

# Durability of Pt/MWCNT Nanocatalyst in High Temperature H<sub>3</sub>PO<sub>4</sub>/PBI PEMFC

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## ABSTRACT

The durability of Pt/MWCNT nanocatalyst was scrutinized by a series of constant life tests (11000 cycle operation) of single proton exchange membrane fuel cell (PEMFC) with phosphoric acid doped PBI (H<sub>3</sub>PO<sub>4</sub>/PBI) membranes at high temperature. The tested anode and cathode catalysts were analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD) to determine the morphology degree of electrocatalyst agglomeration. The XRD results showed that the Pt nanoparticle (Nps) size increased from 2.2 to 6.3 and 9.4 nm before and after single cell life tests for anode and cathode, respectively. The energy dispersive X-ray established the platinum deposition on supporting material. Above results indicated that the agglomeration of Pt Nps should be responsible for the ESA loss of Pt/MWCNT electrocatalyst but not membrane degradation. The further analyses on TEM data suggested that growth of platinum particles occurred via non-spherical shape mechanism on carbon at the nanometer scale.

**Keywords:** Durability, High temperature PEM; Fuel cells, Pt/MWCNT, Catalyst

## 1 INTRODUCTION

Energy and environment are of global concern, which has stimulated worldwide research on efficient and clean energy technologies. Proton exchange membrane fuel cells (PEMFC), among other types of fuel cells, have attracted much attention since their unique and favorable advantages for applications in transportation, stationary, portable and micro-power systems. In general, the PEMFC performance is primarily limited by the slow kinetics of oxygen reduction at cathode. Since the late 1980s the PEMFC performance has been significantly increased from 0.3-0.5 mW/cm<sup>2</sup> to about 1.0-1.5 W/cm<sup>2</sup> today, whereas the noble metal loading has been decreased from 4-5 mg/cm<sup>2</sup> to 0.4-0.5 mg/cm<sup>2</sup> for cathode and <0.03 mg/cm<sup>2</sup> for anode [1]. It is the carbon blacks that suffer from high corrosion, which in turn triggers the agglomeration of platinum particles resulting in reduction of the active surface area and catalytic activity. This is the major mechanism of the catalyst degradation and a key challenge to fuel cell long-

term durability [1]. Improved stability of both supports and catalysts is crucial for the technology.

The newest development in the field of PEMFC aims at higher operational temperatures above 100°C, with new electrolytes e.g. acid doped polybenzimidazole (H<sub>3</sub>PO<sub>4</sub>/PBI) membranes, which have been the main research focus at the Energy and Materials Science Group of DTU [2]. Operating features of the HT-PEMFC include no humidification, high CO tolerance, better heat utilization and possible integration with fuel processing units, as reviewed by the group. Higher operational temperatures impose, however, more challenges for the catalysts and electrodes. First of all, the doping acid has strong adsorption on the surface of catalysts and hinders electrode reactions. As a result, more active catalysts are required to improve the performance. The high temperature obviously aggravates the carbon corrosion. So far, no catalysts with reasonable activity and sufficient long-term stability are available. The stability and durability of Pt/C electrocatalyst in mid-low temperature PEMFCs with Nafion membrane have been widely investigated [2]. However, the systematic study on the durability as well as degradation of Pt/MWCNT nanocatalyst in high temperature PEMFC with single fuel cell test has not been reported. In this study, constant life tests were conducted with a series of PBI/H<sub>3</sub>PO<sub>4</sub> high temperature PEMFC single cells. Constant current performance curves were recorded and electrochemical method (CV) was applied to study the ESA loss of cathode catalysts during the life tests. The transmission electron microscopy (TEM) and X-ray diffractometer (XRD) were used to detect the increase in particle size of the cathode platinum after 3200 cycle operation. The results obtained after three time experiment replicating.

## 2 EXPERIMENTAL

### 2.1 MWCNT Pretreatment

Multiwalled carbon nanotubes (MWCNTs) with outside diameters of <8 nm, length: 0.5-2.0 μm and purity of >95% were purchased from Cheap Tube Inc., in USA. As-received MWCNTs were pretreated to disentangle, purify, and decorate them. Therefore One portion of

MWCNTs was treated by HNO<sub>3</sub> solution; 1.0 g of MWCNTs was mixed with 100 mL of a 65% HNO<sub>3</sub> solution under constant stirring for 20 min and then refluxed at 140 °C for 4 h. The resulting MWCNT was rinsed thoroughly to neutral with deionized water and dried at 80 °C in a vacuum oven overnight.

## 2.2 Catalyst preparation

Modified precipitation method [3] was used to prepare Pt/MWCNT with high loading and good dispersion on the carbon surface. The carbon slurry was prepared by vigorous mixing of carbon nanotube with distilled water. The chloroplatinic acid solution, prepared by dissolving chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, Metalor<sup>®</sup> technologies (UK) Ltd) into the distilled water, was added to the carbon slurry. Then for efficient dispersion, acetic acid was added to the slurry and heated up to a desired temperature up to 90°C. The pH of the slurry was adjusted to the basic using diethyl amine. An excess quantity of 40% aldehyde as reducing agent was then introduced into the slurry for *in situ* liquid-phase reduction. The Pt/MWCNT slurry was filtered, several time washed and then dried at 110°C in a vacuum oven.

## 2.3 Physical characterization

### 2.3.1 XRD Analysis

From Figure 1a it can be seen that there are obvious differences before and after loading platinum on the structures of supporting material (MWCNT). Without Pt, The structure of MWCNT is mostly amorphous carbon black, while after loading Pt; the pattern for Pt/ MWCNT exhibited four characteristic diffraction peaks, at 39.6, 46.7°, 68.5° and 82.6° (2θ) degrees.

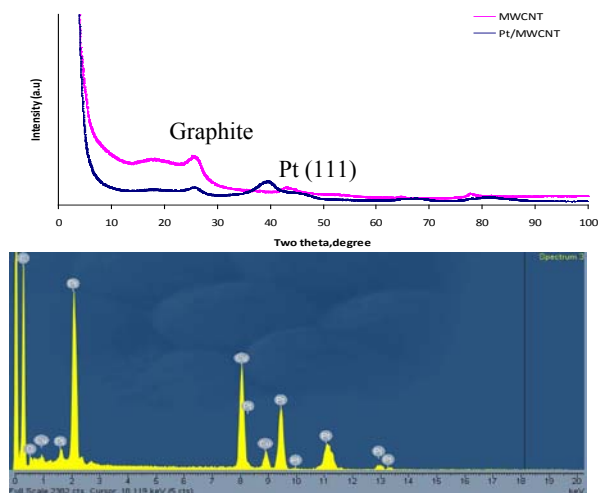


Figure 1: XRD patterns of pure MWCNT and Pt/MWCNT catalyst (a) and EDS image of Pt deposition on MWCNT used as support (b).

Crystallite size determination is performed by measuring the broadening of a particular peak in a diffraction pattern associated with a particular planar reflection from within the crystal unit cell. Using Scherrer equation, average Pt particle sizes of prepared electrocatalyst at wider Pt (111) peak is 2.2 nm. Likewise EDX analysis show that Pt successfully deposited on the carbon nanotube as support material (Figure 1b). These peaks can be attributed to the (111, crystalline facet), (200), (220) and (311) lattice planes of the Pt nanoparticles (Nps), respectively [3].

To obtain a comprehensive analysis, the Pt/ MWCNT catalyst on the electrode endured similar life test durations was characterized by XRD, and the results are shown in Figure 2. X-ray diffraction pattern of the sample was collected using a Huber G670 X-ray diffractometer (XRD) with copper rotating anode (CuK<sub>α</sub> radiation, λ = 1.54056 Å, at 40 kV/20 mA). A continuous scan rate of 5min<sup>-1</sup> from 0° to 90° of 2θ was used for all samples. After single cell series tests, the powder samples of Pt/MWCNT electrocatalyst was scraped from the surface of the anode and cathode sample by a razor blade. The characteristic diffraction peaks of the face centered cubic structure are clearly detected in all the electrode samples. The diffraction peaks at 2θ values of 39.8463°, 67.5° and 81.4° are associated with the Pt (111), (200), (220) and (311) lattice planes, respectively (Figure 2). All the characteristic peaks of Pt in cathode and anode become sharper following the longer test time, which indicates that the Pt particle grew gradually during the lifetime test. It should be noted that the diffraction peaks of Pt in the time tested anode were broader than that tested cathodes, and its particle size had change (d= 6.3 nm) compared with before test (d= 2.2 nm), this suggests that the Pt particle growth in the cathode (d= 9.4 nm) was more serious than that in the anode [3].

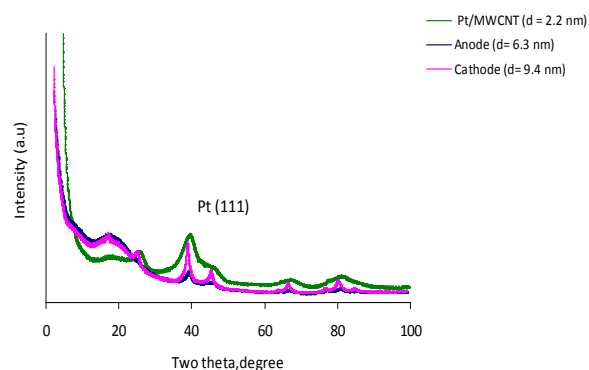


Figure 2: XRD patterns of Pt/MWCNT before and after 3200 cycles single cell test.

### 2.3.2 TEM analysis

Morphology and particles size distribution of Pt/MWCNT catalyst before and after single cell test was performed via High and low magnification transmission electron microscope (HMTEM and LMTEM) images were

observed in a TECNAI T20 TEM equipped with a high-speed slow-scan CCD camera operated with a LaB6 filament at 200 kV. The sample deposited on holey amorphous carbon film on a Cu grid for TEM observation.

Figure 3a presents the TEM images of electrocatalyst before and after the life tests. Their particle size distributions for the electrocatalyst were obtained by manually measuring all the particles from the bright-field micrographs. Also, the diffraction rings in the selected area diffraction pattern (SAD) indicate that the Pt Nps are polycrystalline and randomly oriented, as shown in the inset of Figure 3b.

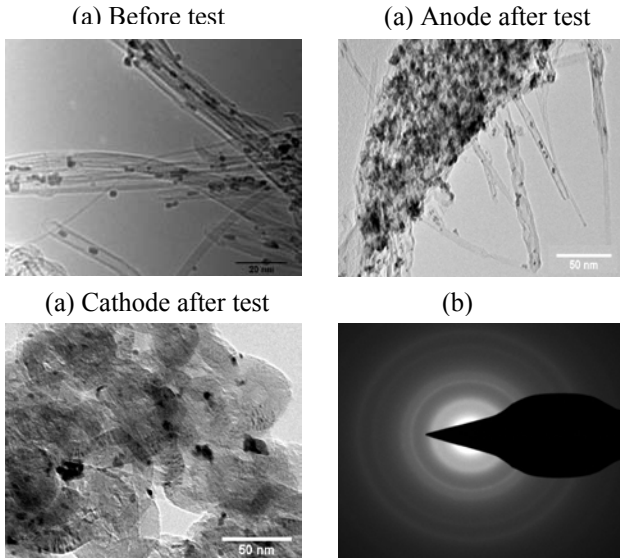


Figure 3: (a) The TEM photographs of Pt/MWCNT in anode and cathode before and after 3200 constant test, (b) the selected area diffraction pattern (SAD) of Pt NPs with the four rings indexed to the {111}, {200}, {220}, and {311} planes.

This result is in good agreement with crystalline fcc structure of XRD prediction. Comparing all the TEM images in figure 3, it is obvious that the size of Pt particles increases after the life tests. In anode some coalescence of particles is apparent; however, numerous small particles are still evident. Evidently, in cathode after 3200 cycles, the mass of small crystallites appear to be absent. From figure 4, it can be seen that the average mean particle size of Pt/MWCNT catalyst is 2.25 nm which is remarkably similar to those obtained in XRD results (Figure 2). At the cathode, due to the TEM images contained some agglomerated or nonspherical Pt particles histogram was not considered in the particle size distribution.

An interesting case is the study of Pt Nps growth mechanism *via* TEM analysis (Figure 3c). After normal operation through fuel cell constant test, HRTEM images revealed that Pt Nps inside the HT PEMFC have a nonspherical (rod and bent) shape typical of either longitudinal or dendrite growth (Figure 3c) [3]. Clearly, at

the cathode, a marked decrease in the density of Pt Nps per  $\text{cm}^2$  of carbon and particle growth was observed.

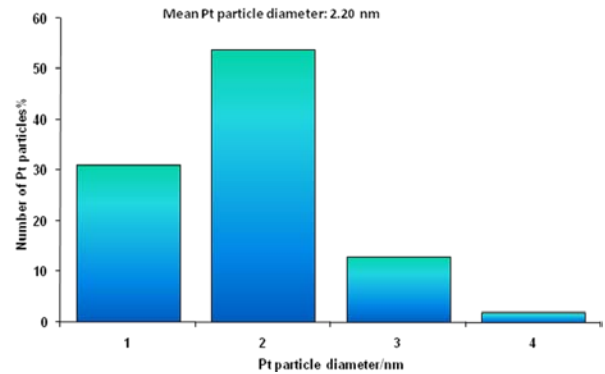


Figure 4: The histogram of Pt/MWCNT particles sizes distribution from the TEM photographs.

### 3 MEA INVESTIGATIONS

In fuel cell the performance loss due to either contribution of catalyst degradation or any of membrane degradation during single cell tests. Understanding features one of them would indicate performance loss origin [4].

#### 3.1 Polarization curve

Polarization curve was obtained by a current step potentiometry with the steady state potential recorded 2 min after each current was set. All polarization curves were measured beginning with the highest currents. The fuel cell polarization at low and medium current densities was dominated by activation losses and ohmic losses. Losses were decided by the electrical resistance of the electrodes. The activation losses were decided by the cell temperature, catalyst activity, reactant concentration and the pressure. The ohmic and the resistance losses were decided by the electrical resistance of the electrodes and the resistance to the flow of ions in the electrolyte [5].

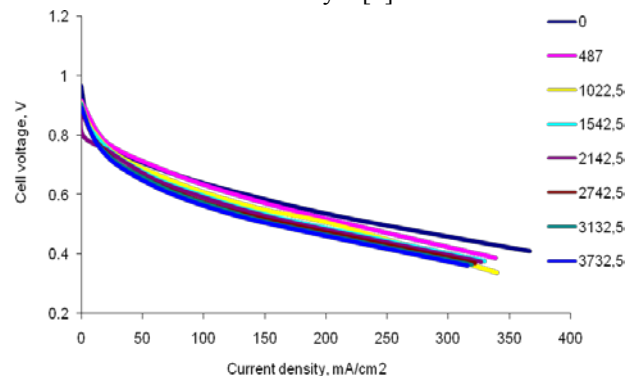


Figure 5: Polarization curves of a PBI fuel cell after different number of cycles (1 cycle = 2 min) constant fuel cell test at open circuit voltage. Platinum loading of the

electrode was  $0.7 \text{ mg Pt cm}^{-2}$  and the active area of the electrode was  $25 \text{ cm}^2$ . Hydrogen and oxygen flow rates were  $100 \text{ ml min}^{-1}$  and the air flow rate was  $200 \text{ ml min}^{-1}$ .

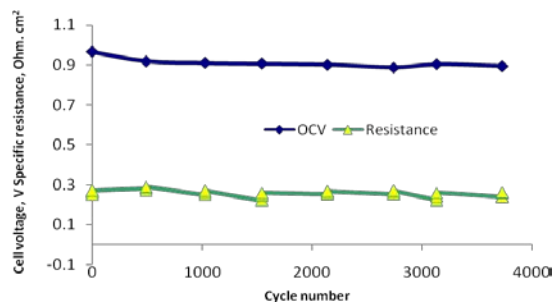


Figure 6: OCV and ohmic resistance of Pt/MWCNT catalyst after 4000 cycles.

Figure 5 shows a set of polarization curves of a Pt/MWCNT operating with hydrogen and air at  $150 \text{ }^\circ\text{C}$ . At the anode side the hydrogen flow was set at  $200 \text{ ml min}^{-1}$ , whereas the air flow at the cathodic side was fixed at  $100 \text{ ml min}^{-1}$ . The numbers shown in the legend are accumulated number of cycles (1 cycle = 2min) at open cyclic voltage (OCV). At lower current densities, the polarization curves have the same behavior. With an increase in the test time of the Pt/MWCNT catalyst has virtually no remarkable influence on the polarization drop particularly when the current density is in a lower, though a better performance is achieved when the current density is close to the limiting value. Clearly, the performance loss occurred throughout the entire current density region, and most of the loss occurred in the first 1500 cycles. Afterwards, the performance decline rate slowed down regularly.

### 3.2 Open cyclic voltage (OCV), specific resistance and degradation

The impact of open circuit voltage (OCV) on the performance and degradation of PBI- $\text{H}_3\text{PO}_4$  membrane of PEMFC operated at  $150^\circ\text{C}$  was investigated. The OCV showed an almost monotonous constant line (Figure 8). However, increasing OCV usually is consisting with performance loss but this outcome is not obtained in our study (Figure 5). OCV graph indicate that MEA degradation is insignificant. Likewise, since the total resistance did not change based on results from Figure 6, the proton conductive with in MEA also inconsequential, hence, OCV and resistance results show that MEA interference in catalyst performance loss insignificant and both increased catalyst activity loss due to mainly catalyst utilization (Figure 7). Finally, one may conclude that catalyst electrochemical surface area (ESA) loss (Figure 8) is likely stem from catalyst durability decrease during fuel cell constant time test.

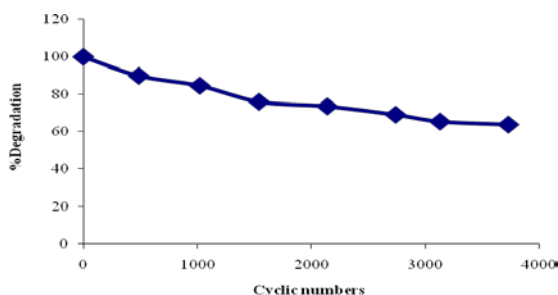


Figure 7: Performance diagram of Pt/MWCNT catalyst after 4000 cycles.

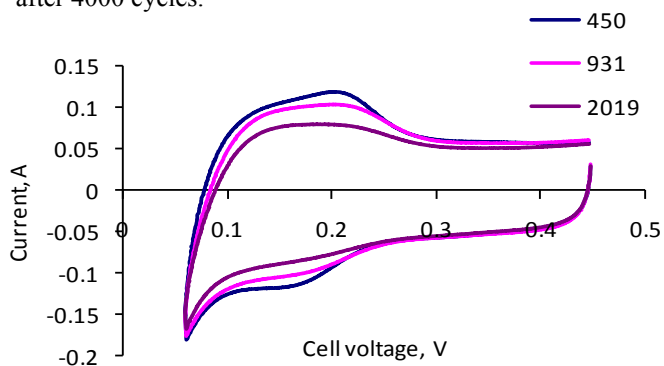


Figure 8: Cyclic voltammetry (CV) data showing catalyst electrochemical surface area (ESA) loss for the Pt/MWCNT catalyst after single cell test.

## 4 CONCLUSION

Durability, Preparation, characterization and of catalyst for  $\text{H}_2/\text{O}_2$  ( $\text{H}_3\text{PO}_4/\text{PBI}$ ) PEMFC -Pt/MWCNT- are presented. Our results indicate that the performance of the prepared catalyst mainly because of catalyst activity loss during single cell test but not membrane. TEM images demonstrate that the shape of Pt Nps change systematically by seeding their growth in non spherical shape (nanorod) after fuel cell test at high temperature.

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