

Preparation of particulate Fuel Cell Electrodes by Electrodeposition Method

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A mixture of MWCNT plus Nafion was prepared and deposited on glassy carbon. Platinum can be deposited directly onto a Nafion+MWCNT-bonded carbon electrode from an aqueous solution consisting of Dihydrogen Dinitrosulfatoplatinate (II). The particle size observed by SEM image was between 810 to 910 nm. We studied the durability of Pt/Vulcan XC-72 and Pt/MWCNT using an accelerated durability tests (ADT). In this test we observed Pt particle dissolution. It can be concluded that multiwalled carbon nanotubes are more resistant to electrochemical oxidation than carbon black (Vulcan XC-72).

Introduction

Proton – exchange – membrane fuel cells (PEMFCs) are considered to provide an environmentally, friendly and sustainable technology. Nevertheless, one of the impediments to their implementation is the cost of manufacturing due to their high platinum content. In order to increase the effective surface area of platinum, several methods have been implemented to prepare the electrodes (1). Among those is electrodeposition of the precious metal onto carbon supports by reduction of platinum salts, such as Na_2PtCl_6 , with the objective of obtaining highly dispersed metal particles (2). It is better does not to use a chloride precursor because chloride is known to poison platinum and impedes the adsorption of oxygen. Thus, any chloride species present must be removed from the PEMFC catalysts before use. Also, $\text{H}_3\text{Pt}(\text{SO}_3)_2\text{OH}$ is not suitable as Thompson (3) has reported. A poisoning species (possibly sulphide or sulphite) was produced with this precursor. To our knowledge, an electroplating bath based on $[\text{Pt}(\text{NO}_2)_2(\text{SO}_4)]^{2-}$ (platinum di-nitro sulfate, Pt-DNS) has not been used to prepare fuel-cell electrodes (1,3). This platinum complex is obtained from $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ by stoichiometric reaction with H_2SO_4 . Sulphuric acid (1N) is used as support electrolyte to maintain pH 2. Recent experiments conducted by Alvarez (4) have revealed that Pt-DNS is a candidate for electrodepositing dispersed platinum onto a composite layer of Nafion – bonded Vulcan XC-72R carbon particles.

The most widely used catalyst support is Vulcan XC-72 carbon black, but Multi-wall carbon nanotubes (MWCNT) are promising in improving the catalytic activity toward fuel cell electrode reactions. In this investigation we examine reduction of Pt-DNS by means of pulse electrodeposition in two carbon supports (Vulcan XC -72R and MWCNT), which was shown to be an attractive technique to replace the conventional preparation methods for powder-type membrane-electrode assemblies (MEAs). The technique of

electrodeposition with pulsed current controls both the size of particles and their adhesion and produces homogeneous deposits selectively. After the electrodes were prepared by pulsed-deposition process, the kinetic parameters of the electrodes were evaluated.

Size distribution is an important characteristic of catalytic materials as it has significant impact on the electrochemical properties. However, commercial software has no automated method for determining this parameter. The main problem is the fact that a general method for segmenting images does not exist; thus, an algorithm must be developed according to the characteristics of the microscopic images to be processed (5). The traditional morphological image-segmentation technique, the so-called watershed-plus-marker approach, was used to segment the images. This technique requires one to identify the appropriate morphological tools for extracting the markers signaling the regions of interest. Then, a procedure, based on morphological filtering, was carried out; next the watershed was applied for segmenting the images. Once the particles in the SEM images were identified, the granulometry was computed.

Other part of this study was the durability of Pt/Vulcan XC-72 and Pt/ MWCNT using an accelerated durability test (ADT) under simulated PEMFC conditions, because oxidation of the carbon catalyst support can result in defects in the support, causes a loss of catalytic activity and decrease the performance of a PEMFC. Degradation of the electrocatalysts is one of the main reasons for the long-term decline in fuel cell performance.

Experimental

Synthesis, Purification and Fuctionalization of Multi Wall Carbon Nanotubes.

Multi-wall carbon nanotubes (MWCNT) were synthesized by spray pyrolysis. Ferrocene (J.T. Baker) was dissolved in toluene (J.T. Baker) and atomized into an argon atmosphere inside Vycor tubing mounted in a tubular furnace held (Barnstead Thermolyne) at 1173 K. The nanotubes were purified by washing in hydrochloric acid (J.T. Baker) solution. This process to eliminate iron ions and functionalized with carboxylic groups by a solution of H₂O₂ (J.T. Baker) (30%V) + H₂SO₄ (J.T. Baker) (70%V). This functionalization was reported by Peng (6) allows to obtain groups -COOH that helped a better anchorage of the Pt ions.

Preparation of Pt/Vulcan XC-72 and Pt/MWCNT Electrodes.

Glassy carbon (GC) electrodes with a geometric area of 0.3848 cm² were used as supports. These were polished to a mirror finish with 0.05μm alumina (Buehler) and cleaned in an ultrasonic bath for 10 minutes. A mixture of Vulcan carbon XC-72 (Cabot) plus Nafion® (ElectroChem, Inc) was prepared, and 5μL were deposited onto the glassy carbon. Another mixture (MWCNT 1mg+ Nafion® 50 μL + ethanol (J.T. Baker) 25 μL) was also prepared with 10μL deposited on glassy carbon. The comparison electrode was fabricated by repeating all procedures with catalysts platinum supported on Vulcan XC-72 (10 and 20 wt.% metal loading). The commercial catalysts platinum were purchased from E-TEK.

The electrodeposition of Pt particles onto the carbon substrates was performed in a conventional cell using a standard three-electrode setup as described by Alvarez (4). The aqueous electrolyte used for Pt deposition contained 10^{-1} M of Dihydrogen Dinitrosulfatoplatinate (II) (Pt – DNS, Alfa – Aezar) at pH 2. The electrochemical deposition was accomplished by cyclic voltammetry with a BAS Epsilon Potentiostat/Galvanostat. After preparation, the electrodes were rinsed with Milli-Q water. During controlled-potential pulse electrodeposition, the current-time behaviour was registered. Based on previous results (4) pulse parameters were chosen as follows: a pulsed step from -0.20 V to -0.81V with a pulse period of 100 ms and 10 cycles of deposition were applied. All potentials are referred to the Normal Hydrogen Electrode (NHE), and all measurements were performed at room temperature.

The effective surface area of the platinum deposit was determined by measuring area under the hydrogen adsorption/desorption peaks during cyclic voltammetry (eliminating the charge for the double layer). Hydrogen adsorption was determined by cyclic voltammogram measurements in 0.5 M H₂SO₄ at sweep rate of 50 mVs⁻¹, with nitrogen atmosphere. The working electrode was cycle in the range of -0.2 to 0.25V.

The oxygen reduction experiments were carried out, using the rotating disk electrode (RDE) technique, in 0.5 M H₂SO₄ saturated with oxygen. The electrochemical kinetics measurements were conducted in a standard electrochemical cell using Pt/Vulcan XC-72 and Pt/MWCNT electrodes as working electrodes. The reduction current on the platinum electrocatalyst electrodeposited on the electrodes Pt/MWCNT in an oxygen-saturated 0.5 M H₂SO₄ solution was recorded under voltammetric conditions between 1 and 0.0 V at a sweep rate of 5mVs⁻¹ for various rotation speeds of the disk electrode.

Accelerated Durability Test (ADT)

Shao (7) and Choo (8) observed that the majority of media corrosion of carbon supports takes place at Open Circuit Potential (OCP) in a PEMFC. On the basis of that, we select a range of potential between 1.0 and 1.2 V in an oxygen atmosphere in 0.5 M H₂SO₄ solution at room temperature (25°C). For intermittent evaluation, cyclic voltammograms were performed in a nitrogen atmosphere in 0.5 M H₂SO₄ after 1000 potential cycles. From these voltammograms hydrogen absorption charge variations were determined during ADT progress. The ADT was carried out in a conventional electrochemical cell connected to an AUTOLAB potentiostat/ galvanostat.

Image Analysis

Scanning electron microscopy (SEM) images and surface mapping by energy dispersive X-ray spectroscopy (EDXS) were performed in a JEOL JSM-5400LV microscope. SEM images permit to detect microstructure variations and to measure the particle size of deposited platinum. An image-analysis system based on a well-known image-processing methodology developed in Visual C++ and called mathematical morphology was used. This software, *SIMM*, (Mexican Register Number 03-2006-060514221100-01) was developed in house. Five SEM images were used to perform the Image Analysis.

Results and Discussion

Electrochemical Evaluation of Pt/Vulcan XC-72 and Pt/MWCNT electrodes.

The process of electrode fabrication consisted of three steps. The first step was to form a particulate-carbon electrode surface without catalyst, the second was deposition of platinum onto the carbon surfaces, and third step was drying. We note that the deposit of platinum was adherent and could be used after several days of exposure to the atmosphere without losing its catalytic properties. During the pulse of potential generation of hydrogen gas was observed on the surface of the electrode immersed in the plating bath. After deposition as quick as possible, the electrodes were moved to the sulphuric acid solution. A typical cyclic voltammogram developed in N_2 -saturated 0.5 M H_2SO_4 is illustrated in figure 1 and it indicates the presence of platinum.

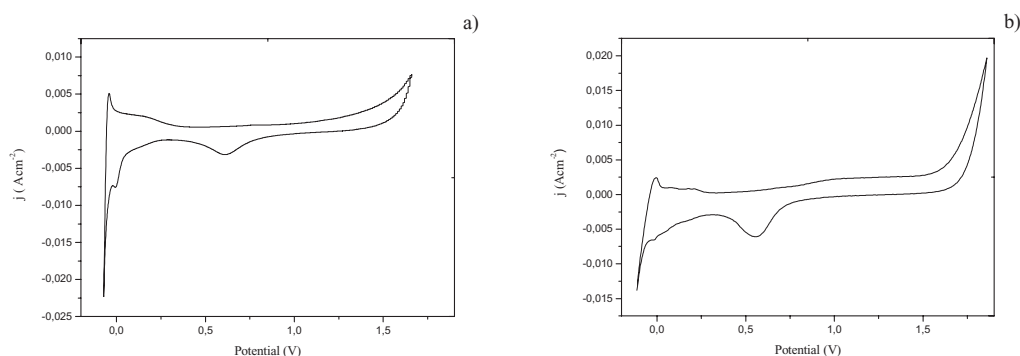


Figure 1. Cyclic Voltammetry of electrodeposited Pt on MWCNT and zone of the determination of electrochemical area of a) Pt/MWCNT, deposition time = 300ms; b) Pt/MWCNT, deposition time = 100ms. Disolution 0.5M H_2SO_4 with N_2 atmosphere.

The specific surface area (m^2g^{-1}) of the electrodes together with the roughness factor (r) and the diameter (d) of the platinum particles were calculated. The specific surface area S (in m^2g^{-1}) was estimated as follows:

$$S = \frac{A_r}{A_g W} = \frac{r}{W} \quad [1]$$

where A_r is the surface area of the clean platinum determined from the charge passed in oxidising a monolayer of adsorbed hydrogen, Pt- H_{ads} (assuming $210 \mu C cm^{-2}$ and an H -adsorption coverage of 77%), A_g is the geometric area of the disc electrode, and W is the platinum loading determined from the charge transferred (assuming a 2-electron transfer per platinum atom deposited). We determined the specific surface area from the adorption/desorption of hydrogen. Assuming spherical particles of uniform shape, particle size (in μm) was calculated from the following equation:

$$d = (6 \times 10^3 S \rho)^{-1} \quad [2]$$

where ρ is the density of Pt, 21.4 g cm^{-3} . The size of the electrodeposited particles obtained with Pt/MWCNT (Table I) is two orders of magnitude greater than the size of particles reported for E-Tek electrodes ($0.0037 \text{ }\mu\text{m}$) (9). Thompson's calculation did not account for a dispersion of sizes in the sample, which will be considered in the section 3.1 on the basis of the SEM results.

TABLE I. Particle size (equation 2) and kinetic parameters (equations 3).

Electrode	Conditions	Tafel Slope (mV decade ⁻¹)	Transfer Coefficient	Exchange Current (Acm ⁻²)	Calculated Particle Size (μm)
Pt polycrystalline	-----	88	0.67	1.10×10^{-9}	---
Pt/Vulcan XC-72 E – Tek	Pt – Vulcan XC-72 (10%) + Nafion	75	0.79	1.93×10^{-10}	-----
Pt/Vulcan XC-72 E – Tek	Pt – Vulcan XC-72 (20%) + Nafion	77	0.76	1.06×10^{-9}	-----
Pt/Vulcan	Vulcan XC-72 + Nafion [Pt - DNS] = 10^{-1} M $t=100$ ms	140	0.42	4.08×10^{-10}	0.59
Pt/MWCNT Deposition time $t=300$ ms	MWNT + Nafion [Pt - DNS] = 10^{-1} M $t=300$ ms	79	0.83	2.59×10^{-12}	0.0226
PT/MWC NT Deposition time $t=100$ ms	MWNT + Nafion [Pt - DNS] = 10^{-1} M $t=100$ ms	77	0.86	1.19×10^{-12}	0.0227
Pt/MWCNT After the corrosion Test	MWNT + Nafion [Pt - DNS] = 10^{-1} M Deposition time $t=100$ ms Range 1 – 1.2V	95	0.69	1.60×10^{-11}	0.0227

We studied the Oxygen Reduction Reaction (ORR) on a high-surface-area platinum catalyst supported on Vulcan XC72 carbon using the thin-film RDE technique. We deposited a mixture of the supported-catalyst powder (E-Tek) with Nafion® onto a glassy carbon disk. This preparation method results in a relatively thick catalyst layer with a relatively high Nafion® content, such that film diffusion resistance could play an important role with detailed mathematical modelling, needed to extract the electrode kinetics from the measured RDE data.

A Koutecky – Levich analysis was used to evaluate the kinetics parameters (Tafel slope and exchange-current density) from the RDE experiments. For Nafion-coated electrodes, besides transport in solution, diffusion in the Nafion film must be considered. Thus, Lawson (10) proposed the following modified equation for Nafion-coated electrodes:

$$\frac{1}{j_{\text{lim}}} = \frac{1}{j_k} + \frac{1}{j_d} + \frac{1}{j_f} = \frac{1}{nFkC_0} + \frac{1}{0.62nAF C_0 D_0^{2/3} \nu^{1/6} \omega^{1/2}} + \frac{L}{nFD_f c_f} \quad [3]$$

where j_k is the kinetically controlled current density at the electrode, j_f is the additional film-diffusion resistance and j_d is diffusion limited current density. F is the faraday constant, n number of electrons exchanged in the electrochemical reaction, k is the rate

constant, C_0 is the bulk concentration, A the surface area, D_0 the diffusion coefficient of O_2 in the bulk, ν the kinematic viscosity, ω the rotation rate in radians per second, L the film thickness, c_f the reactant concentration in the Nafion film and D_f is the diffusion constant in the Nafion film. The film thickness L can be calculated with using the equation reported by Gojkovic (11) :

$$L = \frac{J_L}{\text{Slope}} \frac{c_f}{C_0} \frac{D_f \nu^{1/6}}{0.62 D^{2/3}} \quad [4]$$

The values J_L and slope can be obtained from intercept on the vertical axis and slope of the plot j_{lim} versus $\omega^{-1/2}$, respectively (11). Polarization curves of Pt/Vulcan XC-72 Nafion-coated electrodes on rotating disk electrode are show in figure 2a. The ORR on Pt/Vulcan XC-72 catalysts was diffusion-controlled when the potential was less than 0.55 V and was under mixed diffusion-kinetic control in the potential region between 0.73 and 0.85 V. In consequence, kinetic control was observed at potential higher than 0.85 V. The intercept J_L and slope of the straight line in figure 2b enables one to estimate the thickness of the Nafion film covering Pt/Vulcan XC-72 particles. Using equation 4 and the data reported by Gojkovic (11) $c_f/C_0=1.5$, $D_f=7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $D=1.9 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $\nu 1 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, the film thickness of the film was estimated to be 3.017 μm . With thickness more than 0.2 μm the diffusion of oxygen in the film is the rate determining step (11-12). The film-diffusion resistance (j_f), of the Nafion[®] layer prepared in this work, has to be considered to avoid overestimate the kinetic parameters values. Gojkovic (11) determined Nafion[®] film diffusion limited current densities, j_f , was around 8 mA cm^{-2} (11-13). The kinetic parameters were calculated considering this value only in the case of 20 wt % platinum supported on Vulcan XC-72 (E-TEK) electrodes. In the electrodes prepared by electrodeposition of platinum the film of nafion was to be negligible, because of the Pt was located outer face of agglomerate Vulcan-nafion.

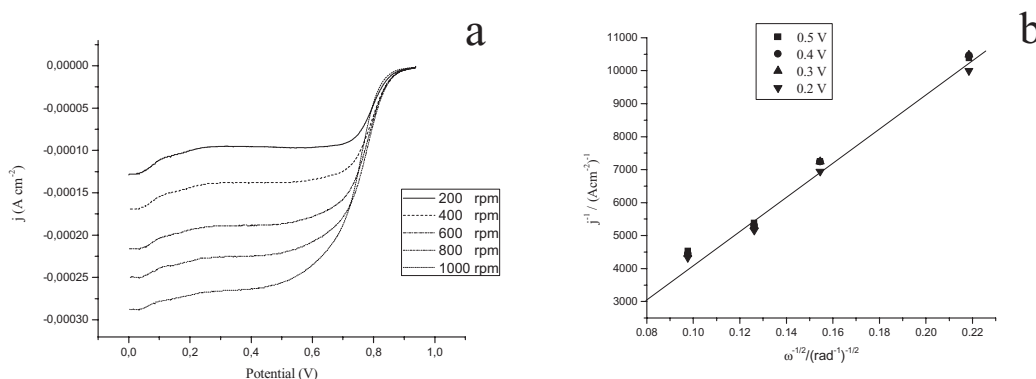


Figure 2. a) Polarization curves on the rotating disk electrodes for the catalysts 20 wt % platinum supported on Vulcan XC-72 (E-TEK). The measurements were performed in 0.5 M H_2SO_4 solution saturated with oxygen at the potential scan rate of 5 mV s^{-1} , b) Koutecky – Levich plot for O_2 at different potential on Nafion-coated Pt supported on Vulcan XC-72 (E-TEK) electrodes, versus inverse of the root rates rotation of electrode.

The Koutecky-Levich analyses of the electrodeposited Pt onto Vulcan XC-72 and MWCNT as substrates is given in figure 3. The Tafel slope b varies from around 60 mV dec^{-1} at low particle size (E-Tek Pt electrodes in Table I) to about 120 mV dec^{-1} at the highest particle size (Electrodeposited Pt/Vulcan XC-72 in Table I). The difference in Tafel slope suggests that the mechanism on a Pt/Vulcan XC-72 (E-Tek Pt electrodes) surface is different from that on an Electrodeposited Pt /Vulcan XC-72 surface. On a Pt/Vulcan XC-72 surface, the rate determining step is a pseudo 2-electron procedure, which gives a Tafel slope of 60 mV/dec . On the contrary, on an Electrodeposited Pt /Vulcan XC-72 surface, the first electron transfer is the rate determining steps, resulting in a Tafel slope of 120 mV/dec (14), see equation 5.

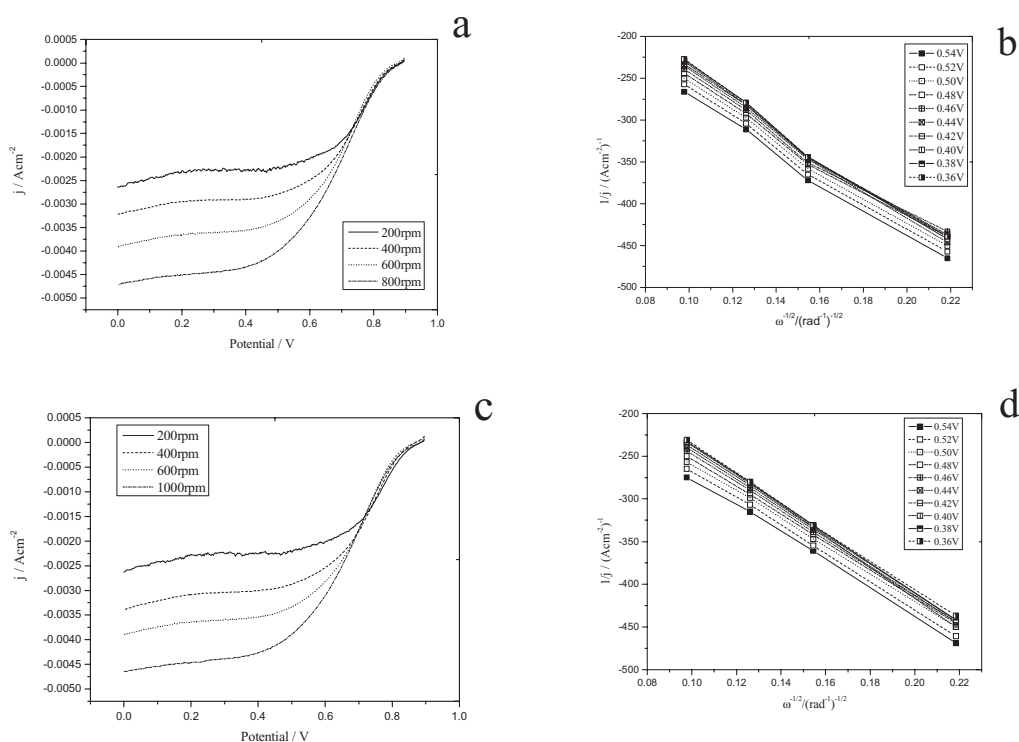


Figure 3. ORR over a) Pt/MWCNT with a deposition time = 300 ms and b) Koutecky – Levich analysis, c) Pt/MWCNT with a deposition time = 100ms, and d) Koutecky – Levich analysis. O_2 flow rate 30 mL min^{-1} , $20 \pm ^\circ\text{C}$, ambient pressure.

The Tafel slope b observed for the Pt/MWCNT was around 80 mV dec^{-1} . The difference in the surface chemistry of the support may also influence in the different Tafel slope between Vulcan XC-72 and MWCNT. Carbon nanotubes are usually considered to be made of rolled-up graphene sheets and Vulcan XC-72 is a carbon black amorphous. It has been shown that the delocalized π electrons of graphene sheets can interact with and stabilize platinum particles (15). The Pt particles deposited on the outer shell of MWCNT are probably to show strong interaction with the support via π -bonding. There may be other specific interactions between Pt and MWCNT, as sometimes postulated to explain the catalytic activity. The value of the exchange-current density

shown in Table I indicates the ORR reaction has a low rate. The low electrocatalytic activity of the Pt deposited from a sulphur containing precursor was also reported by Thompson (3). It is possible that the deposited platinum may have retained poisoning sulphur species or adsorbed these after Pt – DNS reduction. Thompson (3) and Loucka (16) observed this kind of contamination.

Image Analysis

Figure 4a y 4d shows an SEM image of the surface bearing a sample of platinum particles with acceptable dispersion, and figures 4c and 4f shows the particle-size distribution derived from this SEM. A narrow size distribution is observed with particle sizes ranging from 810 to 910 nm. There is an inconsistency between the mean particle size calculated from these SEM observations and that calculated from equation 2. Considering the careful analysis of images made by the *SIMM* software, we accept the mean particle size as determined from the SEM measurements. Although, it is easy and fast to determinate the particle size by means of equation 2, the considerations taken to do this are not proper, hence, it is necessary to develop a more complex model.

The sizes of Pt particles produced by electrodeposition usually fall in the range 20-70 nm (17), much larger than state-of-the-art heterogeneous catalysts (2-4 nm). The particle size obtained in this research is even larger, more than two orders-of-magnitude larger. Nevertheless, although the size of the platinum particles is huge, they are located in the accessible reaction zone. This is the reason that we consider that such electrodes could have practical interest for MEA applications and that it is worth improving the conditions of electrodeposition.

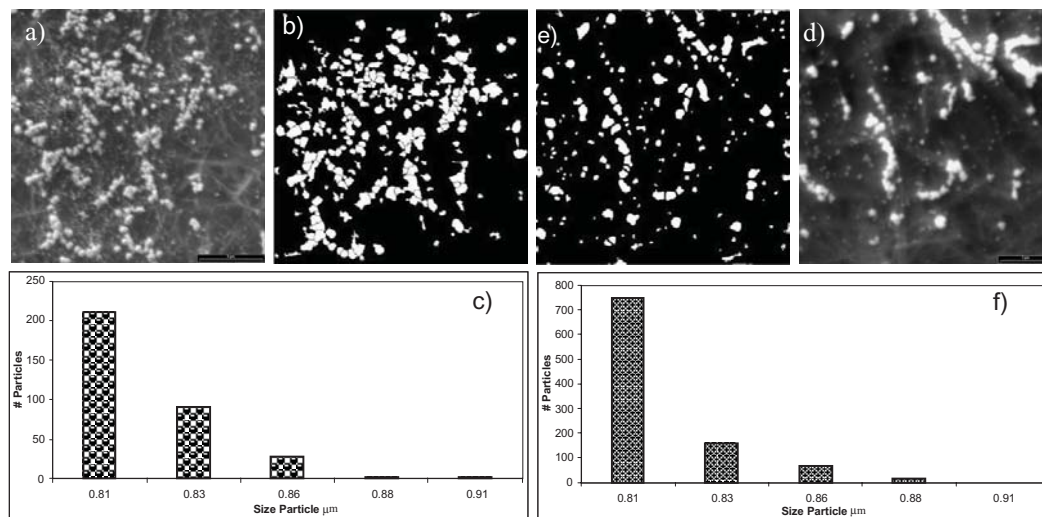


Figure 4. SEM images of a) Pt/MWCNT – ED1(5000x), b) Image analysis by SIMM of Pt/MWCNT, deposition time = 100ms, c) Size distribution of Pt/MWCNT, deposition time = 100ms, e) Pt/MWCNT deposition time = 300ms (20000x), b)Image analysis by SIMM of Pt/MWCNT – ED2, c) Size distribution of Pt/MWCNT, deposition time = 300ms

Accelerated durability test (ADT).

The electrodes evaluated by the accelerated durability test (ADT) were Pt/Vulcan XC-72 and Pt/MWCNT. The ADT was carried out at a potential where most carbon substrates are oxidized to form carbon oxide species (e.g., carboxylates (7)). Moreover, the evaluation conducted after each 1000 cycles showed that the degradation of the carbon had to be very severe (figure 5).

When platinum was deposited on Vulcan XC-72 carbon, the electrochemical surface area (ECSA) decreased by 5% (figure 5b). It is known that the degradation of ECSA may be attributed to several factors: (i) Pt particle dissolution, (ii) loss of electrical contact to the Pt due to carbon-support corrosion (iii) Pt nanoparticle aggregation driven by surface energy minimization or (iv) Platinum Ostwald ripening of Pt nanoparticles. Due to the size of our deposited particles, the ECSA degradation causes should be Pt dissolution and support corrosion. Surprisingly, in the case of MWCNT exposed to the same conditions, the ECSA shows an increase in area of about 80%, see figure 5a and figure 6. Both types of electrode were prepared by the same deposition procedure; thus, we assume that the particle-size distributions were almost the same. Particle size was determined after ADT, observing a decrease in particle number, see figure 6. Furthermore, size distribution histogram also changed (figures 4c, 4f and 6a), the number of particles of the smallest size increased after the ADT, this might be a sign of Pt dissolution during the test. The ECSA change can be explained considering that the Pt initial particles were poisoned with sulphur species, therefore, its electrochemical activity was low. After the ADT, not only particle dissolves but contamination pollutes diminishes also.

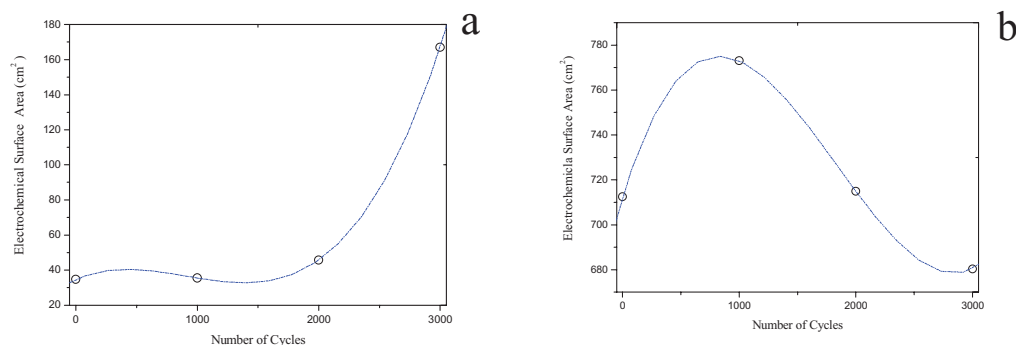


Figure 5. ECSA observed in Accelerated Durability Test (ADT) for a) Pt/MWCNT electrode, and b) Pt/Vulcan XC-72 electrode.

During the ADT, the oxygen evolution process allows oxidation of SO_4^{2-} , $\text{S}_2\text{O}_6^{2-}$, and $\text{S}_2\text{O}_3^{2-}$ ions, and by repeating the oxidation cycles the electrode is cleaned. Despite, the platinum deposited on Vulcan XC-72 and MWCNT electrodes is dissolved and activated; the ECSA on Vulcan XC-72 electrodes diminish due to a high carbon corrosion, which decreases the electric contact with the platinum particles. The ECSA on Pt-MWCNT electrodes increases since the MWCNT is not corroded while the Pt is cleaned. Therefore, the difference in behaviour must be due to the high corrosion resistance of the MWCNT.

The difference in the oxidation degree of the two carbon support can be understood through the difference between their structures. MWCNT are usually made of rolled-up coaxial graphene sheets which offers MWCNT a closed or half-closed structure. It is difficult for oxygen atoms to attack the closed structure and consequently, it is more stable under electrochemical oxidation. Carbon black contains much more amorphous carbon and plain graphite carbon, which has abundant dangling bonds and defects. The dangling bonds easily form surface oxides, which results in a higher corrosion rate.

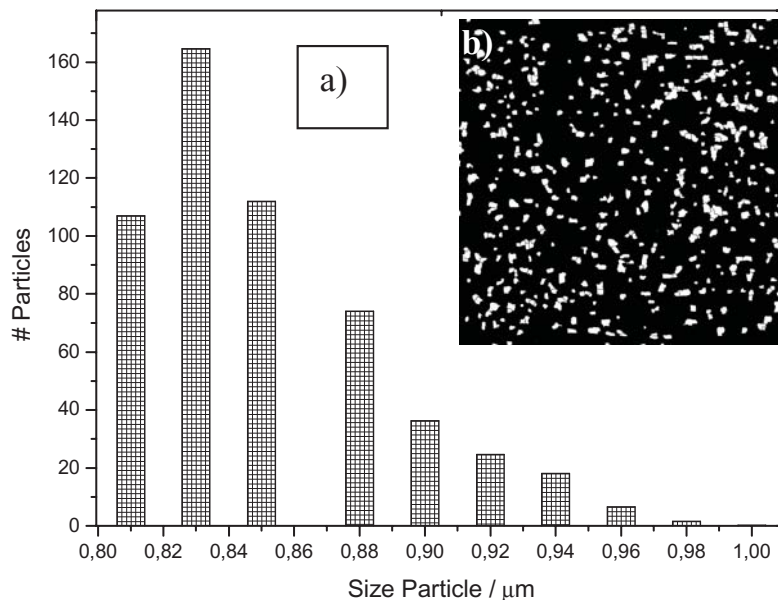


Figure 6. a) Size distribution of Pt/MWCNT, deposition time = 300ms, after ADT (3000 cycles) b) Image analysis by SIMM of Pt/MWCNT, deposition time = 300ms, after ADT (3000 cycles).

We studied the O_2 -reduction kinetics on Pt-MWNT after the ADT, and the mechanism appeared to be the same as initially. The kinetics parameters did not change, see Table I. Thus, the particle size obtained after the ADT does not change the mechanism of the ORR. The large particles were activated under the very harsh anodic treatment that causes degradation of other electrodes (7, 18). EDX measurements gave no evidence of contamination of the surface by nitrogen from Pt – DNS. It is not possible, however, to distinguish whether this comes from exchange with sulfur groups on the Nafion or from the Pt – DNS. We assume that the activation of the electrodes by the ADT may be due to desorption of sulfur contamination that came from Pt – DNS.

Conclusions

Particulate platinum can be deposited directly onto Nafion-bonded carbon electrodes from an aqueous solution of Dihydrogen Dinitrosulfatoplatinate (II) by pulsed electrodeposition. The electrodes modified by electrodeposition exhibit worse catalysis for the ORR than one made of E-TEK Pt/C. This behaviour can be explained by contamination with sulphur from the precursor and by the large Pt-particle size. Further

more work is needed to optimize the Pt particle size produced from this deposition bath and to diminish the amount of poisoning sulphur species.

We studied the durability of Pt/C and Pt/MWCNT using an accelerated durability tests (ADT). Platinum dissolution takes place during the ADT, but may also fall off the support in the case of gasification of Vulcan XC-72 carbon. The electrode prepared with Pt on MWCNT exhibited excellent performance in the corrosion test. Furthermore, the rate for the Pt area loss is small indicating that MWCNT could potentially provide much higher durability than carbon black. It can be concluded that multiwalled carbon nanotubes are more resistant to electrochemical oxidation than carbon black (Vulcan XC-72).

Acknowledgments

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