

# Fabrication of Platinum Nanoparticles Decorated Pyridine-Based Polybenzimidazole-Carbon Nanotube for High Temperature Polymer Electrolyte Membrane Fuel Cells

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**Abstract**—Pyridine based polybenzimidazole (PyPBI) was used as the wrapping polymer onto carbon nanotubes (CNTs) surface. The platinum nanoparticles are then immobilized on the PyPBI wrapped CNTs to prepare Pt on CNT (PyPBI/CNT-Pt) catalysts. The Pt-PyPBI/CNT with Pt loading of 40 wt.% and Pt particle sizes of ~4 nm is used to prepare a PBI based membrane electrode assembly (MEA) and perform fuel cell test at 160°C. We demonstrate that the MEA prepared using the Pt-PyPBI/CNT catalyst has a higher fuel cell performance than that prepared using commercial PtC powder.

**Keywords**—Carbon nanotube, PEM fuel cell, Platinum, Pyridine

## I. INTRODUCTION

POLYMER electrolyte membrane fuel cells (PEMFCs) are being developed as electrical power sources for vehicles and for stationary and portable applications as an alternative to conventional power sources. However, PEMFCs are still far from market launch, which is hindered by two main issues the prohibitive production cost and poor durability and reliability [1-3]. Catalysts exhibit great influence on both the cost and the durability of PEMFCs [1].

Carbon nanotubes (CNTs) appeared to be promising catalyst support for proton exchange membrane fuel cell (PEMFC) because of their unique structure and properties, such as high-surface area, good electronic conductivity, strong mechanical properties and high-chemical stability [2], [3].

Polybenzimidazole (PBI) and its derivative pyridine-PBI (doped H<sub>3</sub>PO<sub>4</sub>) are two of the most promising candidate PEMs of high temperature PEMFCs [4]–[6]. Except using in PEMs of PEMFCs, PBI is also a component in the catalyst layer (CL). It acts as: (1) a metal adsorbing material via the coordination of the metal ion with the aromatic nitrogen of PBI; (2) a Pt carbon support solubilizing material; (3) a binder of PtC (Pt on carbon support), gas diffusion layer (GDL), and PEM; and (4) a proton conductor in CLs. It had been reported that these aromatic

Compounds have a great potential to individually dissolve single-wall CNTs (SWCNTs) and multi-wall CNTs (MWCNTs) through a physical adsorption mechanism based on the  $\pi$ - $\pi$  interactions [6]–[8].

## II. PROCEDURE FOR PAPER SUBMISSION

Py-PBIs was synthesized from tetramine monomer i.e., 3,3'-diamino benzidine (DABD), and two dicarboxylic acid monomers, i.e., isophthalic acid (IPA) and 2,6-pyridinedicarboxylic acid (PyA), with a PyA/IPA molar ratio of 4/6 and a [DADB]/[PyA+IPA] molar ratio of 1/1.

### A. PyPBI wrapped CNTs preparation

MWCNTs (diameter 10-20 nm, length = 5-15  $\mu$ m; CBT Co., Ltd.) mixture in DMAc solutions were prepared with (Table I). The solutions were sonicated at room temperature for 60 min and then filtered. The PyPBI/CNTs were then dried under vacuum.

TABLE I

Sample	PyPBI (mg)	DMAC (mL)
1046PyPBI/CNT-Pt	10	50
2046PyPBI/CNT-Pt	20	50
3046PyPBI/CNT-Pt	30	50
4046PyPBI/CNT-Pt	40	50

### B. Deposition of Pt on PyPBI/CNT support

The deposition of the Pt nanoparticles (NPs) on the PyPBI/CNT was carried out by reducing H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in an ethylene glycol aqueous solution. First, 20 mg of PyPBI/CNT was added to an ethylene glycol aqueous solution (EG/H<sub>2</sub>O = 3/2 v/v, 16.6 mL) and dispersed by sonication. Around 33 mL of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (1.4 mM) in EG aqueous solution was added to the PyPBI/CNT in EG/ H<sub>2</sub>O solution. After stirring for 4 h at room temperature, the mixture was refluxed at 120°C for 8 h. The PyPBI/CNT-Pt catalyst was obtained by filtration, washed with water and dried overnight at 90°C under vacuum

### C. Characterization of PyPBI/CNT-Pt catalysts

The Pt particle sizes and size distributions of PyPBI/CNT-Pt were determined using transmission electron microscope (TEM, JEOL 2100F) and X-ray diffractometer (XRD; Labx

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XRD-6000, Shimadzu). The Pt averaged particle size was estimated from XRD using Scherrer formula [9].

#### D. Preparation of PBI/epoxy membranes

2 g PBI was dissolved in  $N,N'$ -dimethyl acetamide (DMAc, Aldrich Chem. Co.) and mixed with 0.246 g epoxy (Epon-828, diglycidyl ether bisphenol-A). The mixture solution was then cast onto a glass plate with a blade coater to prepare the membrane, and dried in a vacuum oven at  $120^{\circ}\text{C}$  for 24 hr to remove the solvent. The membrane thickness was  $\sim 50\ \mu\text{m}$ . The membrane was immersed in 85wt% of phosphoric acid at  $70^{\circ}\text{C}$  for 24 hr.

#### E. Membrane electrode assembly (MEA) preparations rapped CNTs preparation and single cell test

The PBI/epoxy membrane, Pt-C (carbon supported platinum, Johnson Matthey, 40 wt% Pt) catalyst, Pt-PyPBI-20 (prepared in sec. B), and carbon paper (SGL, GDL-35BC) were used for preparing MEAs. The anode and cathode Pt loadings were both  $0.5\ \text{mg cm}^{-2}$ , and the Pt/C/PBI They were then doped with phosphoric acid by dipping in a 10 wt% phosphoric acid aqueous solution for 24 h and dried in an oven at  $120^{\circ}\text{C}$  for 1 h. The active area of the MEA was  $3.5 \times 3.5\ \text{cm}^2$ .

The performance of the unit cell was tested at  $160^{\circ}\text{C}$  under an ambient pressure using an FC5100 fuel cell testing system (CHINO Inc., Japan). Both the anode  $\text{H}_2$  and cathode  $\text{O}_2$  input flow rates were  $200\ \text{mL min}^{-1}$  and un-humidified.

### III. RESULTS AND DISCUSSION

The TEM images for Pt nanoparticles deposited on Carbon (Johnson Matthey Pt/C) and PyPBI-CNTs supports (this work) are illustrated in Figs. 1. It can be observed that the size of Pt on carbon support was  $\sim 4\ \text{nm}$ . Moreover, Pt nanoparticles were well dispersed and uniformly distributed on the surfaces of the PyPBI-CNT supports. The average Pt particle sizes of the catalysts are estimated from TEM micrographs are summarized in Table II.

TABLE II

PT PARTICLE SIZES ESTIMATED FROM TEM IMAGES AND CALCULATED FROM XRD DATA USING DEBYE-SHERRER FORMULA

Sample	$D_{\text{TEM}}$ (nm)	$D_{\text{XRD}}$ (nm)
Commercial Pt/C	3.21	3.10
1046PyPBI/CNT-Pt	3.98	3.98
2046PyPBI/CNT-Pt	3.50	4.04
3046PyPBI/CNT-Pt	3.98	3.36
4046PyPBI/CNT-Pt	4.02	3.35

The Pt crystallinity and particle sizes of Pt/C and Pt-PyPBI/CNT catalysts were determined using XRD. The Pt particle sizes of the catalysts were also estimated from the half-height of the peak at  $2\theta = 69^{\circ}$  using Scherrer formula [9]. The XRD estimated Pt particle sizes of the catalysts are also shown in Table II.

From TGA data of the four catalysts, we estimated the Pt loadings of each Pt-PyPBI/CNT sample by subtracting the residual wt% of PyPBI/CNT from the residual wt% of Pt-PyPBI/CNT. The Pt loadings of 10PyPBI/CNT-Pt,

20PyPBI/CNT-Pt, 30PyPBI/CNT-Pt and 40PyPBI/CNT-Pt were 41, 43, 45 and 46 wt.%, respectively

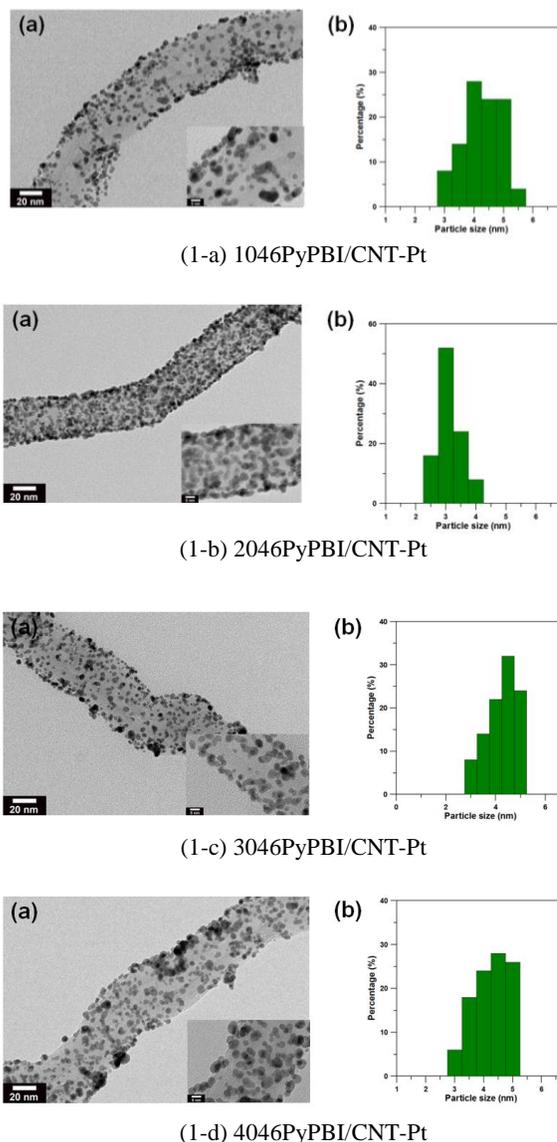


Fig. 1 (a) HRTEM images and (b) Pt particle size distribution histograms of Pt/C and PyPBI/CNT-Pt catalysts.

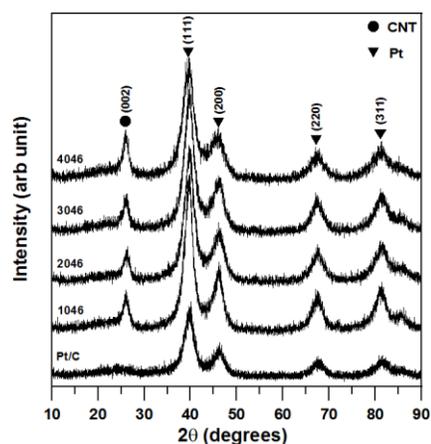


Fig. 2 XRD patterns of Pt/C and PyPBI/CNT-Pt catalysts.

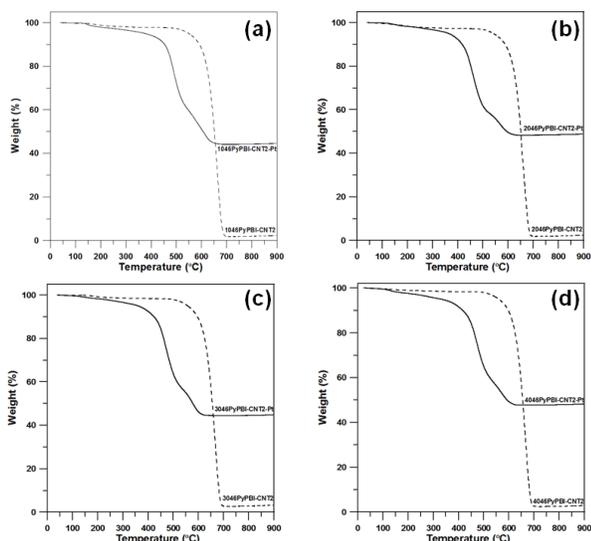


Fig. 3 TGA curves. (a) 1046Pt-PyPBI/CNT-Pt; (b) 2046Pt-PyPBI/CNT-Pt; (c) 3046Pt-PyPBI/CNT-Pt; (d) 4046Pt-PyPBI/CNT-Pt.

Fig. 4 illustrates the  $i$ - $V$  curves of the unit cell tests of these five MEAs. Both the  $i$ - $V$  curves of each MEA at the beginning of cell test and after the cell was activated at a constant current  $i = 200 \text{ mA cm}^{-2}$  for 8 h were recorded. These  $i$ - $V$  data show that the MEA prepared from 20Pt-PyPBI/CNT-Pt has a best fuel cell performance in these five MEAs. All of the MEAs prepared using Pt-PyPBI/CNT had a better fuel cell performance than that prepared from Pt/C catalyst.

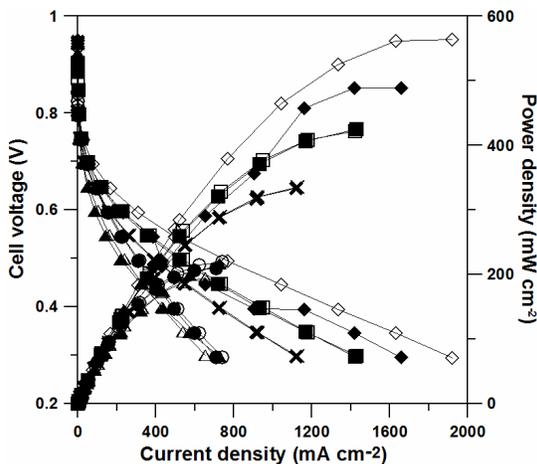


Fig. 4 Fuel cell  $i$ - $V$  curves of MEAs prepared using: (○;●) Pt/C; (△;▲) Pt-PyPBI-10; (◇;◆) Pt-PyPBI/CNT-20; (□;■) Pt-PyPBI-30; (×;×) Pt-PyPBI-40; catalysts. Active area  $12.5 \text{ cm}^2$ , Temp.  $160^\circ\text{C}$ , unhumidified  $\text{H}_2/\text{O}_2$  flow rates  $200 \text{ mL min}^{-1}$ . Open symbols: unit cells

#### IV. CONCLUSION

In this work, we prepared Pt-PyPBI/CNT catalysts by immobilizing Pt nano-particles on the PyPBI wrapped CNTs. The PyPBI/CNT-Pt with Pt loading of 40 wt.% and Pt particle sizes of  $\sim 4 \text{ nm}$ . The Pt-PyPBI/CNT catalyst was used to prepare a PBI/ $\text{H}_3\text{PO}_4$  based MEA and perform fuel cell test at  $160^\circ\text{C}$ .

We demonstrate that the MEA prepared using the Pt-PyPBI/CNT catalyst has a higher fuel cell performance than that prepared using a commercial Pt/C catalyst.

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