OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 5, No. 11, November 2011, p. 1186 - 1189

Pt supported on nanosized oxides for electrocatalyst used in polymer electrolyte fuel cells

N. BANU, E.C. SERBAN, A. MARINESCU, A. M. I. TREFILOV, A. ANDRONIE-BALAN, A. CUCU, S. IORDACHE, C. CEAUS, O. CINTEZA[a], I. STAMATIN*, A. CIOCANEA[b], S. STAMATIN[c]
University of Bucharest, 3Nano-SAE Research Centre, P.O.Box MG-38, 077125 Magurele, Bucharest-Romania
[a]*University of Bucharest, Physical Chemistry Department, Bucharest, Romania*
[b]*Polytechnic University of Bucharest, Faculty of Energetic, Bucharest, Romania*
[c] *University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark*

Even though Pt is a standard catalyst for fuel cells, new advanced materials with low activation energy and high specific surface area are required. Researches proved that conducting oxides are the emerging candidates as support for Pt catalysts targeting replacement of nanocarbons. This paper proposes a study on the properties of a new anode electrocatalyst based on nanosized TiO_2/SiO_2 coated with Pt nanoparticles. Pt catalyst supported on nanoparticles SiO_2 and TiO_2 with different size and morphologies were deposited by sol-gel process. Dimensional analysis on the nanoelectrocatalysts showed a 20-56 nm particle diameter interval. The electrochemical activity of the obtained structures was measured by cyclic voltammetry where high double layer capacity and low electrocatalytic activity has been identified. Large double layer capacity recommends Pt coated SiO_2 and TiO_2 toward photocatalytic applications.

(Received October 24, 2011; accepted November 23, 2011)

Keywords: PEMFC, Mezoporous catalyst support, Nanoelectrocatalysts

---

1. Introduction

Fuel cell electrocatalysts are designed for specific range of temperatures, different types of fuel cell, resistant to CO/ CO_2/ H_2S poisoning and long life cycle. Each type of electrocatalyst depends on the nature of the fuel (the oxidant) and on the working conditions. Thus, at high temperatures, low activity catalysts are accepted since the already high thermal energy reduces the activation barrier. Other properties should be considered as well: solubility, self recovering of the active site and resistance to oxidation or poisoning. Usually in polymer electrolyte membrane fuel cells (PEMFC), the electrocatalyst nanoparticles are spread at membrane-gas diffusion layer interface aiming for a high specific surface area [1]. The fuel splitting into electrons and protons requires a double interface in order to transfer the electrons to the collector electrode and the protons through the electrolyte. This function is accomplished by the catalyst support. At their interface, a phase separation layer appears, known as the *three-phase boundary* [2].

Platinum, the most common catalyst for hydrogen oxidation in fuel cells, has been used in different forms, such as alloyed with Ru [3], Ni [4], Pd [5], deposited on nanocarbon [6] or nanooxides (aluminium oxide [7], silicon dioxide [8], titanium oxide [9], zinc oxide [10], copper oxide[11]) either to decrease poisoning or to increase the electrocatalytic activity. The electrocatalytic activity between nanoxides as support and platinum has been less investigated. While oxides are, in general, catalyst for different chemical reactions, nanooxides have a specific behaviour related to the conduction mechanisms and electrochemical activity via ion and defects on their surface. On the other hand Pt catalyst has a specific behaviour to the hydrogen oxidation via electron transfer. It is expected for systems metal-coated nanooxides to get high electrocatalytic activity for specific applications, particularly to the fuel cells.

The purpose of this work is to study the behaviour of the nanometric Pt particles on nanometric TiO_2 and SiO_2 substrate. Silicon dioxide has good affinity to the hydrogen adsorption leading to hydroxylation and titanium dioxide (rutile and anatase form) are p-type semiconductors. In most catalytic reaction systems, the anatase is accepted as having a better activity than rutile. The obtained structures have been analyzed dimensional and the electrochemical activity by cyclic voltammetry

2. Experimental

2.1 Synthesis of silica nanoparticles

The silica nanoparticles are synthesized in Aerosol-OT (Fluka) surfactant micelles. The micelles systems were prepared by dissolving 0.22 g of Aerosol-OT and 400 μL of 1-butanol (Merck) in 5 mL distilled water under stirring. In the final stage was added in dropwise 30 μL of chloroform (Fluka) and stirring until a transparent solution forms. In the subsequent stage was added vinyl trietoxisilan, (VTES) the precursor for silica sol. 50 μL of VTES (Merck) were added to the micelle system, 30 min continuous stirring. The hydrolysis reaction, in order to initialize the silica polymerization process, was performed by dropwisse of 10 μL of ammonium hydroxide (33%). The sol solution was left to mature under stirring for 20 hours at room temperature, stage where the nucleation and growth of the silica nanoparticles takes place in the micelles solution. The Aerosol-OT surfactant and the 1-butanol co-surfactant were removed by water dialysis through a cellulose membrane between 12-14 kDa for 50 hours. The dialyzed solution was filtered using a 0.2 μ cellulose filter. The filtrate left on membranes was dried and stored at RT.

2.2 TiO_2 nanoparticles

*TiO_2 rutile phase.*The TiO_2 rutile phase structure was obtained by $TiCl_4$ (Fluka) hydrolysis using the sol-gel method similar with the methods described elsewhere [12-13]. The rutile phase was confirmed by Raman spectroscopy.

TiO_2 anatase phase. The anatase form was bought it from TiPe-TitanPE Technologies, grade *TIPE X* 550, yellowish transparent liquid: Nano Titanium Dioxide, anatase <8nm average diameter, dispersant water –based. Coagulation index: 2-4.

TiO_2 anatase, platinum coated. Grade *Pt 600*, from TiPe-TitanPE Technologies, water-based nano TiO_2 sol, yellowish transparent liquid: Nano Titanium Dioxide, Nano Platinum Cluster (not specified concentration), anatase <8nm average diameter. Coagulation index: [2-4].

2.3 The synthesis of a $Pt/TiO_2(SiO_2)$ catalyst by $NaBH_4$ reduction

Pt/TiO_2 and Pt/SiO_2 catalysts were obtained by Pt precipitating on TiO_2 and SiO_2 nanoparticles using the reduction reaction of H_2PtCl_6 (Merck) with $NaBH_4$ (Lachema):

$$2H_2PtCl_6+3H_2O+NaBH_4\rightarrow$$

$$2Pt+NaCl+11HCl+H_3BO_3$$

An H_2PtCl_6 (10%) solution was added, under constant stirring, to a certain amount of TiO_2/SiO_2 for a 20% Pt load. Next, the adequate quantity of $NaBH_4$ (15 *mM*) was added in dropwise under constant stirring at room temperature. After stirring the substance for 1 hour, the suspension was filtered. The solid filtered part was washed until a neutral pH and then, dried at 70 ^{0}C in air for 3 hours [14].

2.4 Characterization methods

To identify the particles size, the obtained samples were investigated by DLS, NanoZeta Sizer (ZEN 3600) with a red laser at 633 nm. The Zetasizer Nano System combines dynamic, static and electrophoretic light scattering technologies enabling the measurement of particle size, zeta potential and molecular weight. The sample solution used in DLS contained: 1 mg sample dispersed in water by ultrasonation for 5 min using ultrasonic processor UIP 1000hd (Hielscher Ultrasound Technology).

Cyclic voltammetry (CV) was performed on a VoltaLab PGZ 301 potentiostat (Radiometer) with a three-electrode electrochemical cell. The working electrode (WE): polished spectroscopic graphite. A mixture containing 1 mg of the sample, 25 μL Nafion and 75 μL isopropyl alcohol was drop cast and dried on 1cm^2 WE. Auxiliary electrode: Pt XM140, Reference electrode: standard calomel electrode (SCE). Measurements were performed at different H_2SO_4- electrolyte concentrations: 0.5 M, 1M and 3 M.

3. Results and discussion

The support material was investigated by DLS in order to determine the dimensional range of the particles (Table 1).

Table 1. DLS dimensional analyses.

Sample	Diameter (nm)
SiO_2	19.86
TiO_2	56.09
X550	25.78

SiO_2 catalytic activity was studied for three different electrolyte concentrations: 0.5M, 1M, 3M H_2SO_4 (Fig. 1). Two peaks assigned to oxidation around 580-600 mV, respective 200 mV for reduction vs. SCE were identified.

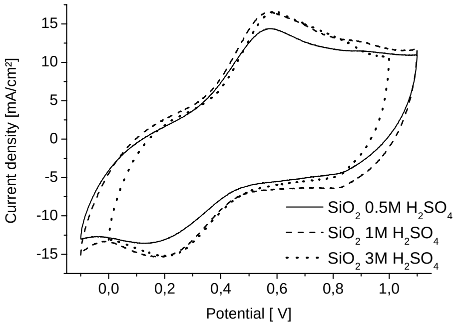

Fig. 1. Cyclic voltammograms for the SiO_2 vs SCE reference electrode.

For Pt supported on SiO_2 the cyclovoltammograms show a specific behaviour (Fig. 2). The hydrogen desorption on Pt sites seems to be independent of the ionic strength of the electrolyte solution.

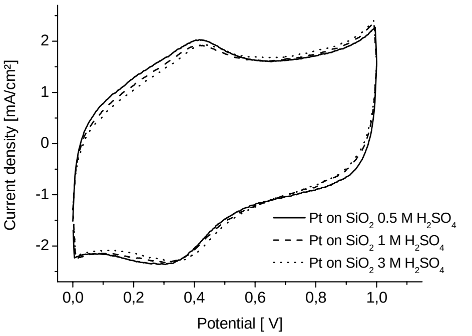

Fig. 2. Cyclic voltammograms for the Pt deposited SiO_2 vs. SCE reference electrode.

Typically, Pt electrode in 1M H_2SO_4 electrolyte presents the oxidation and reduction peaks at 800 mV, respectively at 550 mV [15]. In this case, due to the chemical bonding to SiO_2 which is an ion conductor, the double layer capacity and the magnitude of the peak currents decrease. Having this said the oxidation and reduction peaks are shifted to 400 mV respectively 300 mV.

Table 2.

Sample	H_2SO_4 concentration	C_d ($\mu F/cm^2$)	Q_T (mC/cm^2)
SiO_2	3M	8.5	5.5
	1M	4.0	5.1
	0.5M	7.5	2.5
Pt/SiO_2	3M	1.9	0.70
	1M	1.9	0.71
	0.5M	1.9	1.55

Double layer capacity, C_d, (mF/cm^2) and total specific charge transfer, Q_T, (mC/cm^2) were calculated for each CV corresponding to SiO_2 and Pt deposited on SiO_2 for all electrolyte concentrations (Table 2). Fig. 3 represents the cyclic voltammograms of the rutile, where a very low oxidation and reduction potential are indexed. The sample shows a dynamic double electric layer because the current density increases with applied voltage.

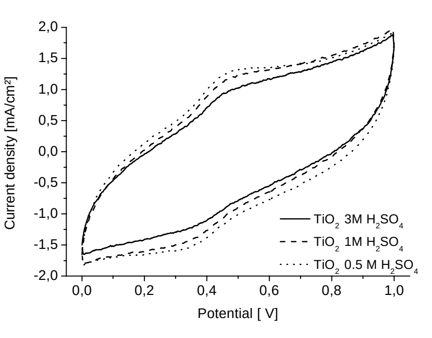

Fig. 3. Cyclic voltammograms of TiO_2 (rutile) response vs SCE reference electrode.

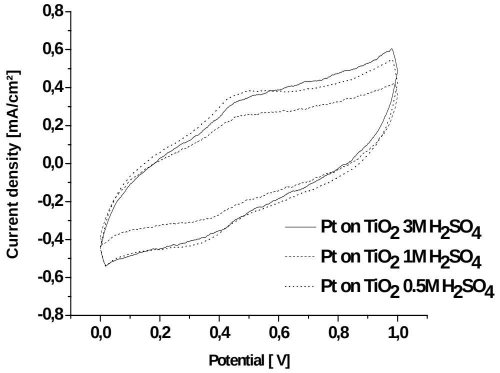

Fig. 4. Cyclic voltammograms on the Pt deposited TiO_2 (rutile) response vs SCE reference electrode.

The curves on Figs. 3 and 4 (rutile and Pt on rutile), has a symmetric oxidation and reduction peaks centred on 0.35mV and 0.45mV. The catalytic activity of both samples depends on the ionic strength of the electrolyte solution.

The samples were prepared differently. On one hand the Pt/TiO_2 sample was doped with Pt by $NaBH_4$ reduction of, while on the other the Pt600 is a solution from TIPE, which has in composition Pt. This solution has a good photocatalytic response, due to its TiO_2 support. The double layer capacity makes the difference between anatase (X550) represented in Fig. 5 and rutile.

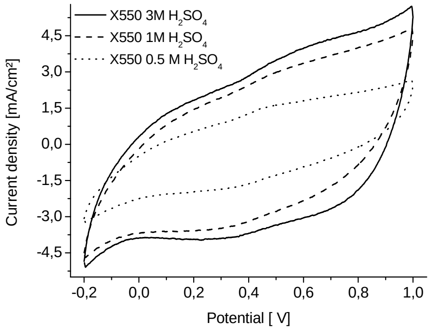

Fig. 5. Cyclic voltammograms of X 550 (anatase TiO_2) vs SCE reference electrode.

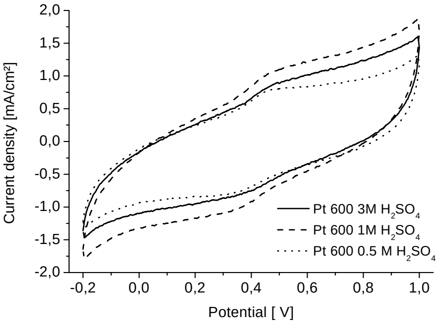

Fig. 6. Cyclic voltammograms of Pt600 (Pt deposited on anatase TiO2) vs SCE reference electrode.

The oxidation and reduction effect is reduced due to the p-type semiconductor character of TiO_2 and due to the interaction of TiO_2 microstructure with protons inside the electrolyte. Data in the Table 3 show that the double layer capacity for Pt/TiO_2 (rutile) is approximately two times lower than the double layer capacity of TiO_2*(rutile*). In case of Pt –anatase (Pt600) the double layer capacity is approximately 3 times higher than regular anatase X550. The double layer is not dependent of acid concentration. A first conclusion is that rutile is more appropriate support for electrocatalyst and anatase form is recommended for photocatalytic activity [16].

Table 3.

Sample	**H_2SO_4 conc**	**C_d (μF/cm^2)**
TiO_2 *(rutile)*	3M	8.6
	1M	9.2
	0.5M	8.0
Pt/TiO_2 *(Pt/ rutile TiO_2)*	3M	4.5
	1M	3.1
	0.5M	4.3
X550 *(anatase TiO_2)*	3M	6.1
	1M	5.3
	0.5M	4.1
Pt 600 *(Pt/anatase TiO_2)*	3M	15.2
	1M	15.9
	0.5M	12.0

4. Conclusions

Pt supported on SiO_2 and TiO_2 nanoparticles are not presenting any specific characteristics for the PEMFC catalyst applications. Even though Pt nanoparticles exhibit high catalytic activity for the oxidation reaction, TiO_2 or SiO_2 are not presenting a good support for Pt, regarding PEMFC applications. Also, Pt 600 did not present any catalytic activity for PEMFC applications. It can be concluded that both TiO_2 and SiO_2 as support for Pt particles are not presenting a good answer concerning the oxidation reaction in PEMFC.

Acknowledgements

The authors acknowledge the financial support from national projects National Program PN-II, contracts 22-136/2008, PN-II-ID-PCE-2011-3-0815.

References

[1] J. M. Song, S. Suzuki, H. Uchida, M. Watanabe, Langmuir, **22**(14), 6422 (2006).
[2] A. J. Dickinson, PhD thesis, University of Newcastle upon Tyne, UK, (2000).
[3] M.-S. Hyun, S.-K. Kim, B. Lee, D. Peck, Y. Shul, D. Jung, Catalysis Today **132**, 138 (2008).
[4] M. K. Jeon, Y. Zhang, P. J. McGinn, Electrochimica Acta **54**, 2837 (2009).
[5] R. S. Jayashree, J. S. Spendelow, J. Yeom, C. Rastogi, M. A. Shannon, P. J. A. Kenis, Electrochimica Acta **50**, 4674 (2005).
[6] A. Pozio, M. De Francesco, A. Cemmi, F. Cardellini, L. Giorgi, Journal of Power Sources **105**, 13 (2002).
[7] S. A. Solov'ev, Y. P. Kurilets, S. N. Orlik, Theoretical and Experimental Chemistry **39**(1), 58(6) (2003).
[8] M. Cai, M. S. Ruthkosky, B. Merzougui, S. Swathirajan, M. P. Balogh, S. H. Oh, Journal of Power Sources **160**, 977 (2006).
[9] A. Fujishima, X. Zhang, D. A. Tryk, Surface Science Reports **63**, 515 (2008).
[10] A. Faur Ghenciu, Current Opinion in Solid State and Materials Science **6**(5), 389 (2002).
[11] T Dittrich, A. Belaidi, A. Ennaoui, Solar Energy Materials & Solar Cells **95**, 1527 (2011).
[12] G. Ramakrishna, A. K. Singh, D. P. Palit, H. N. Ghosh, J. Phys.Chem. B **108**, 4775 (2004).
[13] B. Neppolian, Q. Wang, H. Jung, H. Choi, Ultrasonics Sonochemistry **15**, 649 (2008).
[14] Beyrdbey, B. Corbacioglu, Z. Altin, Journal of Science **22**(4), 351 (2009).
[15] C. H. Hamann, A. Hamnett, W Vielstich. Electrochemistry Wiley-VCH: New York, 423 (1998).
[16] W. J. H. Borghols, M. Wagemaker, U. Lafont, E. M. Kelder, F. M. Mulder, Chem. Mater. **20**, 2949 (2008).

---

[*] Corresponding author: office @3nanosae.org