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Section 5. Carbon and Boron

Platinum / carbon / polyaniline based nanocomposites as catalysts for fuel cell technology

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One of desirable factors in fuel cell systems is to assure a high catalytic activity at the electrode level. This aspect is achieved by depositing the catalyst on high surface area substrate, having the property to be a good electronic conductor and developing in the same time a high ionic conduction. The literature shows different methods of catalyst deposition on carbon substrates, such as Vulcan XC 72R, by a direct chemical reduction of the metallic catalyst, in the presence of a reductant media as formaldehyde solution, or thermal reduction in H_2 / N_2 atmosphere at over 600 ^{o}C. In order to evaluate the catalytic performance of supported Pt, we have investigated a proper method for the noble metal deposition on different substrates such as: Vulcan XC 72R, Ketjen Black EC 300J and PANI, which is suitable to give a close performance compared with commercial one. The catalyst performances were investigated by FTIR, XRD, TEM and Cyclic Voltammetry.

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1. Introduction

Fuel cell is a power device that produces electricity without combustion. Chemical energy is converted directly into electrical energy and heat when hydrogen fuel is combined with oxygen from the air [1–4].

In working conditions, the hydrogen and oxygen are piped into the fuel cell's porous electrodes. On the anode side, the molecular hydrogen is catalyzed giving a stream of electrons ($2e^-$) and protons ($2H^+$). The electrons pass through an external circuit from anode to cathode giving an electrical current, while the protons pass through membrane towards cathode. On the cathode side, the piped oxygen combines with the protons ($2H^+$) to form water.

The functions of porous electrodes in fuel cells are: (1) to provide a surface site where gas/liquid ionization or de-ionization reactions can take place; (2) to conduct ions away from or into the three-phase interface once they are formed (so an electrode must be made of materials that have good electrical conductance) and (3) to provide a physical barrier that separates the bulk gas phase and the electrolyte [1].

In order to increase the rates of reactions, the electrode material should be catalytic as well as conductive, porous rather than solid. This technical aspect could be achieved by depositing the catalyst on a high surface area substrate, having the property to be a good electronic conductor and developing in the same time a high ionic conduction.

Usualy, the authors use to disperse the catalyst on the surface of a conducting nanocarbon like commercial Vulcan - XC 72R or Ketjen Black - EC 300J. The ionic conduction is given by impregnation of the carbon supported catalyst with a proton conductive polymer, like Nafion®. The literature shows different methods of catalyst deposition on carbon substrates, such as Vulcan XC 72R, by a direct chemical reduction of the Pt catalyst, in the presence of a reductant media as formaldehyde solution, or thermal reduction in H_2 / N_2 atmosphere at over 600 ^{o}C [5,6]. Other authors reported methods were electrochemical techniques for Pt deposition on polyaniline (PANI) [7-13] or even direct chemical reduction of Pt from H_2PtCl_6 in the presence of a reductant media as $NaBH_4$ / NaOH [13].

The aim of our research is obtaining a conductive and stable electrode, with a high surface area, improving thus the catalytic activity and the ionic changes at a high speed on the surface of the electrode. Our purpose is to use a highly conductive polymer (e.g. polyaniline) in order of achieving these desirable features. On the other hand, polyaniline is attractive for our purpose due to: high conductivity upon doping with acids (10^{-1}-10^{2} S/cm); good electrochemical behaviour; easy preparation under reproducible conditions by both electro-polymerization and chemical oxidation of aniline; chemical, electrical and environmental stability.

In order to evaluate the PANI performance as catalyst support, we have investigated a proper method for the catalyst preparation, which is suitable to give a catalyst with close performance compared with commercial one (e.g. E-TEK). Considering the technical routes reported in literature, we used a suitable method of Pt deposition, being adequate for all kinds of substrate as PANI, Vulcan XC 72R and Ketjen Black – EC 300J.

2. Experimental

2.1 Polyaniline Synthesis by Self Assembly Polymerization Method

Polyaniline was prepared by chemical oxidation of 0.2 M of aniline sulfate with 0.25 M ammonium peroxydisulfate according to literature procedure [14,15]. Aniline sulfate (3.82g, purum, Aldrich) was dissolved in 50 mL of 0.2 M sulfuric acid, in a volumetric flask. Ammonium peroxydisulfate (5.71g, purum, Aldrich) was dissolved in 50 mL of 0.2 M sulfuric acid. Both solution were kept for 1h at the room temperature, then mixed in a beaker, briefly stirred and left to polymerize for 24h. The green precipitate was collected on a filter, washed with 300 mL of 1M sulfuric acid to removes the residual monomer, the oxidant and its decomposition products. Supplementary, the precipitate was washed with 300 mL acetone to removes the low molecular weight organic intermediates and oligomers. The resulting polyaniline salt (C_6H_5-NH-HSO_4) was dried at the room temperature for 3h and further in an oven at 70 °C for 3 h.

2.2 Pt loading Carbon / PANI substrates

1g of commercial Ketjen Black – EC 300J, Vulcan - XC 72R and in-lab fabricated PANI were dispersed by ultrasonication for 15 min in 50 cm^3 D.I water, producing a homogeneous slurry. 1g sodium bicarbonate was added to the slurry and ultrasonicated for 15 min. The slurry was boiled for 30 min at 80 °C, under continues stirring. A solution of 1.5 g chloroplatinic acid in 60 ml D.I. water was added to the slurry, keeping the ultrasonication for 15 min. The slurry was boiled for 60 min at 80 °C, under continues stirring. 3 cm^3 of formic acid solution in 25 cm^3 D.I. water was added to the slurry, ultrasonicating for 10 min. The slurry was boiled for a further 60 min at 80 °C, under continues stirring and then filtered and washed with D.I. water to pH 7. The precipitate was dried in vacuum at 100 °C for 60 min and then supplementary dried for 12 hours at about 100 °C in an oven.

A supplementary reduction of Pt at temperatures over 600 °C was avoided, taking into account that PANI begin to decompose at over 200 °C.

2.3 Investigations

Have been prepared and investigated:

- PANI supported Pt 40%
- Ketjen Black – EC 300J supported Pt 35%
- Vulcan – XC 72R supported Pt 35%

Have been investigated also:

- Commercial Pt 60% on Vulcan (E-TEK)
- Commercial Pt 30% on Vulcan (E-TEK)

The obtained nanocomposites were characterized by using different methods:

- X-ray diffraction (XRD) data were obtained by using a Bruker D8 Advance equipment with Cu Ka radiation;
- SEM images were colected on JEOL Model JSM-5400 Scanning Electron Microscope;
- TEM images were obtained by using a LEO 912AB-B Electron Microscop.
- Cyclic Voltammograms were obtained with a Sycopel Potentiostat / Galvanostat, at a scan rate of 50 mVs in deaerated 1 M H_2SO_4 solution, between +0.8 and – 0.6 mV vs. Mercury / Mercurous Sulphate electrode (MMS).

The obtained PANI support was characterized by Fourier Transform Infrared Spectroscopy (FT-IR) with a Perkin Elmer 2000 equipment, in the region of 2000 – 600 cm^{-1} using KBr pellets.

3. Results and discussions

Generally, our work is characterized by implementation of polyaniline as conducting polymer in fuel cell technology. The performance of this technology is supported by the achievement of the desirable features such as: high surface area electrodes, high catalytic activity, very good electronic and protonic conductivity at the electrode level, good stability at elevated temperatures, acceptable cost etc.

If we are considering the surface area and electronic conductivity in fuel cells, many of these features are supported by the special carbon blacks used: Vulcan XC-72R and Ketjen Black EC 300J. On the other hand, the desired properties could be achieved by developing new materials with a good protonic conductivity, being possible to remove some expensive components from a fuel cell (e.g. Nafion membrane) with another cheaper. New and cheap catalyst or catalyst supports development which can assure a high catalytic activity is an also big issue of the fuel cell technology.

A key property of using a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized “pi” (π) bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition – and this is what the dopant does – charge carriers in the form of extra electrons or ”holes” have to be injected into the material. A hole is a position where an electron is missing. When such a hole is filled by an electron jumping in from a neighboring position, a new hole is created and so on, allowing charge to migrate a long distance.

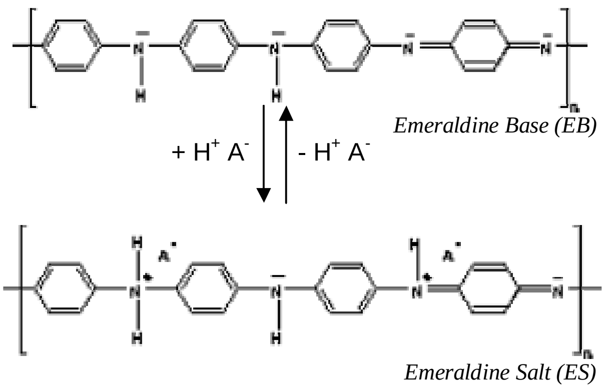

Fig. 1. Polyaniline transition between conducting (Emeraldine Salt – acidic medium) and no conducting form (Emeraldine Base – alkaline medium), where A^- = anion species (e.g. HSO_4^-) [15].

By doping the polyaniline in sulfuric acid media, actually we introduce some charge carriers which make possible the electrical conduction along the polymer chain. Controlling the pH, we can switch very easy between the conducting and no conducting forms of polyaniline, Fig. 1.

In fuel cell technology, the commercial carbon used both as gas diffusion layer (GDL) and catalyst support (Ketjen Black EC 300J) is considered being a conductive carbon, with a high surface area, of about 600 m^2/g. The measured electrical conductivity is about 5 S/cm. This lack of conductivity compared with a graphite is given by the morphology of the respective carbon. Other types of nanostructured carbon, used by the researchers in the fuel cell technology, are the nanotubes or the fullerenes. These structures could offer a very high surface area but are not proper for utilization as a catalyst support due to a very small particle size of about 1 nm. If we consider the reported optimum crystallite size of 3-4 nm for Pt particles dispersed on a carbon support, we can conclude that a deposition of Pt catalyst using carbon nanotubes or fullerenes as supports will determine the catalyst clusterization, decreasing the surface area and the catalytic efficiency. Also, taking into account the morphology, conduction properties and chemical inactivity, we consider the utilization of nanostructured carbon in fuel cell technology being almost limited.

The electrical conductivities of Ketjen Black EC 300J and PANI were measured in a special designed two-point probe equipment, Fig. 2, in a range of temperatures between 25 ^oC and 120 ^oC. In this measurement we have been using a cylinder mold, composed by two SS electrodes and a teflon tube having the inner diameter of 1 cm^2. Applying DC current by a power supply (PS), in a range between 20 mA and 1 A, we measured the voltage as response of the passing current through the particulate conductive / resistive sample.

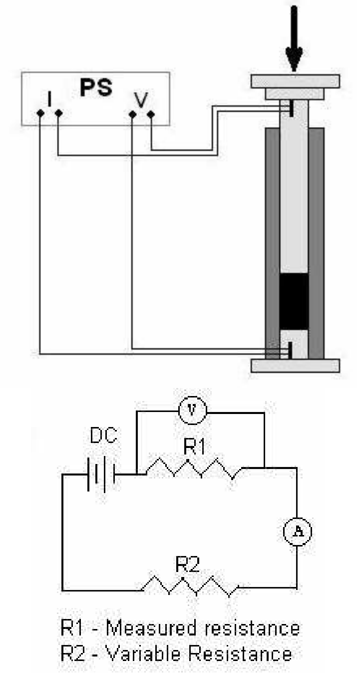

Fig. 2. Designed two-points probe equipment for electrical conductivity measurement.

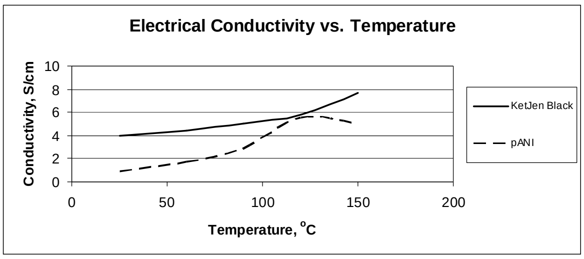

Fig. 3. Dry state electrical conductivity comparison: Ketjen Black EC 300 J vs. PANI (two points probe measurement).

The obtained electrical conductivity of PANI is about 3 S/cm, Fig. 3, acording to different reports relating the conductivity of Emeraldine Salt (ES), doped with sulfuric acid [15]. In dry state, the conductivity of polyaniline, is in the same range relating the carbon black conductivity. However, taking into account the literature reports [15,18], the polyaniline's conductivity increases about 5 times in wet conditions compared with dry state.

Moreover, by controlling the pH and aniline polymerization parameters, we can change the morphology of polyaniline, passing from amorphous clusterized structure, Fig. 4, to nanotubes/ nanofibers with a diameter of about 80 nm and a length of about 300 nm, Fig. 5, and thus controlling the surface area of PANI.

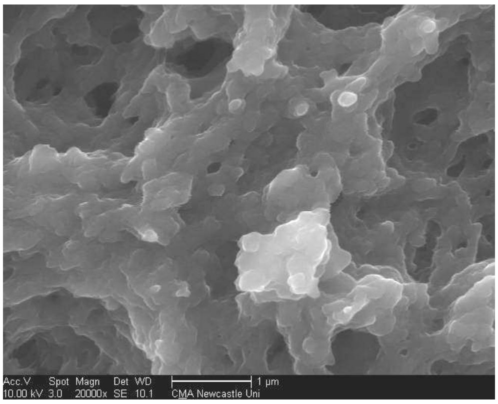

Fig .4. SEM on an electrodeposited PANI sample by Cyclic Voltammetry Method x 20000.

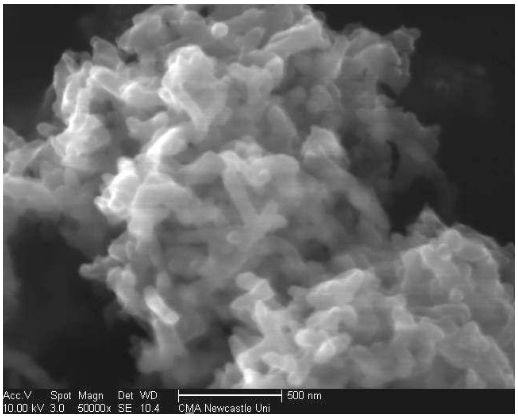

Fig. 5. SEM on a PANI sample obtained by Self Assembly Polymerization Method × 50000.

The FTIR spectra of a PANI sample obtained by Self Assembly Polymerization Method shows similar characteristics with literature reports [19,20], with characteristics bands of a doped polyaniline structure at 1610, 1570, 1480, 1300, 1240, 1139, 1050, 870 and 820 cm^{-1}, Fig. 6.

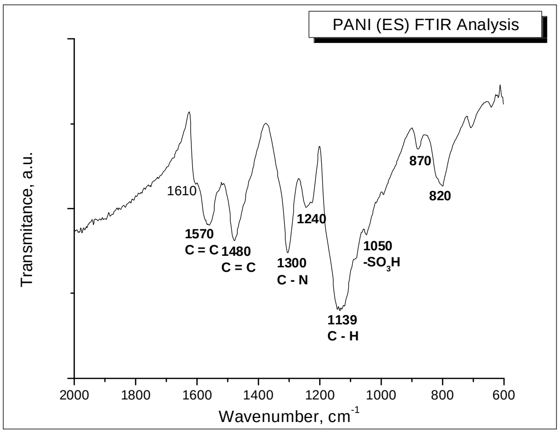

Fig. 6. FTIR Analysis of a PANI sample obtained by Self Assembly Polymerization Method.

The XRD patterns for supported Pt catalysts are shown in Fig. 7. All catalysts exhibit the diffraction peaks of the fcc structure. The mean particle size in all catalysts was estimated from the broadening of 220 reflection. The particle sizes were found to vary between 3-5 nm, Table 1.

Table 1. Particle sizes evaluation by XRD for in-lab supported catalysts.

Catalyst type	Metal loading, %	Particle size, nm
Pt on Ketjen Black	35	5.4
Pt on Vulcan	35	5.5
Pt on PANI	40	3.7
Pt on Vulcan (E-TEK)	30	4
Pt on Vulcan (E-TEK)	60	7

The mean size of Pt clusters evaluated by TEM is compared with that of XRD, Fig. 8-12. The two data agree reasonably well and corresponds with the literature reported values [21,22].

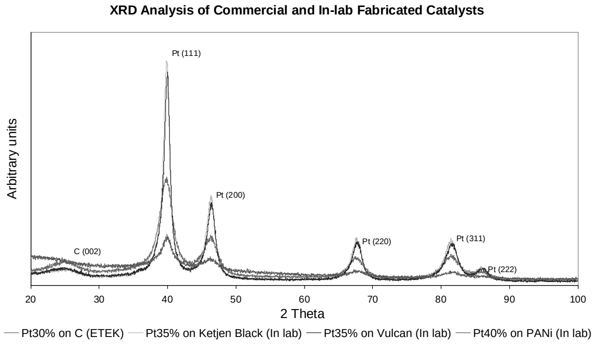

Fig. 7. XRD Analysis of commercial and in-lab made catalysts on C / PANI supports.

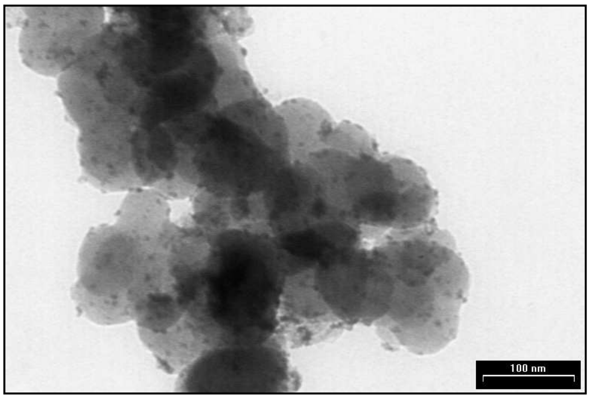

Fig. 8. Pt 35% on Vulcan, in-lab.

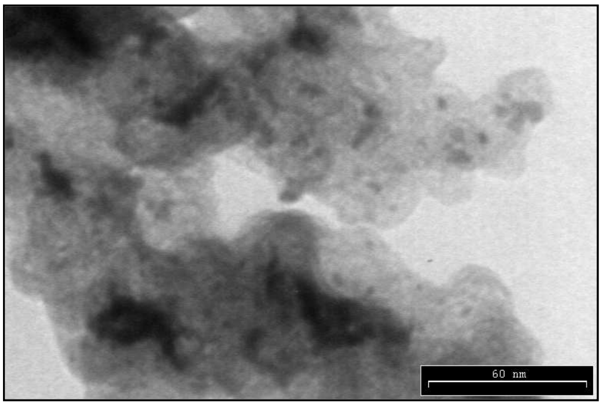

Fig. 9. Pt 35% on Ketjen Black, in-lab.

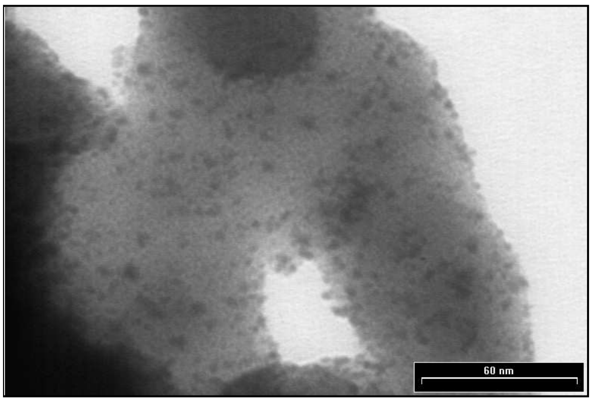

Fig. 10. Pt 40% on PANI, in-lab.

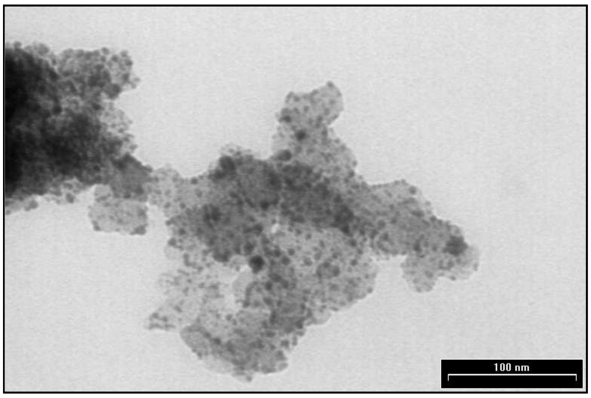

Fig. 11. Pt 30% on Vulcan, ETEK.

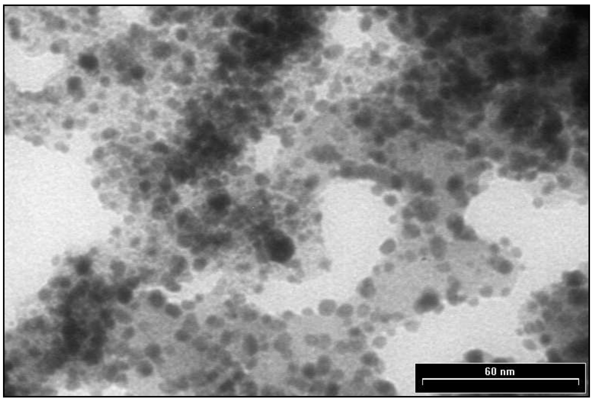

Fig. 12. Pt 60% on Vulcan, ETEK.

In order to establish the catalytic activity of in-lab fabricated supported catalyst, cyclic voltammograms were obtained between +0.8 and - 0.6 mV vs. Mercury/Mercurous Sulphate electrode (MMS), at a scan rate of 50 mVs in deaerated 1 M H_2SO_4 solution. Fig. 13 shows the cyclic voltammograms of the catalysts in gas diffusion electrodes.

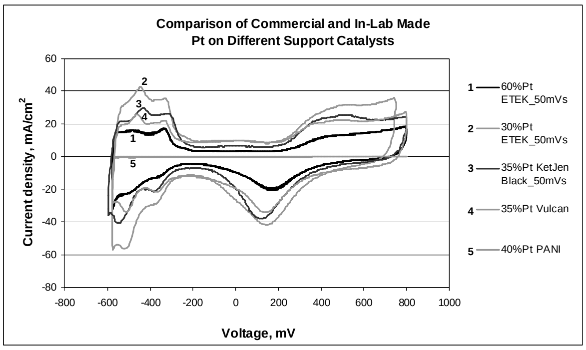

Fig. 13. Cyclic Voltammetry Analysis of commercial and in-lab made catalysts on C / PANI supports.

The cyclic voltammograms reveal that the surface area decreases while the particle size increases, corresponding with the peak around - 550 mV vs. MMS. Voltammograms for the commercial catalyst were most similar to those for the in-lab fabricated catalyst, although showed somewhat higher currents over the whole potential range. These current enhancements are due to increases in the electrochemically active surface area of the catalyst, and are direct related to the particle size.

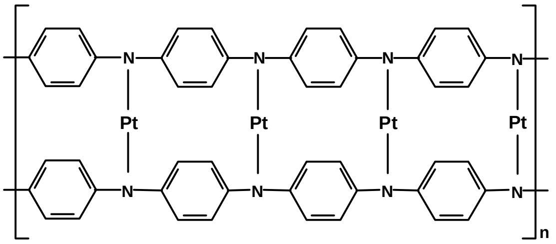

Fig. 14. Pt/PANI Complex [13].

In spite of very good dispersion of Pt on the polyaniline support, poor PANI supported catalyst performance in terms of CVs, Fig. 16, and polarizations was experienced, although correct particle size was achieved, of 3–5 nm considering the TEM and XRD data. Hence poor performance may be due to chemical incorporation of Pt inside the PANI particles, forming a kind of Pt/PANI complex, Fig. 14 [13]. This remains to be confirmed, but PANI may be chemically deactivated prior to deposition and provide a useful support structure.

4. Conclusions

We consider that the above described method is suitable for the catalyst deposition on the carbon supports. By this method can be prepared both Pt and Pt alloys based catalyst. The method is simple and gives catalysts with comparable performances to commercial catalysts.

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