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Structural and electrochemical characterization of TiO_2/Pt hybrid catalyst system for direct bio-ethanol fuel cell

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This paper is focused on preparation and microstructure and electrochemical characterization of carbon-TiO_2/Pt catalyst used as electrode in fuel cells applications. The platinum deposition was comparatively studied on graphitized carbon substrate and carbon substrate covered with titanium oxide. A strong influence on the platinum deposition, depending of the TiO_2 presence, was found. The platinum nanoparticles about 5 nm in size are dispersed in aggregates of 50 to 100 nm on the catalyst surface. This dispersion is strongly affected by the titanium oxide and the substrate porosity. The Pt/TiO2/G and Pt/G electrodes were tested for their catalytic activity in the oxidation of ethanol. The prepared Pt/TiO_2/G electrode show higher active surface area than for the Pt/G electrode, this increase in the surface area could be explained to be due to a spreading of wetting or the formation of new active sites at the Pt/oxide interface.

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1. Introduction

Pt and Pt-based catalysts have been extensively investigated as electrocatalysts for the oxidation of liquid fuels such as methanol and ethanol. However, the high price and limited supply of Pt constitute a major barrier to the development of direct alcohol fuel cells - DAFC.

For the best performance, DAFC electrode should consist of two or more phases, such as a nanosized catalyst and a porous material as a support for the catalyst. The general requirements of support materials for their applications to platinum-based electrocatalyst are a high surface area for a high level of dispersion of nanosized catalysts, a pore structure suitable for maximum fuel contact and by-product release, and good interactions between the catalyst nanoparticles and the support [1,2].

In particular, oxide supports are widely used in heterogeneous catalysis and have an excellent stability in oxidizing environments [3]. Recently, more works have been focused on the system of combining metal oxides, carbon and Pt [4,5].

Until now, titanium oxides have been potentially attractive as supports due to strong catalyst-support interaction, stability in fuel cell operation atmosphere, low cost, commercial availability and the ease control of size and structure [6.7].

The present paper has as a main objective the structural characterization of titanium oxide platinum hybrid catalyst system electrochemically obtained on a graphitized carbon surface.

2. Experimental

2.1 Catalysts preparation

Two types of catalyst were prepared: the first one, electrodeposited platinum on graphitized carbon sheet (Pt/G) and the second one, hybrid titanium oxide/platinum on a similar supporting electrode (TiO_2/Pt/G).

The preparation of the Pt/G catalyst was done from a 0.1M $HClO_4$ and 2.4mM H_2PtCl_6 solution at a constant potential of -0.1 V/AgCl on a working surface area of 0.7cm^2 for 180s. After platinum deposition, the electrode's surface was rinsed with bi-distilled water and dried at room temperature.

The preparation of the second catalyst Pt/TiO_2/G was also done by electrochemical method in two steps. In the first step, the electro-deposition of TiO at a constant potential of 0.7 V/AgCl on carbon substrate from 10 % $TiCl_3$ and 0.1M KCl 0.1M solution at the pH of 2.2 for 200s was performed. The pH value correction was realized using saturated Na_2CO_3 pro analysis grade. After TiO_2 deposition, the electrode was rinsed with bi-distilled water and covered with platinum using electrochemical method described above.

2.2 Electrode characterization

The electrodeposited Pt and TiO_2/Pt electrodes were characterized by surface structural analysis and electrochemical techniques.

The surface structural analysis of the electrodeposits was achieved by scanning electron microscopy (SEM) energy dispersing X-ray spectrometry (EDX), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). The TEM specimens were prepared by extracting micrometric fragments from the sample surface and mounting these fragments on holey carbon grids for TEM.

Jeol 200CX and INSPECT S FEI electron microscopes were used for investigations and the images processing was performed with AnalySIS Olympus software for phase analysis.

In addition, the catalytic responses toward ethanol oxidation were measured by chrono-amperometry technique in a 3.75 M ethanol in 0.5M H_2SO_4 solution of.

3. Results and discussion

3.1 Microscopic characterization

3.1.1 Pt/G electrodeposition

The graphitized carbon has a major advantage as a supporting electrode because it's homogeneous structure at the micrometric scale. However, at the nanometric scale this material presents an interesting morphology consisting in aggregates of nanocrystalites of graphitized carbon of about 100-300 nm in diameter as shown in figure 1, linked by quasi-amorphous carbon, where the graphitic planes are in a random arrangement.

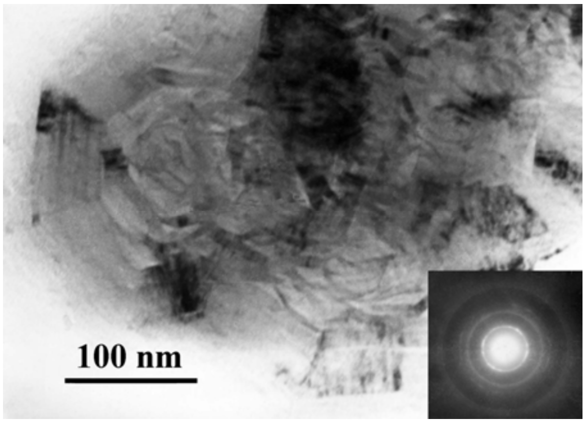

Fig. 1. TEM image and the corresponding SAED showing the nanostructure of the graphitized carbon supporting electrode.

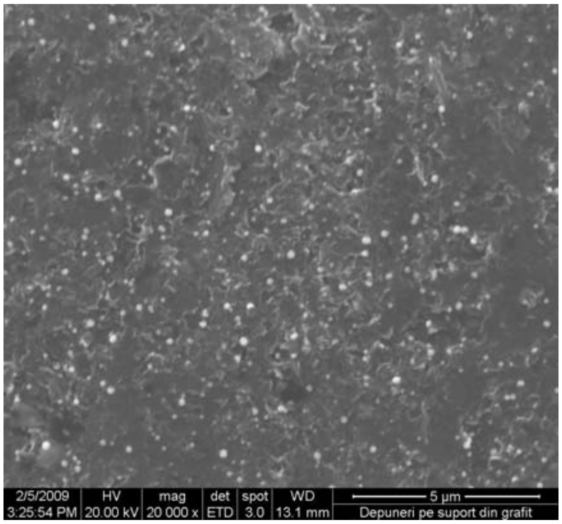

Fig. 2. The SEM image of carbon electrode decorated with small platinum particles

After platinum electrodeposition from hexachloride platinum acid (H_2PtCl_6) solution at -0.1V/AgCl, the electrode surface shows a relative homogeneous aspect with small platinum particles (Fig. 2).

Using image analysis software AnalySIS Olympus, was appreciate the coverage percentage of the carbon electrode surface with platinum at about 10-11%. That will not influence significantly the real area of the surface and its roughness. The platinum particles are present on the catalyst surface in quite large aggregates, about 50 – 100 nm in size as show in figure 3. However, the average size of the platinum nanoparticles are about 5 nm, as can be seen in high resolution image in figure 4 showing some platinum particles dispersed in the quasi-amorphous carbon matrix.

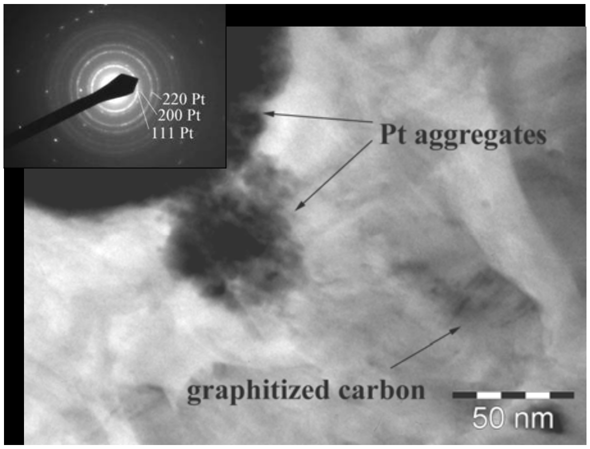

Fig. 3. TEM image and SAED pattern of platinum aggregate on carbon substrate.

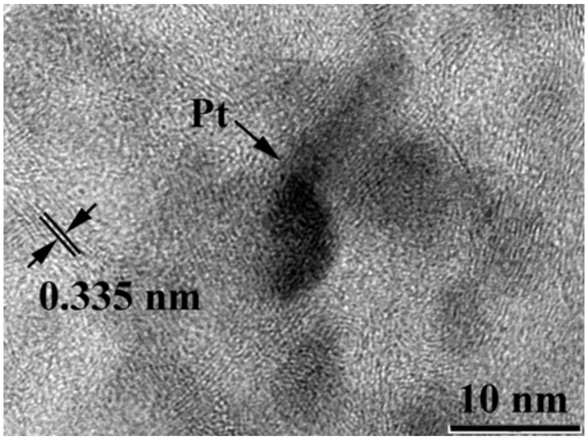

Fig. 4. High resolution TEM aspect of platinum nanoparticle enbeded in the graphitized carbon matrix, which show the (0001) lattice fringes (0.335nm) characteristic for graphite.

3.2 Hybrid TiO_2/Pt Electrodeposition

As is shown in the figure 5, the graphitized carbon electrode surface is quasi totally covered with TiO_2. The microanalysis of this coating shows a very small area of micropores, which was appreciated by image analysis at about 5% from the electrode surface.

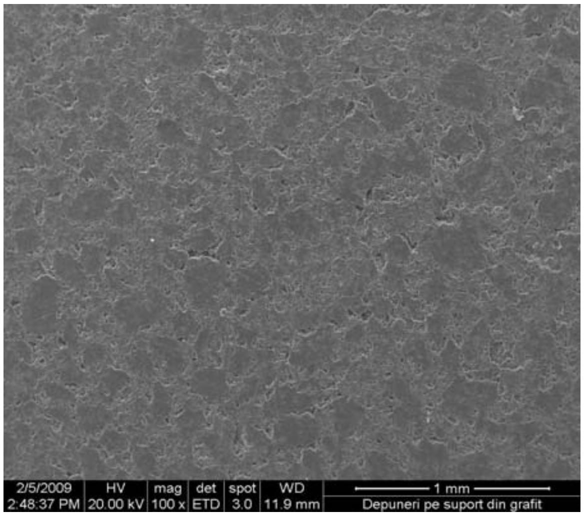

Fig. 5 Low magnification SEM image of the electrode covered surface with TiO_2 coating by electrochemical oxidation from $TiCl_3$ based solution at 0,7V/AgCl

Titanium oxide and carbon are hydrophobic materials. Because its well wet-ability on carbon substrate, the initial TiO_2 oxide thin film tend to cover the surface. However, the electrodeposited titanium oxide coating consists from nanosized hydrated TiO_2 particles [8], can influence its hydrophility. The high magnification SEM analysis of the surface show a non homogeneous grows and a porous structure formation in the coating out layer (see figure 6). The size of the deposited TiO_2 particle aggregate grows three dimensionally from hundred of nanometers to micrometer, forming a porous surface morphology.

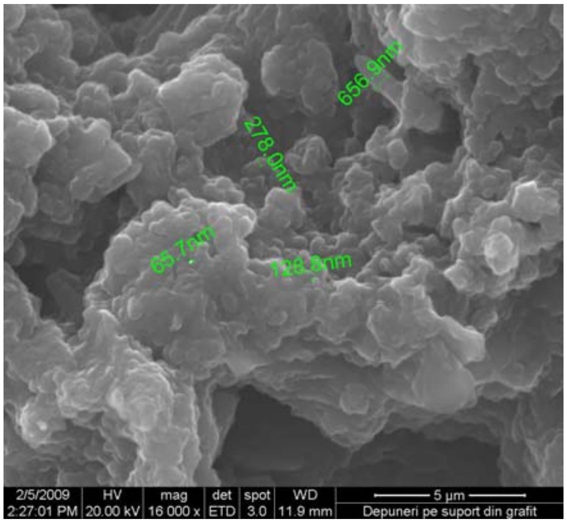

Fig. 6. SEM image of the three- dimensional grow of titanium dioxide coating.

The electrochemical deposition of platinum catalyst on TiO_2 covered electrode is in this case available only on non covered carbon sites areas as is shown in Fig. 7.

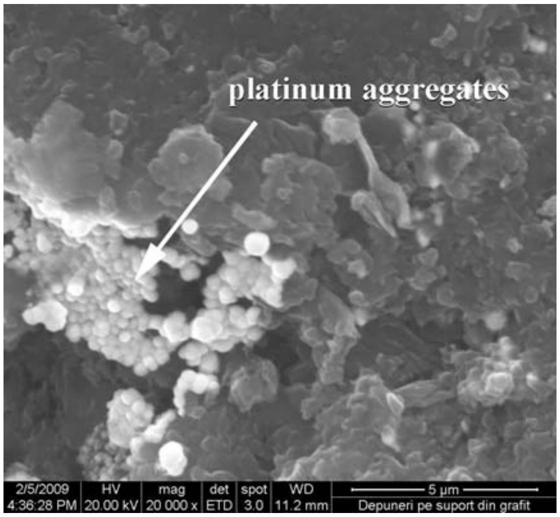

Fig. 7. SEM image of platinum electrodeposited catalyst in a micrometric porous sites of the carbon electrode with TiO_2 coating.

The phase's analysis using Olympus software reveals very small platinum coverage degree of about 3%. That is in a well concordance with carbon surface area non covered with titanium oxide, estimated at about 5% , mentioned above. The EDX analysis of platinum covered sites show a very small TiO_2 signal compared with platinum and carbon signals, as shown in figure 8.

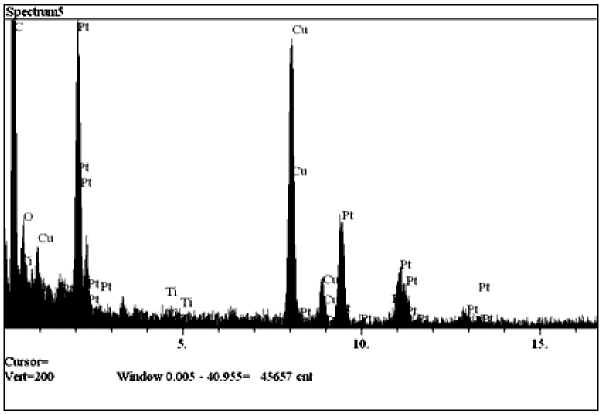

Fig. 8. EDX Spectrum of TiO_2/Pt hybrid system on the platinum covered sites.

Because of the very small electrochemical working surface exposed by the TiO_2 non covered porous sites, we suppose a big current density on these sites and a bigger platinum particle aggregates formation, up to 500 nm in size , as seen in Fig. 7.

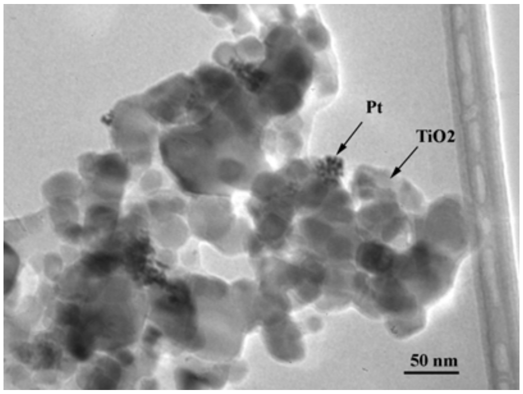

Fig. 9. High magnification TEM image showing platinum particle aggregate on the TiO_2 particles.

However, the TEM study of some fragments extracted from the Pt/TiO_2/G electrode, show the presence of small aggregate of platinum on the TiO2 nanoparticles (figure 9). This means that some platinum particles are deposited or dispersed in smaller pores of the covered electrode, non visible on the SEM low magnification images.

The TEM study revealed also that the titanium oxide deposition is composed from crystallites of anatase and rutil having sizes between 30 and 80 nm.

3.3 Electrochemical characterization

From the CVs (fig 10), can be seen that the platinum oxide potential for the Pt/TiO2/G electrode increases compared to those of Pt/G, which is in agreement with the literature data [8]. The real electrochemical active surface area, Ar, and Roughness factor, *Rf* calculated from the region of hydrogen desorption [9] are summarized in table 1 [**]. The Pt/TiO_2/G electrode shows higher active surface are than Pt/G, probably because of wetting spreading [10] or because of new active sites at the Pt/oxide interface formation [11].

Table 1. Roughness factor of Pt/G and TiO2/Pt/G electrodes as determined from charges corresponding to the hydrogen adsorption peaks [**].

Electrode	*Ar* (cm^2/mg)	Rf (cm^2Pt/cm^2)
Pt/G	141,87	11.109
Pt/TiO_2/G	323,56	34.557

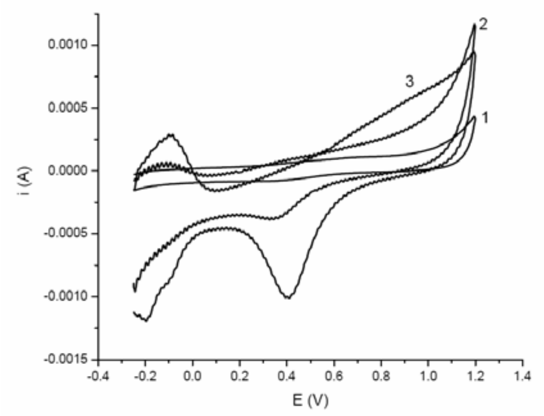

Fig. 10. CVs of the graphite (1), Pt/G (2) and the Pt/TiO_2/G electrodes (3).

The real surface area of a catalyst can be orders of magnitude greater than the geometric area. Since the extent of adsorption and catalytic reaction rates depend on real surface area, it is important to measure this value. A measure of the real electrochemical surface area can be obtained from the charge corresponding to the area under the hydrogen adsorption peaks.

3.4 Ethanol electrooxidation

The as-prepared Pt/TiO2/G and Pt/G electrodes were tested for their catalytic activity in the oxidation of ethanol. Figures 11 and 12 shows cyclic voltammetry curves recorded for both electrodes in a 0.5 M H_2SO_4 solution containing 3.75 M C_2H_5OH.

It can be seen that Pt/TiO_2/G displayed a 2.8 times higher current compared to Pt/G electrode. Considering that Pt/TiO_2/G and Pt/G had near Pt loading (see table1), the Pt/TiO_2/G appeared significantly more active for ethanol oxidation. Furthermore, the onset potentials of Pt/TiO_2/G (0.35V vs Ag/AgCl) were lower than those of Pt/G (0,2V) though the peak potentials were a little higher (0,55 V) than Pt/G (0,75V), this fact indicated that Pt/TiO_2/G have higher catalytic activity for ethanol oxidation at low potential than Pt/G.

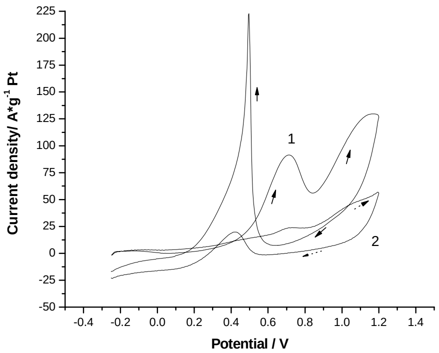

Fig. 11. Cyclic voltammograms for ethanol electro-oxidation at Pt/TiO$_2$/G, (1) and Pt/G,(2) electrode in 3,75 M C_2H_5OH and 0.5 M H_2SO_4 solution with a scan rate of 50 mV/s.

The peak current measured ethanol oxidation during the forward scan, and corrected for the double layer charging contribution, is generally used for the evaluation of the so called "mass activity", an important parameter for the characterization of an electrocatalyst [13]. In our case, for Pt/TiO2/g and Pt/G electrodes the mass activity calculated from fig.3 was ca. 63.8 A/g , respective 15,9 A/g.

A plot of oxidation current vs. time (chronoamperometry) was measured in 2.75 M ethanol + 0.5 M H_2SO_4 for the two electrodes at a constant potential of 0.6 V vs. Ag/AgCl. As shown in Fig.12 the TiO$_2$/Pt/G electrode reveals much higher steady- state current than Pt/G electrode. This is a direct evidence that TiO$_2$/Pt/G have higher catalytic activity then Pt/G electrode.

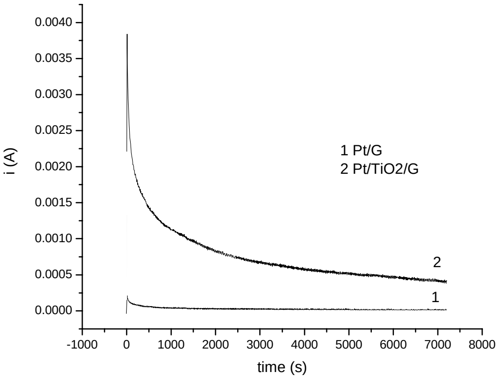

*Fig. 12. Chronoamperometric response of Pt/G (1) and TiO$_2$/Pt/G (**2**) electrodes of the ethanol oxidation in 0.5 M H_2SO_4 solution at an applied potential of 0.6 V vs. Ag/AgCl.*

4. Conclusions

The platinum nanoparticles, about 5 nm in size, are deposited in the both electrodes, graphitized carbon and graphitized carbon covered with TiO$_2$, in aggregates with dimensions from 30 to 500nm. The electrodeposited titanium oxide coating consists from crystallites of anatase and also rutil structure, with size between 30 to 80 nm.

The TiO$_2$ electrodeposited layer shows a three dimensional growth forming a porous surface morphology. The phase's analysis reveals very small platinum coverage degree, about 3% for the TiO$_2$/G electrode, in a well concordance with carbon non covered surface by titanium oxide, about 5%.

Electrodeposited platinum catalyst on titanium oxide porous coating is formed from very small nanosized particles spherical aggregates, comparing with the much larger platinum aggregates deposited in the TiO$_2$ non covered pores sites of the carbon electrode. As a conclusion of this work, the particles of platinum embedded in the film of titanium oxides have a better catalytic effect then the particles of platinum deposited directly on the support of graphite.

Acnowledgement

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References

[1] E. S. Steigerwalt, G. A. Deluga, D. E. Cli.el, C. M. Lukehart, J. Phys. Chem. B **105**, 8097 (2001)
[2] W. D. King, J. D. Corns, O. J. Murphy, D. L. E. Boxall, A. Kenik, K.C. Kwiatkowski, S.R. Stock, C.M. Lukehart, J. Phys. Chem. B 107, 5467 (2003).
[3] B. Rajesh, K. R. Thampi, J.-M. Bonards, H. J. Mathieu, N. Xanthopoulos, B. Viswanathan, J. Power Source. **141**, 35 (2005).
[4] L. H. Jiang, G. Q. Sun, Zh. H. Zhou,W. J. Zhou, Q. Xin, Catal. Today **93–95**, 665 (2004) .
[5] Y. X. Bai, J. J. Wu, J. Y. Xi, J. Sh. Wang, W. T. Zhu, L. Q. Chen, X. P. Qiu, Electrochem. Commun. **7**, 1087 (2005).
[6] M. Hepel, I. Kumarihamy, C.J. Zhong, Electrochem. Commun. **8**, 1439 (2006).
[7] J. Tian, G. Sun, L. Jiang, S. Yan, Z. Mao, Q. Xin, Elecrochem. Commun. **9**, 563 (2007).
[8] A. Manivanan, N Spataru, K Arihara, A Fujishima, Electrochemical and Solid state Letters, E **8** (10), (2005).
[9] S. S. Gupta, J. Datta. J.Chem. Sci., **117**, 337 (2005),
[10] A. Pozio, M. De Francesco, A. Cemmini, F. Cardellini, L. Giorgi, J. Power Sources, **105**, 13 (2002).
[11] G. Tamizhmani, G. A. Capuano, J. Electrochem. Soc. **141**, 968 (1994).
[12] V. S. Bogotzky, Y. B. Vassilyev, Electrochim. Acta **12**, 1323 (1967)
[13] F. Gloaguen, J. M. Leger, C. Lamy, J. Appl. Electrochem. **27**, 1052 (1997)

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