibility of direct use of the natural gas by steam internal reforming which avoids external reforming and hydrogen storage [1-4]. Yttria stabilized zirconia (YSZ) material is a promising solution for electrolyte, while the most used anodic material for SOFC is the Ni/YSZ cermet due to its convenient properties and low cost [5].

The anode microstructure and thickness are characteristics which governs its efficiency in the fuel cell. Therefore, the nanostructured materials obtained by tailoring these characteristics during synthesis are of particular interest [10, 11]. The main research direction is oriented towards the development of synthesis techniques which would allow the decrease of the operating temperature below the actual range (600 – 800 °C - Intermediate Temperature - SOFC) and the use of dry hydrocarbons [12-14]. This would lead to more freedom in choosing appropriate materials for interconnections, electrical connections, and to an important increase of the device lifetime.

The synthesis methods are in their majority classical ones, like precipitation and co-precipitation [6], sol-gel [7], dip coating [21] and the solid phase reaction [8,9]. However, in the last years other deposition methods have been investigated for thin film based SOFC, the most investigated including vapor deposition [15, 16], vacuum plasma spraying [17-20], and sputtering [22].

The present work is proposing the use of RF assisted pulsed laser deposition technique for fabrication of thin films electrodes to be used in low temperature SOFC's based on YSZ electrolyte. It presents a comparison between the characteristics of SOFC based on thin film (RF-PLD) and respectively thick film (chemical synthesis) with similar composition.

2. Experimental

2. 1 Material preparation

Mesostructured xNiO-Y_2O_3-ZrO_2 with 8 % (molar ratio) yttria and various nickel oxide content (x = 0, 5, 10%), were prepared by self assembling method associated with hydrothermal treatment, using cationic surfactant - cetyltrimethylammonium bromide (CTAB) as template agent. The surfactant was dispersed in water under strong stirring up, and the water solution of inorganic precursors (zirconium oxichloride –$ZrOCl_2$ (Riedel de Haën), yttrium nitrate hexahydrate –$Y(NO_3)_3 6H_2O$ (Merck) and nickel (II) nitrate - $Ni(NO_3)_2$ (Merck)) has been added after two hours. Urea (Sigma – Aldrich) was added as hydrolyzing agent and temperature was increased at 353K, for 4 hours. The obtained gels with 1/0.36/7 oxide/surfactant/urea molar ratio were loaded into Teflon link steel autoclave and heated 3 days at 373 K. The solids were washed with ethanol, dried and calcined in air at 873K. The resultant ZrO_2-8%Y_2O_3 oxidic materials (obtained when x=0) has been used as electrolyte, while the NiO–YSZ materials have been used as anode. Similar procedures have been followed for synthesizing the oxide material for cathode - a ceramic composite - CeO_2-PrO_2 with 10% molar ratio – starting from cerium nitrate hexahydrate – $Ce(NO_3)_3 6H_2O$ (Merck) and praseodymium nitrate pentahydrate $Pr(NO_3)_3 5H_2O$ (Flucka).

In order to realize the SOFC, the obtained ZrO_2-8%Y_2O_3 powder has been used as electrolyte pellet after pressing at 30 atm and sintering at 1273 K. The oxides used for anode – x NiO-8% Y_2O_3-ZrO_2 with (x = 5, 10%), and cathode - CeO_2-PrO_2 with 10% molar ratio, respectively, were also pressed at a pressure of 200 atm and thermally treated at a temperature of 873 – 973 K in order to obtain targets for the laser ablation experiments. They were irradiated at 45° incidence by the fourth harmonic of a Nd: YAG laser (wavelengths 266 nm, pulse length 5 ns, repetition rate 10 Hz, number of pulses 20000) at a constant fluence of 3 J/cm^2. The ablated material has been collected on the YSZ pellet or Si (100) substrate placed at 4 cm in front of the target, under continuous oxygen flow, at a constant pressure of 5 Pa. An additional oxygen radiofrequency plasma beam (13.56 MHz, 100 W), which proved to be beneficial for similar materials [23], has been assisting the growth both in case of anode and cathode thin film deposition. It insures an enhanced reactivity at the substrate level due the presence of an excited and ionized beam of oxygen atoms and molecules and reduces the oxygen deficiency in the obtained film, which is typically encountered in PLD technique.

2. 2 Material characterization techniques

The obtained materials were characterized as regarding their structure, morphology and chemical composition by specific investigation techniques.

The thin films topography as resulted from RF-assisted PLD deposition was investigated by a NOMAD Quesant Instrument Atomic Force Microscope (AFM) in intermittent contact mode (WaveMode™) on areas of 20 x20 µm^2 with an image resolution of 1024×1024 pixels. The surface morphology of SOFC were determined by Scanning Electron Microscopy (SEM) using a Carl Zeiss apparatus model EVO LS10.

Surface analysis performed by X-Ray Photoelectron Spectroscopy (XPS) was carried out on VG Scientific ESCA3 equipment, with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was AlK_α (1486.6 eV) with an overall energy resolution of about 1.1 eV. Survey scans (0 – 1100 eV) were recorded for each sample in order to evidence all the XPS features of the elements found out on the surface, while high resolution scans have been performed around each peak of interest. The charging effect was compensated using the C1s line (BE = 284.8 eV) of the adventitious hydrocarbon on the sample surface.

The crystalline structure of the powders obtained by chemical synthesis was determined by X-ray diffraction (XRD) using a Philips PW 170 diffractometer with Cu K_α radiation, $\lambda = 0.15405$ nm, in Breg-Brentano geometry.

Secondary Neutral Mass Spectrometry (SNMS) analyses have been performed with a Hiden Analytical System with sensitivity at ppb level, using Ar ion gun for sputtering and a MAXIM - Quadrupole mass spectrometer for species detection (mass range up to 300 amu).

The electrocatalytic properties were studied in a solid oxide membrane reactor. The system based on CeO_2-PrO_2 cathode-YSZ electrolyte –NiO-YSZ anode was inserted into a ceramic tube and connected with two platinum sieves which ensure the electrical contact between the electrodes and the reactor body itself. The experimental arrangement is shown in Fig. 1.

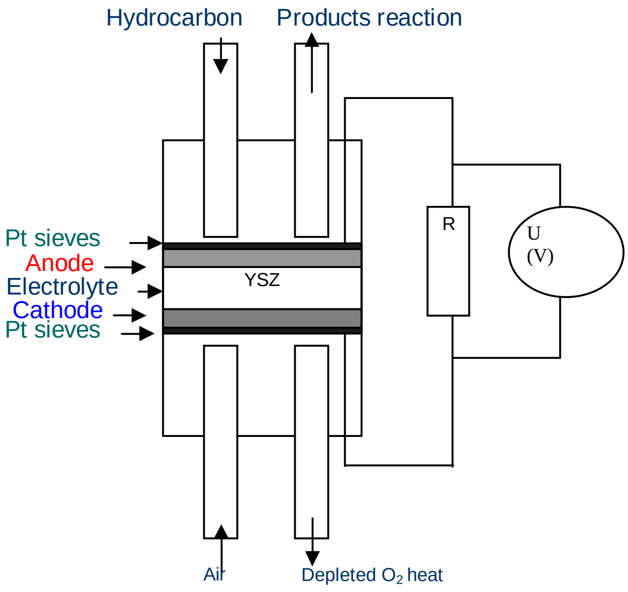


Fig. 1. Schematic of the home-made SOFC membrane reactor.

A mixture of 10% methane in nitrogen at a CH_4 flow rate of 100 sccm and respectively 50 sccm air as oxidant agent at the cathode were used for testing the SOFC efficiency.

The voltage was recorded with a Fluke processmetter connected across a 1 MΩ load resistance. The measurements were performed in the temperature range 450 – 700 °C.

3. Results and discussion

In the typical approach the cell was made by assembling a thick anode layer of NiO-YSZ materials and a thick cathode layers of CeO_2-PrO_2, in between with the electrolyte YSZ pellet. A SEM cross-section image of such a structure, obtained by pressing the electrodes materials on the electrolyte is presented in Fig. 2, from which one can see the mesoporous structure of the anode with a thickness around 200 μm on top, the electrolyte pellet (1 mm) and respectively the cathode thick layer on the bottom (300 μm).

In the RF assisted PLD approach, the cell is made from thin electrodes (around 200 nm thickness each) deposited on the same type of electrolyte pellet (1 mm thick).

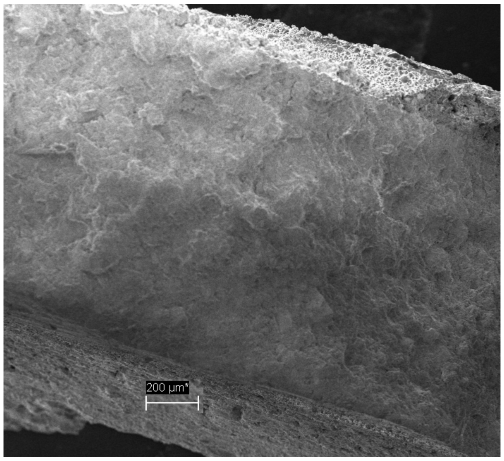


Fig. 2. SEM cross-section image of a membrane prepared by pressing the powders.

3.1 Characterization of powders and thick electrodes

The X-ray diffraction patterns of the NiO– YSZ and CeO_2-PrO_2 materials, which were used, respectively, for anode and cathode formation by chemical and RF-PLD targets are presented in Fig. 3. From the wide-angle XRD patterns, in the range 2θ = 3 – 70 degrees, one can find that all the samples obtained by hydrothermal treatment are crystallized in a cubic phase which corresponds to that of structurally distorted ZrO_2 and CeO_2, respectively. Still, the broadness of the peaks which stands for the nanocrystallinity of the materials prevents from a clear discarding between cubic and tetragonal peaks. The (200) reflection is slightly larger suggesting a possible split in tetragonal (002) and (110) peaks, but considering the broadness of the others peaks one could assume the formation of a predominant cubic phase. The shift of diffraction peaks is related to Y and Ni incorporation, and respectively to Pr incorporation. Previously it was reported [24] that the hydrothermally synthesized mesoporous YSZ is structurally stabilized in cubic phase as result of Y_2O_3 addition. The small grain (nanocrystallites) effects and/or the Y^{3+} dissolution in the ZrO_2 matrix is conducting to a lattice dilatation (considering the Shanon radii $Y^{3+}/Zr^{4+}=0.90/0.59$). CeO_2 is stable in the cubic fluoride phase and Pr^{4+} substitution is leading to a lattice contraction ($Pr^{4+}/Ce^{4+}=0.85/0.97$ [25]). Moreover, the absence of Y_2O_3, NiO, and PrO_2 phases indicate that the distribution of the doped element(s) is rather homogeneous.

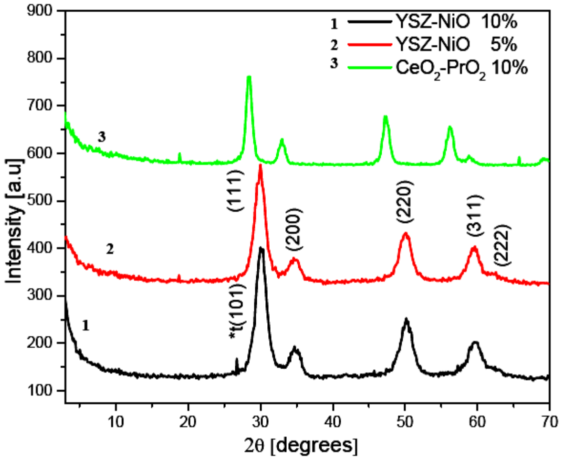
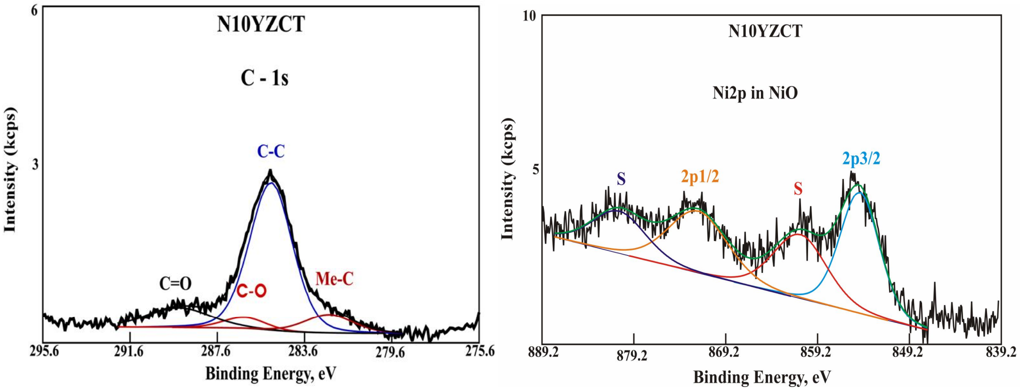


Fig. 3. XRD patterns of the hydrothermally synthesized materials used for anode and cathode deposition.

The XPS measurements have been performed on the powders. They also give information on the initial concentration of elements in the targets. The deconvoluted spectra in the region of C1s binding energy presents (Fig. 4, left), besides the usual C–C, C–O, C=O bonds, some Ni-C bond which could lead to an improvement of the electrical conductivity [26]. The Ni 2p deconvoluted photoelectron line for the sample YSZ modified by 10% NiO is clearly attributed to the Ni^{2+} oxidation state without any contribution from the elemental Ni. Moreover, the Ni chemistry is identical for YSZ samples modified with 5%.



(a) *(b)*

Fig. 4. The XPS spectra of YSZ modified by 10% NiO powders in the binding energy regions corresponding to (a) C1s;(b) Ni2p regions – S corresponds to satellite bands.

In Table 1 are presented the binding energies for all the peaks of interest, while in Table 2 are presented the calculated relative elemental concentration of the materials used as targets for depositing the anode of SOFc's.

Table 1. Binding energies of the peaks corresponding to O1s, Ni2p, Y3d and Zr3d for NiO-YSZ powders synthesized by hydrothermal treatment.

Element	O(1s)	Ni (2p)		Y(3d)		Zr(3d)	
		2p3/2	2p1/2	3d5/2	3d3/2	3d5/2	3d3/2
Binding Energies (eV)	529.8 532.6	854.3 861.4	872.4 880.9	157.3	159.3	182.2	184.6

Table 2. Experimental and calculated atomic percentage of the metals in the Ni-YSZ powders synthesized by hydrothermal treatment.

Relative element concentrations (atom%)		Ni	Y	Zr
YSZ with 5% NiO powder	experimental XPS	4.5	15	80.5
	calculated	4.6	14.8	80.6
YSZ with 10% NiO powder	experimental XPS	5	19	76
	calculated	9.3	14.8	75.9

Within the limit of the experimental errors, the sample doped with 5% Ni exhibits a surface stoichiometry very close to the calculated (intended) one. One can notice for the sample with 10% Ni a significant diffusion of Ni from the surface into the bulk accompanied by a segregation of Y from the bulk to the surface, as noticed also in ref. [27] which showed that the Ni^{2+} ions may diffuse into Y_2O_3 lattice leading to the lattice contraction of Y_2O_3.

3. 1 Characterization of thin electrodes

The AFM investigations of the RF assisted PLD films deposited on Si substrates prove the formation of smooth and dense structures, with only small particulates on the surface having typical dimension no larger than 50 nm, as can be seen in Fig. 5.

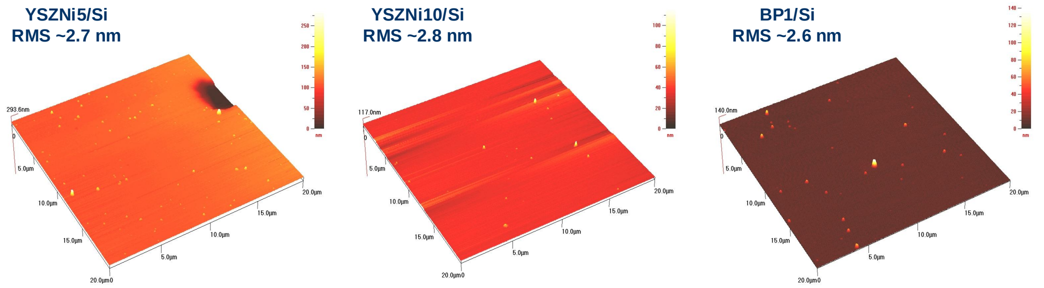


Fig. 5. AFM images of anode and cathode materials deposited by RF assisted PLD on Si substrate.

The typical roughness is around 2.7 nm for all the obtained films. Still, the sandwich structures anode-electrolyte-cathode with thin film electrodes could not be investigated by this technique due to the intrinsic surface roughness of the YSZ electrolyte. Indeed, the SEM pictures of samples deposited on Si substrate and respectively on YSZ electrolyte, presented in Fig. 6 (a) and (b), respectively, prove that the NiO-YSZ thin film is conformal to the substrate.

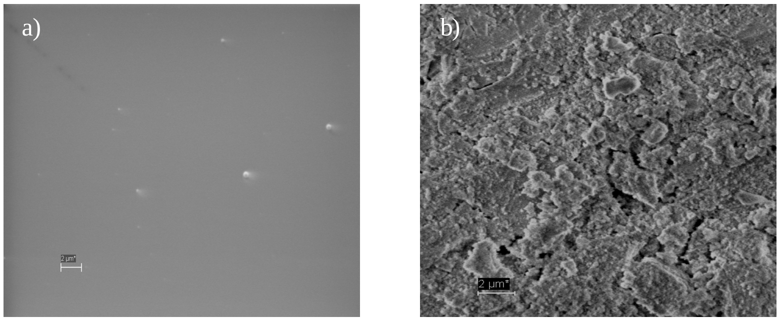


Fig. 6. SEM images of the RF assisted PLD 5% NiO – YSZ thin films deposited on (a) Si substrate; (b) YSZ electrolyte.

The XPS measurements in the binding energy corresponding to Ni 2p state, performed on RF-PLD thin films deposited on silicon are presented in Fig. 7. They reveal the presence of Ni^{3+} oxidation state as Ni_2O_3 with the Ni2p3/2 binding energy at 856.5 eV [28], in comparison to the starting powder where only the Ni^{2+} oxidation state with the 2p3/2 energy of 854.3 eV was observed (see Table 1). The feature at 848.7 eV is assigned to the F Auger line which appears as a contaminant, and is not affecting the Ni chemistry on the surface.

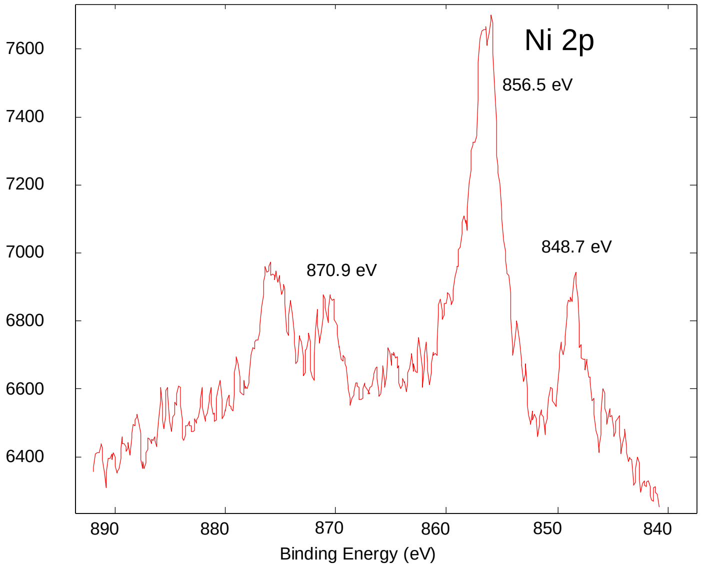


Fig. 7. XPS spectra of 10% Ni –YSZ thin film deposited by RF-PLD in the Ni2p binding energy region.

The in-depth quantification of the material composition of the RF assisted PLD deposited thin films have been performed by SNMS analyses. In Fig. 8 are presented the obtained compositional profiles for the materials used as anode and cathode, respectively. The sputtering time is proportional to the depth of removed material, namely initial time (0) corresponds to the surface while the maximum sputtering time corresponds already to a level inside the substrate. All the investigated films show a constant in-depth composition and the existence of a rather large interface to the substrate. The samples deposited starting from higher Ni content in the target present a higher signal associated to Ni atoms, similar values of the Y and smaller signal associated to the Zr presence in the film. The stoichiometry calculations show an accurate preservation of initial concentration for the Pr – modified CeO_2 cathode.

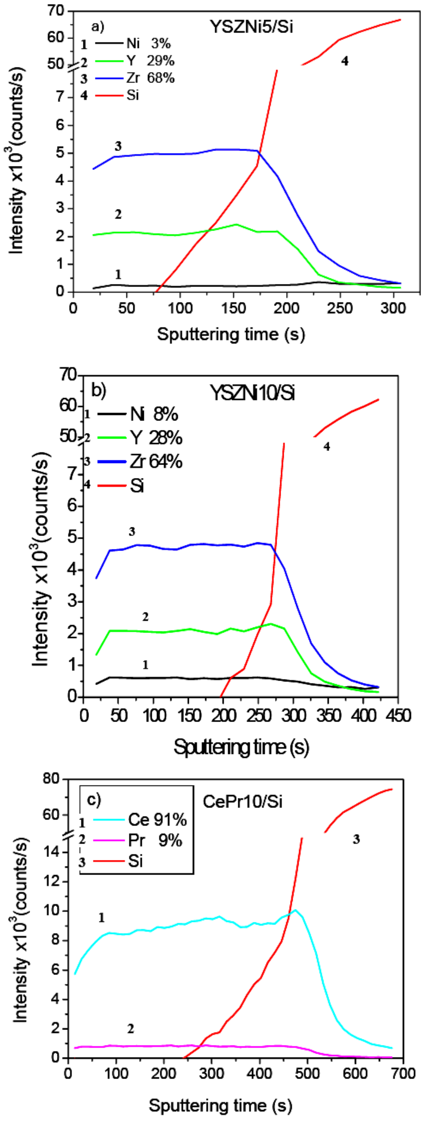


Fig. 8. SNMS measurements on RF-PLD thin films of: (a) 5% NiO doped YSZ; (b) 10% NiO doped YSZ; (c) PrO_2 doped CeO_2.

In Table 3 are comparatively presented the atomic percentages of the metals in the NiO-YSZ anode as determined by XPS (surface) and SNMS (bulk) analyses of the samples. The differences can be explained by considering the possible diffusion of Ni from the ZrO_2 matrix towards the surface with the formation of Ni_2O_3, but one should consider that the concentration evaluations by SNMS have been performed without any correction of sensitivity to different elements and without considering the possible preferential sputtering.

Table 3. Surface and bulk elemental concentration of Ni-modified YSZ thin films.

Relative element concentrations (atom%)		Ni	Y	Zr
YSZ with 5% NiO RF-assisted PLD thin film	XPS - surface	13.5	28.2	58.3
	SNMS - bulk	3	29	68
YSZ with 10% NiO RF-assisted PLD thin film	XPS – surface	21.9	22.9	55.2
	SNMS - bulk	8	28	64

3.2 Investigation of SOFCs based on thick and thin electrodes

The electrocatalytic activity of the membranes obtained by chemical synthesis starts at temperatures above 600 °C (See Fig. 9 (a)), a maximum voltage of 40 mV being measured for the sample with 10% Ni at 700 °C. Instead, as can be seen from Fig. 9 (b), the cell performance is increased for the systems based on electrodes deposited by RF-assisted PLD, which are already functioning at temperatures around 450 °C. The higher measured voltages in the case of RF-PLD technique are related to higher values of the generated current inside the reactor, which correlates to a higher hydrocarbon conversion in the anodic space. The electrocatalytic reaction implies the simultaneous existence of the three phases [29] (TPB = three phase boundary) in the reaction center: a gaseous phase represented by the used fuel, an electron conductive phase, represented by the YSZ material and a metallic phase with electronic conduction, represented by Ni. The high dispersion of Ni in the YSZ matrix of anode and the homogeneous and continuous thin film favor the increase of the active centers number and the rapid desorption of the by-products. This leads to a higher methane conversion and respectively, to the increase of the electric current produced in the SO membrane reactor.

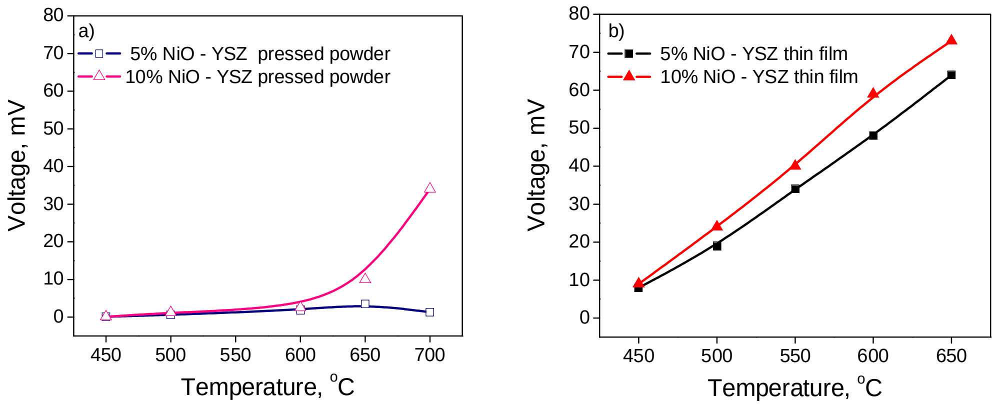


Fig. 9. Measured voltage across the SOFC as function of temperature for the (a) thick film based membrane and (b) RF-PLD based membrane.

4. Conclusions

Solid oxide fuel cells with thick and thin electrodes have been realized by two techniques: powder pressing and RF assisted PLD, respectively.

The starting materials, namely yttria stabilized zirconia as electrolyte, NiO-Y_2O_3-ZrO_2 for anode and CeO_2-PrO_2 for cathode have been prepared by self assembling method associated with hydrothermal treatment. They present cubic structures and compositions similar to the intended, theoretical ones.

The RF assisted Pulsed Laser Deposition led to films which are smooth, compact and conformal to the substrate. The anode composition is enriched in Ni at surface, which partially appears in different oxidation state in comparison to the target, (XPS data) and slightly depleted in bulk (SNMS data).

An operating temperature as low as 450 °C and an increased fuel conversion efficiency were determined for the SOFC's based on the thin films grown by RF-assisted PLD, in comparison to the thick based SOFCs. RF assisted PLD appears as a promising technique for obtaining thin film solid oxide fuel cells based on YSZ electrolyte.

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