Annals of the Academy of Romanian Scientists
Physics Series
ISSN 2559-1061 Volume **2**, Number **1/2017**

NANOSTRUCTURED CATALYSTS FOR HYDROGEN FUEL CELLS

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December 2016

1. Introduction

As the necessity for energy keeps on growing it has become a pressing concern the development of new methods of producing energy both efficient and harmless for our environment. In the past the limiting factors of renewable energy were the storage and transport of that energy. By using fuel cells and hydrogen based technology the electrical energy from renewable sources can be distributed where and when is needed, clean, efficient and sustainable.

Nanotechnology is the area of interest in the research of new methods of improving the performance and reducing the costs of the catalysts used in fuel cells. Fuel cells are devices that convert chemical energy from a fuel such as hydrogen into electricity through chemical reactions with oxygen or other oxidizing agents. The source of energy for these cells is situated at the anode, the oxidant at the cathode while the electrolyte allows the ions to flow between these two parts of the fuel cell.

According to the U.S. Department of Energy, these have a typical efficiency of 40 to 60% [1]. By comparison, the typical internal combustion engine of a car has between 14 and 30% efficiency [2]. The maximum theoretical yield of a fuel cell is 83% when it operates at low power densities and uses pure hydrogen and oxygen as reactants at a temperature of 25 °C [3]. The main factors that contribute to a reduction in fuel cell voltage output are: *activation losses, fuel crossover and internal currents, ohmic losses* and *concentration losses* respectively.

2. Thin Films Deposition

Nanotechnology is the science that develops materials at atomic and molecular level in order to improve their properties, in particular the electric and magnetic ones. One scientific discovery with considerable potential in modern industry is the technology of thin films [4].

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The deposition by thermionic vacuum arc method (TVA) was developed at Naţional de Fizica Laserilor, Plasmei şi Radiaţiei). INFLPR (Institutul Due to the bombardment by the ions of the same material, the resulting films are compact, smooth and without columnar structures.

The physical properties of thin films are similar to those of the material, while their rugosity can reach values in the order of nanometers. Additionally, no droplets are formed and the film adherence to the Si or glass substrate is very high. Moreover the plasma plume ignition in high vacuum conditions assures a very high purity of the deposited films (Fig. 1).

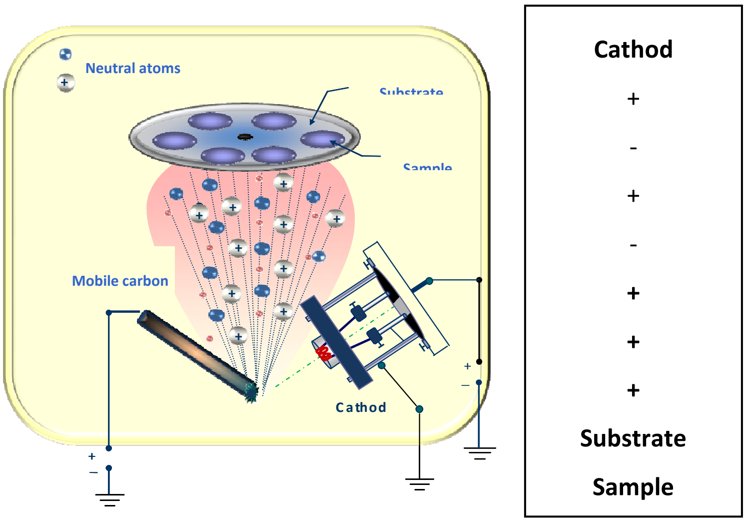
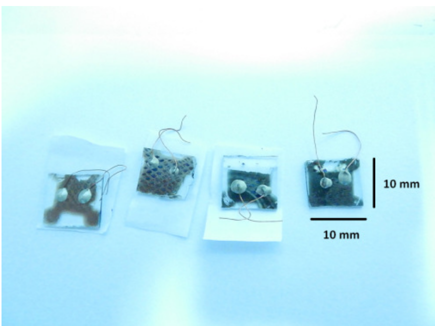


Fig. 1. TVA Deposition – Plasma ignition and substrate deposition [5].

3. Carbon – Platinum Thin Films on Glass Substrate

The C–Pt nanostructured composite on glass substrate has been obtained by the Thermionic Vacuum Arc method in one electronic gun configuration and the deposition consisted of two stages: the *carbon deposition* and the *platinum deposition* (Fig 2).



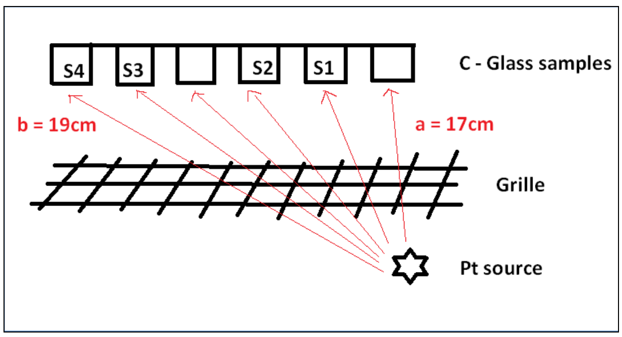


Fig. 2. The platinum deposition on C–Glass samples. **Fig. 3.** The four C–Pt samples.

Table 1

Sample	Estimated Pt Thickness (nm)	Distance between contacts (mm)
S1	3.8	2.872
S2	3.6	3.245
S3	3.3	2.596
S4	3.2	1.697

Ohmic contacts were attached to the samples for use in electrical measurements. The electrical contact on the samples was performed by a product consisting of 80% silver-filled two-component epoxy-based glue (0.0025 Ω/cm specific resistance) [6]. The resistance was calculated by comparing the voltage drop on the specimen to the voltage drop on a standard (control) resistor ($\boldsymbol{R_x = R_e \cdot UR_x/UR_e}$).

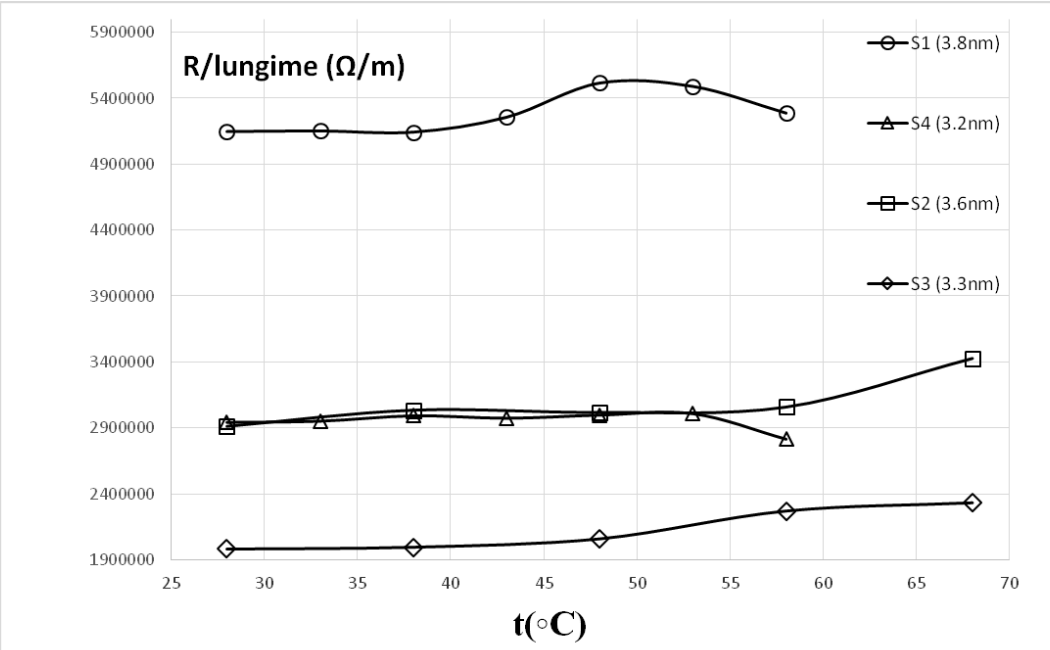


Fig. 4. Resistance/distance ratio vs. temperature for samples S1(○), S2(□), S3(◊) and S4(Δ) respectively.

It can be seen that sample S1, even if it has isles of Pt with 3.8 nm thickness, has the highest resistance per distance ratio of all 4 samples. By contrast sample S3 with only 3.3 nm has the lowest ratio of all. These measurements lead to the conclusion that the *surface* of platinum between contacts is responsible for the decrease in electrical resistance.

4. Nickel – Platinum and Palladium Thin Films

The NiPt + Pd thin films were deposed by the TVA method described above but in a three electronic gun configuration. The deposition consisted of two stages: the *platinum – nickel deposition* and the *palladium deposition*.

The formation of 5 nm diameter Pd nanoparticles that nucleate in the NiPt matrix was intended. The reason is Pd increases the overall surface of the catalytic reactions in the NiPt matrix, one of the possible explanations is the transfer of electrons between the Pd nuclei and the matrix (Fig 5) [7].

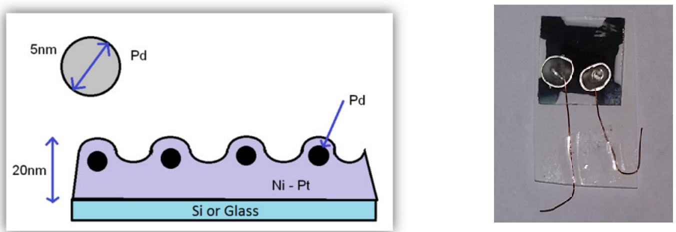
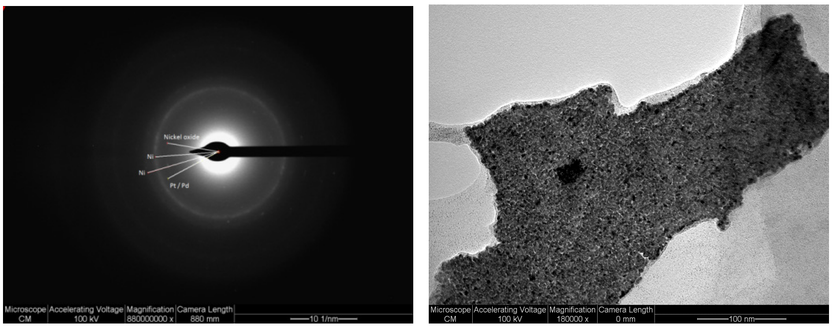


Fig 5. Inclusion of palladium nanoparticles in platinumnickel matrix (left) and the specimen used in investigations (right).



(a) **(b)**

Fig 6. (a) TEM image obtained at 100 kV and 180000× magnification at the surface of the film; **(b)** Electron diffraction reveals the presence of Ni and Pt or Pd.

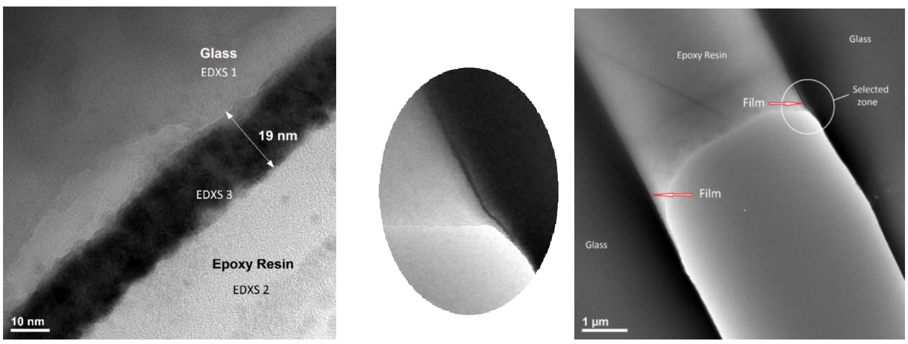


Fig 7. The selected zone shows the thin film.
The NiPt matrix thickness is 19 nm. A columnar growth of the thin film is observed.

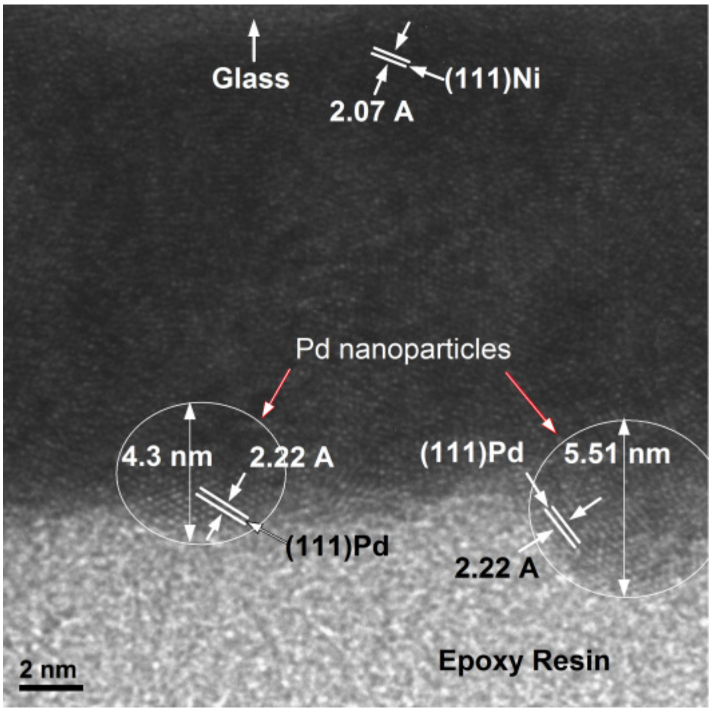


Fig. 8. The presence of Ni is identified by the 2.07 Å spacing between bright interference fringes while Pd is located by the 2.22 Å interplanar spacing between two parallel planes. These values are compared to the ICDD database (The International Centre for Diffraction Data) [8, 9]. The inclusion of spherical Pd nanoparticles approximately 5 nm in diameter in the NiPt matrix can be noticed.

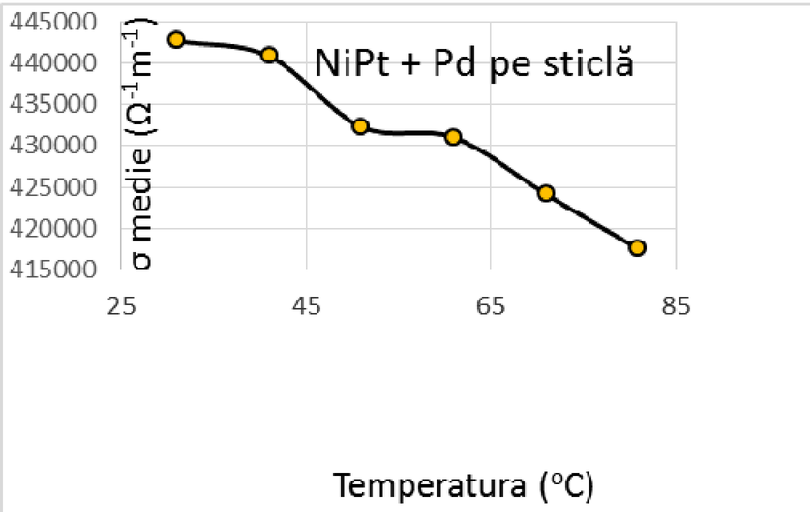


Fig. 9. The sample's average conductivity vs. temperature graph illustrates the conductor behavior of the thin film σ average (Ω-1m-1) Temperature (°C) NiPt + Pd on glass substrate.

5. Conclusions

The decrease in electrical resistance is caused by the surface and not the thickness of platinum between contacts for the four C – Pt samples that were investigated.

In the case of the nanostructured NiPt + Pd on glass substrate thin films deposed by the TVA method, the HRTEM analysis reveals the nucleation of spherical Pd nanoparticles approximately 5 nm in diameter in the NiPt matrix as intended. Electron diffraction also indicates the presence of chemical elements Ni, Pt and Pd. The conductor behavior of the tested NiPt + Pd specimen is proved by the decrease in average conductivity with temperature.

R E F E R E N C E S

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[9] ICDD for cubic palladium reference number 04-015-0494.

6 List of Original Contributions

6.1 Papers Published in ISI - Indexed Journals

[1] **L. Petrasescu, V. Ciupina, S. G. Tutun, R. Vladoiu, G. Prodan, C. Porosnicu, E. Vasile, I. Prioteasa, R. Manu**, *Carbon - Platinum nanostructured catalysts for hydrogen fuel cells*, Journal of Optoelectronics and Advanced Materials; **Vol 17**, Issue: 9-10, Pages: 1464-1470, September – October **2015**.

[2] **Ş. G. Tutun, L. Petrăşescu, R. Vlădoiu, G. Prodan, C. Poroşnicu, E. Vasile, I. Prioteasa, R. Manu, V. Ciupină**, *Application of some carbon-aluminium based nanostructures obtained by tva method in divertors coating from fusion reactor,* Journal of Optoelectronics and Advanced Materials; **Vol 17**, Issue: 7-8, Pages: 1064-1069, July – August 2015 3. **Victor Ciupina, Iulian Prioteasa, Daniela Ilie, Radu Manu, Lucian Petrăşescu, Ştefan Gabriel Tutun, Paul Dincă, Ion Mustață, Cristian Petrică Lungu, Ionuț Jepu, Eugeniu Vasile, Virginia Nicolescu, Rodica Vladoiu,** *Synthesis and Characterization of Copper/Cobalt/Copper/Iron Nanostructured Films with Magnetoresistive Properties,* AIP Conference Proceedings, Volume 1815, Issue 1, 10.1063/1.4976370, Published Online: February 2017, 040001 (**2017**); doi: http://dx.doi.org/10.1063/1.4976370.

6.2 Posters Presented in International Conferences

[1] V. Ciupina, R. Vlădoiu, G. Prodan, Ş.G. Tutun, L. Petrăşescu, C. Poroşnicu, E. Vasile, *Application of carbon based nanostructures in divertors coating from fusion reactor*, **13th International Balkan Workshop on Applied Physics**, July **2013**.

[2] V. Ciupină, R. Vlădoiu, G. Prodan, L. Petrăşescu, Ş.G. Tutun, C. Poroşnicu, E. Vasile, *Nanostructured catalysts for hydrogen fuel cells*, **13th International Balkan Workshop on Applied Physics**, July **2013**.

[3] V. Ciupină, R. Vlădoiu, G. Prodan, Ş.G. Tutun, L. Petrăşescu, C. Poroşnicu, E. Vasile, *Application of some carbon-aluminium based nanostructures in divertors coating from fusion reactor*, **14th International Balkan Workshop on Applied Physics**, July **2014**.

[4] V. Ciupină, R. Vlădoiu, G. Prodan, L. Petrăşescu, Ş.G. Tutun, C. Poroşnicu, E. Vasile, *Carbon – platinum nanostructured catalysts for hydrogen fuel cells*, **14th International Balkan Workshop on Applied Physics**, July 2014.

[5] V. Ciupină, G. Prodan, R. Manu, Ş.G. Tutun, L. Petrăşescu, N. Vineticu, O. Brancoveanu, I. Prioteasa, *Contributions in the optimization of the electron diffraction precession system for the examination of thin films*, **14th International Balkan Workshop on Applied Physics**, July **2014**.

[6] V. Ciupină, I. Prioteasa, R. Manu, L. Petrăşescu, Ş.G. Tutun, C. Poroşnicu, I. Mustata, C.P. Lungu, E. Vasile, G. Schinteie, *Thermally treated CuCoFe thin films obtained by tva method*, **14th International Balkan Workshop on Applied Physics**, July **2014**.

[7] L. Petrăşescu, V. Ciupină, Ş.G. Tutun, R. Vlădoiu, A. Mandes, V. Dinca, G. Prodan, C. Poroşnicu, E. Vasile, I. Prioteasa, R. Manu, *Nucleation of palladium nanostructures in platinum-nickel matrix*, **15th International Balkan Workshop on Applied Physics**, July **2015**.

[8] L. Petrăşescu, V. Ciupină, G. Prodan, C. Poroşnicu, E. Vasile, *Inclusion of palladium nanoparticles in platinum-nickel thin films*, **16th International Balkan Workshop on Applied Physics**, July **2016**.

[9] V. Ciupină, I. Prioteasa, R. Manu, L. Petrăşescu, Ş.G. Tutun, C. Poroşnicu, I. Mustata, C.P. Lungu, E. Vasile, G. Schinteie, D. Ilie, *Sythesis and characterization of some Cu/Co/Cu/Fe thin films with special magnetoresistance properties*, **16th International Balkan Workshop on Applied Physics**, July **2016**.

[10] R. Manu, V. Ciupină, G. Prodan, Ş.G. Tutun, L. Petrăşescu, N. Vineticu, O. Brancoveanu, I. Prioteasa, *Contributions to optimization of the quality of electron diffraction image in characterization of thin films using the precession system*, **16th International Balkan Workshop on Applied Physics**, July **2016**.