



## Activity and stability studies of platinumized multi-walled carbon nanotubes as fuel cell electrocatalysts



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### ABSTRACT

A non-covalent functionalization for multi-walled carbon nanotubes has been used as an alternative to the damaging acid treatment. Platinum nanoparticles with similar particle size distribution have been deposited on the surface modified multi-walled carbon nanotubes. The interaction between platinum nanoparticles and multi-walled carbon nanotubes functionalized with 1-pyrenecarboxylic acid is studied and its electrochemical stability investigated. This study reveals the existence of a platinum-support interaction and leads to three main conclusions. First, the addition of 1-pyrenecarboxylic acid is improving the dispersion of platinum nanoparticles, leading to an improved electrochemical activity towards oxygen reduction reaction. Second, the investigations regarding the electrochemical stability showed that the platinum-support interaction plays an important role in improving the long-term stability by as much as 20%. Third, post-mortem microscopy analysis showed a surprising effect. During the electrochemical stability investigations concerned with carbon corrosion it was found that the multi-walled carbon nanotubes were undergoing severe structural change, transforming finally into carbon spheres.

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### 1. Introduction

Efficient electrochemical conversion of energy has an utmost importance in answering the needs of future energy supply and demands. In this respect, polymer electrolyte fuel cells (PEMFCs) represent a research avenue, due to the fact that it can produce electrical and thermal energy in a versatile way. Usually, low temperature PEMFCs are using electrocatalysts in the form of nanoparticles supported on high surface area carbons. Pt based materials are the most used electrocatalysts in a real PEMFC. Even with the steady decrease in the Pt price over the last 2 years [1], Pt price is still one of the main drawbacks for PEMFC commercialization. Having these said, huge efforts have been made for developing PEMFC with non-precious metal catalysts [2,3]. However, from the performance point of view the Pt based materials supported on high surface area carbons have a superior activity compared to the non-precious metal catalysts. In order to achieve

the US Department of Energy mass activity targets [4], Pt alloying with several transition metals has been explored [5–8]. Nevertheless, the deployment of PEMFCs is still limited by several key aspects related to overall cost and performance loss during extended operation time. It was proven recently that Pt dissolution is a major degradation mechanism along with Ostwald ripening, support corrosion, particle migration and coalescence [9]. Nonetheless, one should consider the degradation mechanisms associated with the electrocatalyst/support system.

Even though the direct degradation of Pt is the most studied phenomenon, carbon corrosion can play an important role in the overall degradation of the catalyst especially when potential spikes up to 1.44 V<sub>RHE</sub> are occurring during start-up/shutdown [10]. During these periods the high surface area carbon undergoes severe electrochemical corrosion. According to its Pourbaix diagram, carbon is not stable under PEMFC operating conditions when exposed to potentials larger than 0.207 V<sub>RHE</sub> [11]. Yet, no corrosion is taking place at these low potentials due to the sluggish kinetics, but carbon corrosion is accelerated by the presence of Pt at larger potentials and elevated temperature. In this respect, much effort has been made for replacing the carbon support with different ceramics [12–18]. From the research point of view, the ideal

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support should have a property matrix consisting of high surface area, high electronic conductivity and high resistance towards corrosion under PEMFC operating conditions. Even if an alternative material to carbon is found having the above mentioned property matrix, it will probably still take some time before it may be replaced in a real PEMFC manufacturing industry due to the membrane-electrode assembly (MEA) optimization and probably higher costs of the support, itself. This is why carbon materials with alternative structures [19–22] are still the most viable solution. Multiwalled carbon nanotubes (MWCNTs) were among the first alternative carbon nanostructures to be tested as PEMFC electrocatalyst support [23,24] due to their large surface area and remarkable electronic conductivity.

Electrochemical corrosion of carbon is known to take place during PEMFC operating conditions, even though the full corrosion process is not completely understood. It is widely acknowledged that amorphous carbon defects are formed at large potentials and corroded at lower potentials [25]. Carbon oxidation starts with the presence of defects or at the kinks of the basal planes which have unsaturated valences and free  $\sigma$ -electrons [26]. The defects are crystallographic sites with different reactivity. Considering that MWCNTs have a relative defect-free structure it should be a rather stable material which does not undergo severe corrosion under PEMFC operating conditions. However, this defect-free structure translates into no anchoring points for Pt, thus functionalization is needed prior to Pt deposition. Covalent functionalization has been widely used in this respect [27], where the use of highly concentrated sulphuric acid, nitric acid, or a mixture between these two, oxidizes the MWCNT surface creating different oxygen functional groups. Nonetheless, this harsh treatment causes permanent damage to the MWCNT structure resulting in a large amount of surface defects which may be one of the starting points for the overall carbon oxidation.

There are several studies available in literature which consider MWCNT as possible electrocatalyst support for PEMFC. For example, heat treated MWCNTs perform better than the untreated MWCNTs in terms of activity and durability [28]. Another study shows that the diameter of the MWCNTs plays an important role, MWCNTs with a larger diameter have an increased specific activity and improved durability [29]. Zhao et al. showed that MWCNT with a specific surface area of  $120 \text{ m}^2 \text{ g}^{-1}$  are the most suitable MWCNTs as PEMFC electrocatalyst support [30]. It is difficult to compare results among different research groups for several reasons. First, most of the studies are performing cyclic voltammograms in either sulphuric acid or perchloric acid which results in different oxygen reduction reaction (ORR) activity. Since anion adsorption may influence the catalyst activity [31], it is preferred to electrochemically test the materials in perchloric acid and not in sulphuric acid. Second, the lack of similar Pt nanoparticle size supported on different supports can result in different degradation mechanisms which may lead to an erroneous conclusion. It is a well-known fact that smaller nanoparticles increase the surface energy leading to a faster Pt degradation rate [32]. Modifying both the particle size and the support will result in ambiguous conclusions. Supports which have a large difference in surface area in comparison to the reference support may automatically result in a preferential degradation mechanism. Third, the use of different accelerated stress test (AST) might have a different outcome for identical materials, which makes it difficult to compare results among different research groups. Therefore this paper aim is to prove that it is possible to increase the durability and ORR activity of Pt supported on MWCNTs just by enhancing the nanoparticle dispersion on the support without modifying the particle size or subjecting the MWCNTs to harsh acid treatments.

In this work, a non-covalent functionalization with 1-pyrenecarboxylic acid (PCA) has been used in order to maintain the

pristine MWCNT surface characteristics. Pt in the form of nanoparticles has been synthesized beforehand and subsequently deposited on the non-covalently functionalized MWCNT surface. The present study focuses on the interaction between the Pt nanoparticles, MWCNTs and the PCA which is attached on the carbon nanotubes. In this respect, a wide range of physico-chemical characterization techniques were used to explain the findings resulted from the electrochemical activity and stability measurements. In our attempt to provide proof that the interaction between Pt, MWCNT and PCA is enhancing the electrochemical stability, we have observed an unexpected effect, mainly segmenting the graphene layers constituting the MWCNT.

## 2. Experimental

### 2.1. Materials

MWCNTs (BET:  $270 \text{ m}^2 \text{ g}^{-1}$ ; VGCF-X<sup>TM</sup>, Showa Denko, Japan) were used as starting support material and have been used without further purification. Ethylene glycol (EG, 99%, VWR),  $\text{K}_2\text{PtCl}_4$  (46.75%, Alfa-Aesar) polyvinylpyrrolidone with  $M_w = 55,000$  (PVP, Sigma Aldrich), 1-pyrenecarboxylic acid (PCA, 97%, Sigma-Aldrich), acetone (99%, VWR) and ethanol (96%, VWR) were used for platinization of MWCNT without any further purification. Perchloric acid (TraceSelect<sup>®</sup>, Sigma Aldrich) and ultrapure water ( $18.2 \text{ M}\Omega$ , Millipore) were used for the preparation of the electrolyte.

### 2.2. Synthesis

150 mg of MWCNTs were added to 10 ml of ethanol along with 0, 1.5, 3 and 7.5 mg of PCA and ultrasonicated (Bandelin SONOREX<sup>TM</sup>) for 1 h in order to produce MWCNT with 0%, 1%, 2% and 5% PCA, respectively. The solvent was evaporated prior platinization. PCA was previously used to obtain a better dispersion of MWCNT in different solutions [33]. Pt nanoparticles were synthesized via a modified polyol method previously reported elsewhere [17]. Briefly, a volume of 20 ml of 9.6 mM  $\text{K}_2\text{PtCl}_4$  in EG was vigorously stirred at room temperature with 20 ml solution of 6 mM PVP in EG until complete dissolution of PVP and  $\text{K}_2\text{PtCl}_4$  in EG was achieved. The resulting mixture was refluxed at  $160^\circ\text{C}$  with Ar purging. After 3 h, the mixture was cooled to room temperature, and 150 mg of the desired support material was added along with 300 ml of acetone and magnetic stirred for 12 h. The final solution was centrifuged 6 times at 4500 rcf (Eppendorf 5804) and vacuum dried for 12 h at  $90^\circ\text{C}$ . The final samples were denoted as Pt/MWCNT-PCA-0%, Pt/MWCNT-PCA-1%, Pt/MWCNT-PCA-2% and Pt/MWCNT-PCA-5%, respectively.

### 2.3. Physical characterization

Thermo gravimetric analyses (TGA) were performed using a Netzsch STA-449-F3 equipped with a Pt sample carrier placed vertically in a furnace. The samples were placed in an alumina crucible and heated to  $1000^\circ\text{C}$  with a  $20 \text{ K min}^{-1}$  heating rate in a gas mixture consisting of nitrogen supplied at  $40 \text{ ml min}^{-1}$  and oxygen supplied at  $10 \text{ ml min}^{-1}$ .

X-ray diffraction (XRD) analysis was carried out by means of X'Pert Pro PANalytical X-ray diffractometer. The analysis took place between  $10^\circ$  and  $85^\circ$  glancing angles with a  $0.02^\circ$  step and a dwelling time of 12 s per step. The peaks were compared against the powder diffraction files (PDF) standardized by the International Centre for Diffraction Data (ICDD) for phase identification purposes.

The surface studies were carried out by using X-ray photoelectron spectrometer (XPS) from SPECS<sup>®</sup> by using the Mg  $\text{K}\alpha$  source and the data was analysed by using CasaXPS<sup>TM</sup> software. The survey spectra (resolution of 2.5 eV) were recorded for kinetic energies

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