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Determination of the Electrochemical Surface Area for CNF-Pt Electrocatalyst Using Cyclic Voltammetry

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Abstract: Carbon Nanofibers (CNF) are considered to be a promising catalyst support material due to their unique characteristics, excellent mechanical, electrical and structural properties, high surface area and nevertheless, good interaction with metallic catalyst particles. The possibility of preparing CNF decorated with platinum by an electrochemical method was tested, using a hexachloroplatinic bath solution. The experiments were carried out with the aid of a Potentiostat/Galvanostat Ivium Technologies Vertex, in a three – electrode cell. The aim of the present work was to determine the electrochemical surface area (ECSA) of the CNF-Pt catalysts in relation to the functionalization treatment of fibers, using an electrochemical method. ECSA for different functionalized CNF-Pt catalysts was determined by cyclic voltammetry in 0.5 M H_2SO_4 solution. The highest active surface of platinum was obtained for the samples with CNF functionalized by plasma treatment using 80 W for 1800 s. The obtained results correlate very well with the particles size and distribution of platinum, revealed by scanning electron microscopy (SEM) and the quantity of deposited platinum determined by thermo gravimetrical analysis (TGA) respectively. Cyclic voltammetry (CV) has been proven to be a suitable method for estimation of the ECSA of the electrocatalysts.

Keywords: carbon nanofibers, platinum electrodeposition, electrochemical surface area.

1. Introduction

Obtaining electric energy through different methods than conventional ones has been an extensively studied subject during the last period. Replacing the fossil fuels and developing new, more efficient and eco-friendly materials and applications is a real challenge among the scientists [1-4]. Such applications are fuel cells, which are considered to be a promising power source for the future. Lately, these are assessed to be very performant and convenient due to the possibility of using them as portable devices. An important aspect for the proper conversion of chemical energy into electricity is the catalyst type, more exactly the efficiency of the catalyst, lifetime and stability. Intense studies in this field have revealed that platinum is the metal with the highest catalytic activity for electrode processes within a fuel cell [5-10], but due to its prohibitive price, the use of this metal in industrial purposes is limited. As a consequence, during last years, several materials, which can replace the expensive platinum but preserve the same properties (high electrical conductivity, structural stability and good corrosion resistance) have been investigated. Moreover, reducing the platinum amount by depositing nanoparticles onto a suitable support material has been proven to be another efficient method.

One of the most important parameters for catalyst materials is the electrochemical surface area (ECSA) of the catalyst material, which has a strong influence on the reaction rate, catalytic activity inside a fuel cell and also on the obtained current and power density [10-15]. An effective method to reduce the amount of platinum, without diminishing the fuel cell performances is to deposit metal nanoparticles onto a compatible support that exhibits a large surface area. Lately, the studies revealed a considerable decrease of the platinum amount (100 times lower) and these improvements led to important cost reduction. Suitable materials as support for platinum deposition are carbon based materials, as carbon nanofibers (CNF), carbon nanotubes or carbon black due to their unique characteristics, excellent mechanical and electrical properties and good interaction with the metal particles [15-20].

The present work deals with the possibility of combining the noble properties of platinum with the special properties of CNF. The aim of this work is to develop catalysts materials for electrochemical cell applications by electrodeposition of platinum particles onto the surface of CNF support material. The uniform distribution associated with reduced particle size confers a very high active surface area for the catalyst and an increased sensitivity, which leads to a high performance of the fuel cell. The characterization of CNF electrochemically decorated with platinum nanoparticles was performed using SEM and EDX for morphology and chemical composition of the obtained structures, TGA for platinum content determination and CV measurements in 0.5 M H_2SO_4 solution for ECSA estimation.

2. Experimental

2.1. Functionalization of CNF

In order to develop platinum based catalysts, CNF with a high graphitization degree (up to 75%) with a large specific surface area 115 m^2 g^{-1} produced on industrial scale and commercially available (GANF) from the Grupo Antolin (Spain) were used as support material.

It is well known that CNF are hydrophobic and inactive. Thus to improve considerably the amount of platinum which will be subsequently reduced on the nanofibers surface, a functionalization process is necessary in order to increase the surface energy by attaching different functional groups on their graphitic surface. Currently, several functionalization methods are available, as chemically (using different acids), electrochemically, or applying plasma treatments. Plasma functionalization is an efficient method for surface modification, being a quick and environmental friendly process which can induce different functional groups on the CNF surface, by interaction of the plasma-generated excited species with the exposed solid interface. The type of the functionalization groups depends on the gas mixture used in the process. Applying oxygen, the C=C bond is broken and different types of functionalities like hydroxyl, carbonyl or carboxyl groups can be generated onto the outer surface of the CNF, resulting a chemical/physical modification on the first atomic layers [6-10]. Moreover, this type of functionalization creates nucleation anchors for the metal which is going to be deposited onto the CNF and furthermore increases the wettability and the surface energy of the fibers respectively. Various studies proved that beside the increased quantity of metal which has been reduced on the surface of the treated fibers, the distribution was also improved and as a consequence, the utilization degree became higher [8, 9].

In this regard, CNF were treated in oxygen plasma using a microwave plasma reactor (Plasma Finish RFG 300 RF), at room temperature, by varying the process parameters, like exposure time and power. The high density of electrons generated in microwave plasma leads to efficient chemical reactions, which are developed in a very short time compared to another functionalization methods. Two different sets of parameters were applied, being presented in Table 1. The oxygen plasma functionalized samples are investigated in comparison to untreated CNF samples.

TABLE 1. Optimized plasma treatment parameters

Samples	Exposure time [s]	Power [W]
CNF-Pt-0	0	0
CNF-Pt-80	1800	80
CNF-Pt-100	1200	100

2.2. CNF-Pt electrodes preparation

After the functionalization process, 0.05 g of CNF were dispersed in 50 mL isopropanol, the resulted ink was ultrasonicated for 30 minutes and then deposited onto a carbon paper - gas diffusion layer (GDL) commercially available by Freudenberg type H2315I2C6. The morphology of the GDL material before the CNF application is presented in Fig. 1. The samples were dried in an oven for 15 minutes at 50°C. Subsequently, on the surface of the freshly prepared CNF-GDL samples, platinum nanoparticles were deposited applying an electrochemical pulse plating method. This step was performed with a Potentiostat/Galvanostat Ivium Technologies Vertex, in a three-electrode cell, using a saturated calomel electrode (SCE) as reference and a platinum disk as counter electrode.

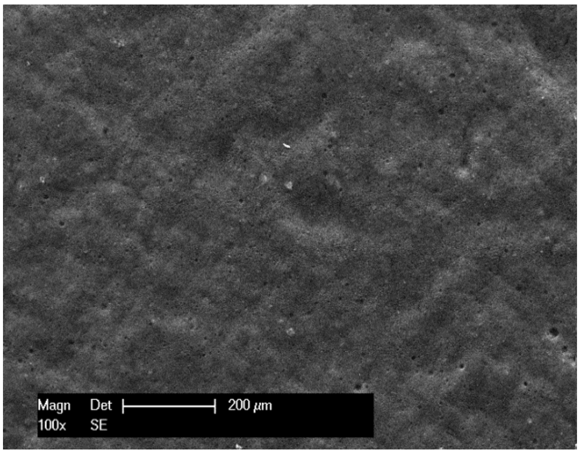

Figure 1.SEM micrograph of the GDL surface without CNF before platinum deposition

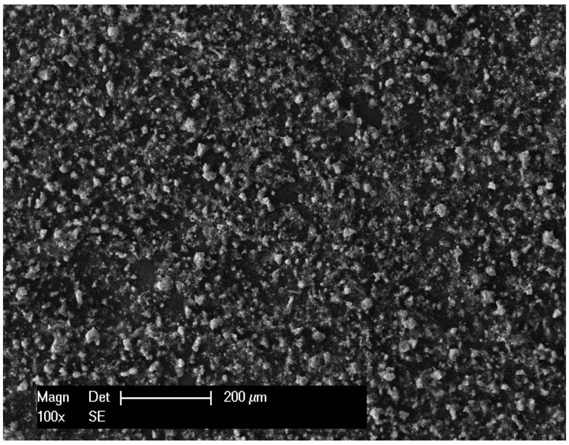

Figure 2. SEM micrograph of the electrode surface with CNF and after platinum deposition

The electrolyte used for the platinum electrodeposition was a 10^{-3} M H_2PtCl_6 solution, adjusted with HCl in order to reach a pH value of 2. The optimal deposition parameters were 0.05 A cm^{-2} current density (i) applied for 1 second (t_{on}) and OCP measurement for 59 seconds (t_{off}), repeated for 12 cycles. The deposition was carried out at 50°C and the parameters were kept constant for all the investigated samples. This type of electrodeposition leads to a mean platinum loading of 0.3 mg cm^{-2}. The morphology of an electrode after platinum deposition is shown in Fig. 2.

2.3. CNF-Pt electrodes characterization

The platinum decorated CNF samples are analyzed by SEM using a Philips XL 30 ESEM equipped with energy dispersive X-Ray analyzer for morphological and structural characterization. Platinum loading of the prepared samples is determined by TGA measurements carried out with a Netzsch STA 449F1 Jupiter instrument. Samples were placed in an Al_2O_3 ceramic crucible and heated up from 30°C to 1200°C with a rate of 20 K min^{-1} under controlled atmosphere consisting of N_2 and synthetic air with a flow of 20 mL/min. The electrochemical surface area (ECSA) was determined from the cyclic voltammetric curves carried out in 0.5 ´M H_2SO_4 using a Potentiostat/Galvanostat Ivium Technologies Vertex, in a three-electrode cell, a SCE served as reference electrode and a 1 cm^2 platinum disk as counter electrode. The CV measurements were carried by sweeping the potential between -0.2 V to 0.8 V vs. SCE, with a linear potential sweep rate of 0.1 V s^{-1} for 200 cycles.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM)

The structure and the morphology of the resulted CNF-Pt electrodes are very important characteristics because they have a considerable influence on the catalytic activity of the electrodes After the CNF spray deposition onto the GDL support material, the electrode surface becomes significantly higher (Fig. 2). This aspect is very important in catalyst development procedure. A higher available surface has a positive effect on the activity of the catalyst. Moreover, by deposition platinum nanoparticles onto the CNF surface, the ECSA in additionally increased. Fig. 3-5 reveals the morphology of the CNF-Pt electrodes with or without functionalization treatment. Untreated CNF based sample presents a poor platinum distribution and the particles are agglomerated in clusters due to the low surface energy of the support material. The hydrophobicity of the support material provides only few active sites for platinum nucleation process. By applying a functionalization treatment, the number of active sites is increased and the platinum particles are evenly distributed. The dimension of platinum particles is smaller in comparison to those deposited onto the untreated samples. The appearance of the Pt particles on the both functionalized CNF is the same, but the amount of platinum slightly changed in respect to the treatment parameters. A higher treatment power leads to a decrease in the functionalization degree of the fibers and consequently the platinum particles tend to agglomerate. The platinum nanoparticles can be seen as clusters on the surface and individual particles as bright spots. When the applied power of the functionalization treatment is increased to 100 W, an increase in platinum particles size can be observed. This fact can be attributed to a decrease in the functionalization degree, which favors the growth mechanism of the catalyst particles during deposition.

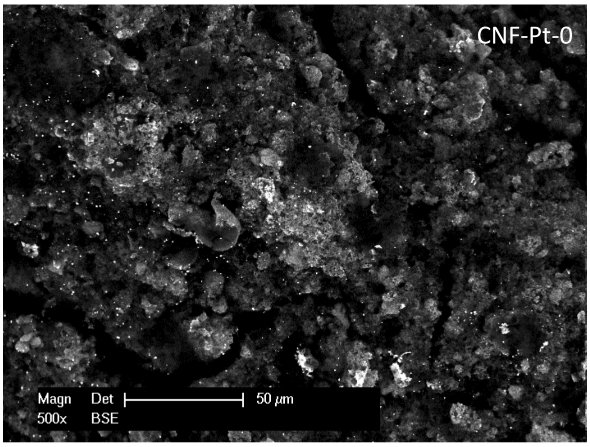

Figure 3. SEM micrograph of CNF-Pt-0 electrode

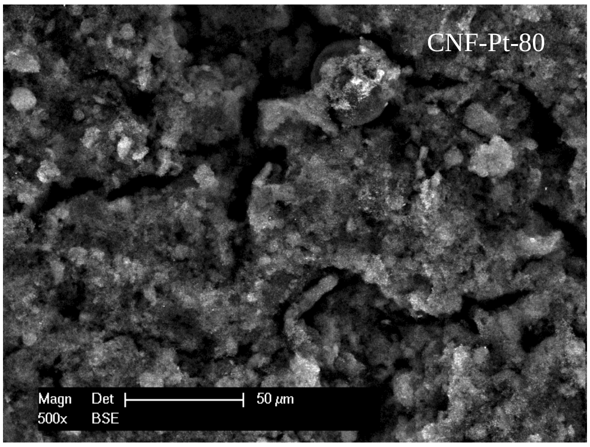

Figure 4. SEM micrograph of CNF-Pt-80 electrode

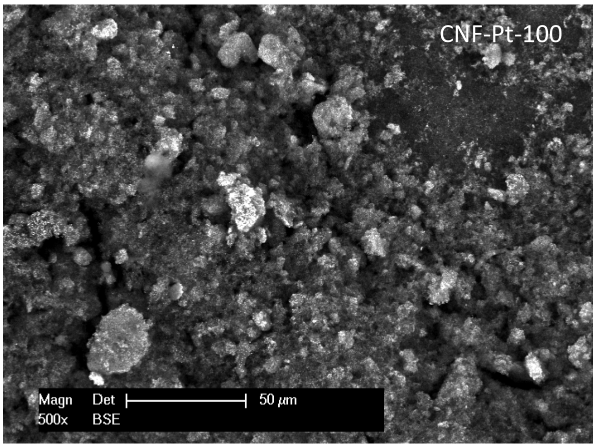

Figure 5. SEM micrograph of CNF-Pt-100 electrode

3.2. Thermogravimetrical Analyze (TGA)

The values obtained for platinum loading and ECSA related to 1 cm^2 for each of the samples are presented in Table 2.

Fig. 6 displays the weight loss for 3 of the analyzed samples. A minor weight loss at lower temperatures is assigned to decomposition of the organic phases and amorphous carbon from the GDL structure. The major weight loss is attributed to combustion of carbon from the support material. The rest mass corresponds to platinum amount deposited on each of the samples. The quantity of deposited platinum onto the CNF surface increases considerably for samples which were previously treated in oxygen plasma. The best results were obtained for CNF-Pt-80, on which, a higher amount of platinum was found. The lowest amount of platinum was obtained for CNF-Pt-0 sample.

TABLE 2. Platinum loading, ECSA of the CNF-Pt electrodes

Sample	Rest mass [%]	Platinum loading [mg cm^{-2}]	ECSA [cm^2 mg^{-1}$_{Pt}$]
CNF-Pt-0	1.24	0.26	12
CNF-Pt-80	1.46	0.31	24
CNF-Pt-100	1.97	0.29	21

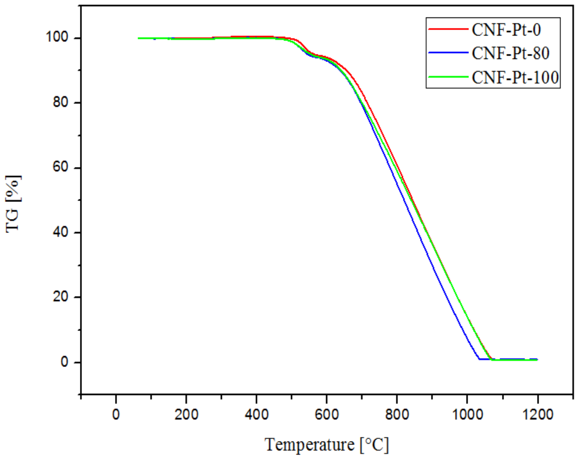

Figure6. TGA measurements of the CNF-Pt samples

3.3. Electrochemical measurements

The cyclic voltammetry (CV) was performed in 0.5 M H_2SO_4 solution. The maximum potential value was set to 0.8 V in order to avoid the corrosion of carbon from the support material. The last cycle from each measurement was further used for ECSA determination. The polarization curves for the last cycle of each sample are presented in Fig. 7.

The CV method based on hydrogen adsorption on the surface of the platinum was used to determine the ECSA of CNF-Pt electrodes. Applying sufficiently negative potentials to the working electrode, the hydrogen adsorption and desorption region is achieved. When platinum is in contact with an acid solution, the reduction of H^+ and the adsorption of [H] atoms is achieved. The reaction is presented in (1):

$$H^+ (aq) + e \rightarrow H (ad) \qquad (1)$$

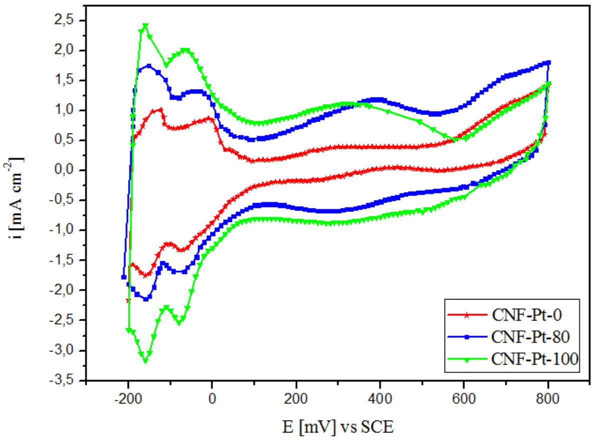

Figure 7. CV in 0.5 M H_2SO_4 solution of the CNF-Pt electrodes

As the potential is getting more negative, the whole platinum surface is covered with hydrogen atoms and after this step, the adsorption of H_2 molecules occurs (2):

$$2H (ad) \rightarrow H_2 (ad) \qquad (2)$$

All the adsorbed molecules are forming hydrogen bubbles, which leave the platinum surface, and instead of them, other hydrogen molecules are adsorbed with a high rate, increasing also the cathodic current (hydrogen evolution). This process is used for platinum electrode electrochemical surface area determination. The charge for hydrogen adsorption/desorption on platinum can be calculated by integrating the voltammetric curves between the potentials where the hydrogen evolution occurs. The electrochemical surface area can be calculated from (3):

$$ECSA = Q_H / Q_C \qquad (3)$$

where, Q_H (mC) is the charge for hydrogen adsorption/desorption and Q_C is 0.21 (mC cm^{-2}).

The results show that the electrode CNF-Pt 80 presents the largest electrochemical surface area of 24 cm^2 mg^{-1} Pt. As the platinum loadings are not significantly different, the difference between the surface electrodes can be justified by smaller platinum particles and a better distribution onto the surface. This fact can be attributed to the different amounts of functional groups available on the CNF surface which provide more active sites and consequently to the plasma activation parameters.

4. Conclusions

In the present work, three different CNF-Pt electrodes have been prepared using the electrochemical pulse plating method. The work aimed to investigate the influence of the plasma functionalization parameters of the CNF on the platinum deposition process and on the electrochemical surface area respectively. The SEM investigations confirm the presence of platinum particles and their uniform distribution onto the substrate. TGA investigations brought information about the quantity of platinum deposited onto the CNF layer and the highest value for the platinum loading was around 0.3 mg cm^{-1}. As the CV measurements present, the reduced particle sizes obtained from the electrochemical pulse plating method correlated with a suitable functionalization treatment significantly enhanced the electrochemical surface area of the electrodes. Additionally, this improvement has also an important influence on the catalytic activity of the electrodes.

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