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## Nanocatalysts for Low Temperature Fuel Cells

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### Abstract

Zeolitic Imidazolate Frameworks (ZIFs) are one of the potential candidates as highly conducting networks with surface area with a possibility to be used as catalyst support. In the present study, highly active state-of-the-art Pt-NCNTFs catalyst was synthesized by pyrolyzing ZIF-67 along with Pt precursor under flowing Ar-H<sub>2</sub> (90-10 %) gas at 700 °C. XRD analysis indicated the formation of Pt-Co alloy on the surface of the nanostructured catalyst support. The high resolution TEM examination showed the particle size range of 7 to 10 nm. Proton exchange membrane fuel cell performance was evaluated by fabricating membrane electrode assemblies using Nafion-212 electrolyte using H<sub>2</sub>/O<sub>2</sub> gases (100 % RH) at various temperatures. The peak power density of 630 mW.cm<sup>2</sup> was obtained with Pt-NCNTFs cathode catalyst and commercial Pt/C anode catalyst at 70 °C at ambient pressure. ■

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*Keywords:* ZIF-67; ORR catalysts; Membrane-Electrodes Assembly; PEM Fuel Cell

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## 1. Introduction

Proton exchange membrane fuel cell (PEMFC) is the most promising energy conversion technology for stationary as well as automotive applications due to its advantages such as lower operating temperature and higher power density as compared to other types of fuel cells. However, for wide-scale commercialization of PEMFCs, it should overcome several challenges including reducing the cost, maximizing the utilization of platinum catalyst, improving the performance and durability of the membrane electrode assembly. Oxygen reduction reaction (ORR) is the most important one due to the potentially lower exchange current density value in the PEMFC [1,2,3]. In order to have reasonable reaction kinetics, noble metals based nanocomposites are the most efficient electrocatalysts towards ORR. However the noble metal ORR catalysts are highly expensive and are the leading barriers for the PEMFC commercialization [4,5]. In this context, it is important to develop highly efficient and durable electrocatalysts for ORR [6]. Recently, metal-organic frameworks (MOFs) have emerged as a novel class of porous crystalline materials both as template and precursor to produce nanoporous carbons for gas storage [7], catalyst support [8], and electrode materials for lithium batteries [9], sensors [10], and supercapacitors [11]. Zeolitic imidazolate frameworks (ZIFs) as a subclass of MOFs are excellent materials for the synthesis of nanocarbon electrocatalysts with abundant carbon and nitrogen [12,13]. MOF-derived nanocomposites reported as poor ion and electron transport materials due to poor graphitic degree and microporous structures [14-16]. The use of ZIFs as a precursor for the synthesis of N-doped CNTs (NCNTs) structures has rarely been reported as ORR electrocatalyst [17-19]. In the preliminary study, cathode with ultra-low loading of Pt on N-doped carbon nanotube frameworks (Pt-NCNTFs) was developed and evaluated towards ORR catalyst in the PEMFC. The Pt-NCNTFs nanocatalyst was characterized using x-ray diffraction, scanning electron microscope and transmission electron microscope for composition, and nature of particle morphology and distribution. Membrane electrode assemblies fabricated with Pt-NCNTFs cathode nanoelectrocatalyst catalyst (loading of 0.12 mg Pt per cm<sup>2</sup>) showed a peak power density of ~630 mW.cm<sup>-2</sup> at 70 °C with H<sub>2</sub> and O<sub>2</sub> gases at 100 % RH under ambient operating pressure, with excellent performance stability.

## 2. Experimental

### 2.1 Synthesis of ZIF-67 particles

ZIF-67 samples were synthesized as described in the published literature [3]. In a typical synthesis, 2-methylimidazole (1.97 g) was dissolved in a mixed solution of 20 ml of methanol and 20 ml of ethanol. Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (1.746 g) was dissolved in another mixed solution of 20 ml of methanol and 20 ml of ethanol. The above two solutions were then mixed under continuous stirring for few minutes and held for 20 h at room temperature. The purple precipitate was collected by centrifuging the solution, washed in ethanol several times and dried at 80 °C overnight. The flowchart in Figure 1 provides the process steps sequentially.

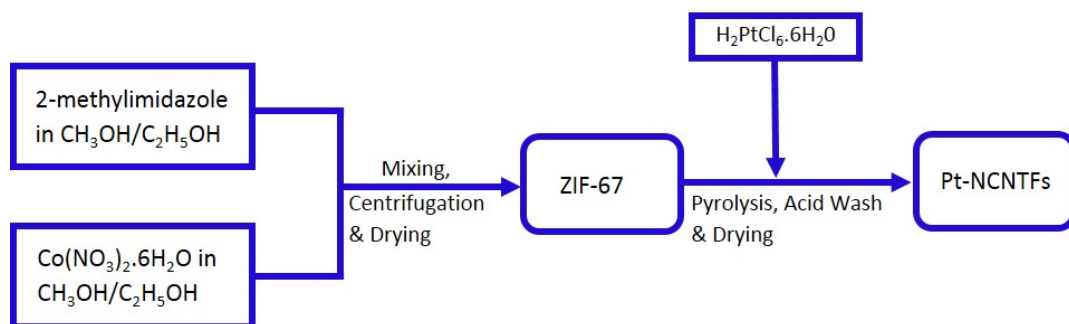


Figure 1. Process flowchart for Pt-NCNTFs Synthesis.

### 2.2 Synthesis of Pt-NCNTFs

The ZIF-67 particles were soaked with H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O solution (5 wt % solution in DI water) and the resulting material was dried at 80 °C for 1h. The dried powder was heated at 350 °C for 1.5 h then raised to 700 °C at a ramp rate of 2 °C per minute and pyrolyzed for 3.5 h under flowing Ar/H<sub>2</sub> (90%/10% in volume ratio) atmosphere (see

Figure 1). The as-prepared black powder product after cooling down to room temperature naturally was treated in 0.5M H<sub>2</sub>SO<sub>4</sub> solution for 6 h. The resulting sample was collected by centrifugation, repeatedly washed with DI water, and then dried at 80 °C. NCNTFs were synthesized by following same protocol without adding Pt precursor. The synthesis process reported here used only single precursor as carbon, nitrogen and Co source.

### 2.3 Catalyst Characterization

The morphology and structure of the Pt-NCNTFs were characterized by Scanning Electron Microscopy (SEM, Hitachi S-3500 N) and Transmission Electron Microscopy (TEM, Philips CM200, 200 kV). Powder X-Ray diffraction (XRD) are recorded using SIEMENS D5000 X-Ray Diffractometer with Cu K $\alpha$  radiation (Cu K $\alpha$ ,  $\lambda$  = 1.54, 40 kV and 30 mA).

### 2.4 Electrochemical single cell measurements

#### 2.4.1 Catalyst Coated Membranes

The cathode catalyst ink was prepared by dispersing Pt-NCNTFs (or Pt/C for anode) in Nafion solution (Ion Power, Inc., LQ-1005-1000 EW, 5% wt.) and isopropyl alcohol. The catalyst coated membrane (CCM) was fabricated coating the catalyst ink by micro-spray method on Nafion-212 (Ion Power Inc., USA) membrane and vacuum-dried at 70 °C. The catalyst loading was 0.2 and 0.12 mg Pt per cm<sup>2</sup> on the anode and cathode sides of the CCM, respectively.

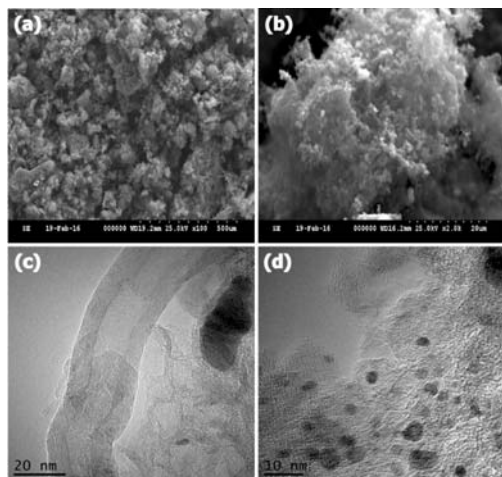
#### 2.4.2 Gas diffusion layer

Teflonized non-woven carbon paper (GD07508G, Hollingsworth & Vose Company) was used as a substrate for fabricating gas diffusion layers (GDLs). Nano-chain Pureblack carbon (grade 205-110) from Superior Graphite Co., VGCF from Showa Denka, Teflon dispersion (TE-3859) from DuPont Fluoroproducts and SDS (C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>Na) from Fisher Scientific were used for carbon slurry preparation. 0.5 g of carbon powder (73.16 wt.% Pure black carbon powder and 26.84 wt.% VGCF) was dispersed in 8 ml DI water containing 120 mg of SDS by stirring the mixture for 10 min and sonicated for 30 min. PTFE (34 wt.%) dispersion was added into the mixture and followed with the magnetic stirring for 10 min. The carbon slurry (micro-porous layer) was coated onto the non-woven carbon paper substrates using Easycoater equipment (EC26, Coatema) and sintering at 350 °C for 30 min in air.

#### 2.4.3 Fuel cell assembly and Testing

The MEAs were assembled by sandwiching the CCM with the gas diffusion layers on both sides in the PEMFC test cell (Fuel Cell Technologies Inc., USA) of the CCM. Silicone coated fabric (Product # CF1007, Saint-Gobain Performance Plastics, USA) gasket used and the cell was tightened with a uniform torque of 40 lb-in. Single cell fuel cell performance was evaluated using Greenlight Test Station (G50 Fuel Cell Test Station, Hydrogenics, Canada) at 50, 60 and, 70 °C with H<sub>2</sub>/O<sub>2</sub> at ambient pressure by galvanostatic polarization. The relative humidity of the reactant gases were maintained at 100 % by controlling the humidity bottle temperatures (both at 400 SCCM, respectively).

## 3. Results and Discussion



The surface morphology as well as the physical dimension of the NCNTFs and Pt-NCNTFs cathode catalysts as examined under SEM and TEM are shown in Figure 2(a and c) and 2(b and d), respectively. As can be seen clearly from the SEM images, the carbon nanotubes are grown on the surface of ZIF-67, which is slightly different from the published literature [20].

Figure 2. Scanning Electron Micrographs of (a,b) Pt-NCNTFs, and Transmission Electron Micrographs of (c) NCNTFs and (d) Pt-NCNTFs.

The possible reason for the growth of carbon nanotubes is due to the more reducing environment under flowing Ar gas with 10 % H<sub>2</sub> during the pyrolysis, similar to a CVD process. As evident from the TEM image shown in Figure 2c, the presence of well-defined multiwall carbon nanotubes is confirmed, as observed in the surface examination by SEM. The darker spot located at upper right is Co particle as measured by EDS analysis with ~15 nm in diameter. As seen in Figure 2d, the average Pt particle sizes are in the range of 7-10 nm, which could lead to fairly high performance and longevity. The catalyst particles are in the range of 4 to 8 nm yielding good performance and improved durability [21]. In addition, graphitic lattice fringes (with 0.34 nm) are also evidenced for providing superior conducting network as well as electrochemical stability.

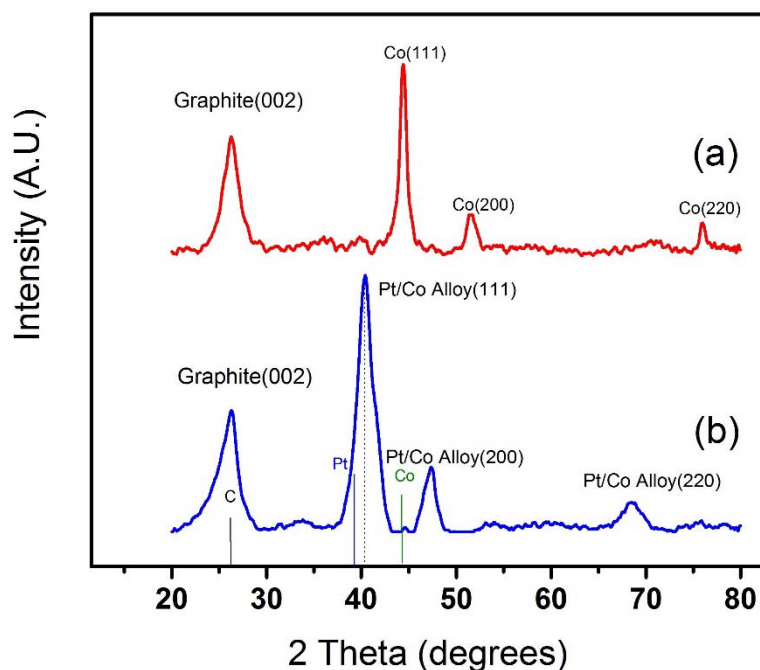


Figure 3. X-Ray diffractograms of (a) NCNTFs and (b) Pt-NCNTFs.

XRD patterns for NCNTFs and Pt-NCNTFs are given in Figure 3. As clearly observed, both the NCNTFs and Pt-NCNTFs show the presence of graphitic carbon at  $2\theta$  value of  $\sim 26.3$  (hkl value: 002), confirming the graphitized CNTs under TEM examination. Other 3 diffraction peaks in the NCNTFs (Figure 3a) are identified as Co (111), Co (200) and Co (220) planes at the  $2\theta$  values of 44.36, 51.67 and 75.98, respectively. In the case of Pt-NCNTFs, the presence of Pt-Co alloy is identified and is expected to exhibit enhanced electrochemical performance towards ORR [22]. Based on the lattice parameters of Pt (3.92 Å) and Co (3.53 Å), the composition of the Pt-NCNTFs (3.86 Å) is estimated to be 84 - 16 atomic wt. % Pt-Co alloy using

Vegard's law [23]. From the Scherrer Equation the average crystallite size was calculated by FWHM, for the Pt-NCNTFs as 10.5 nm which is nearly identical to the values estimated from TEM images.

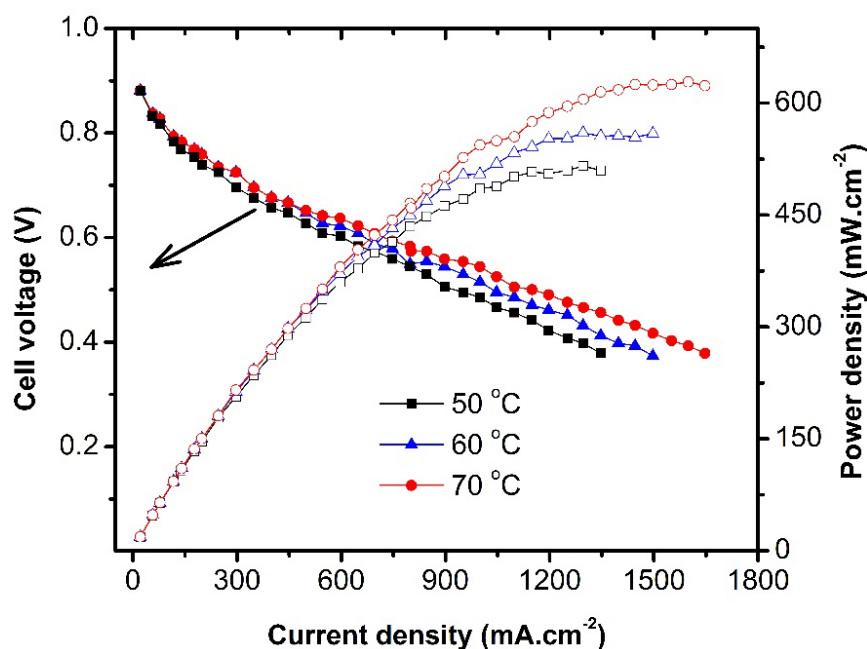


Figure 4. Fuel Cell Performance using Pt-NCNTFs cathode catalysts at various temperatures with H<sub>2</sub> and O<sub>2</sub> gases, 100 % RH at ambient pressure. The open symbols represent the power density values.

Figure 4 shows the PEM fuel cell performance of the MEAs with Pt-NCNTFs cathode and commercial Pt/C anode catalysts using H<sub>2</sub> and O<sub>2</sub> at various temperatures up to 70 °C. It is very encouraging to observe that the cathode with extremely low

loading of 0.12 mg Pt per cm<sup>2</sup> showed a peak power density of 630 mW per cm<sup>2</sup> at 70 °C with H<sub>2</sub> and O<sub>2</sub> gases at ambient pressure at 100 % RH. Further evaluation of the Pt-CNTFs nanocatalysts under various operating conditions as well as durability is in progress.

#### 4. Conclusions

Pt nanoparticles of size 10 nm were supported on nitrogen doped carbon nanotubes framework prepared from pyrolysis of ZIF-67 at 700 °C in an Ar/H<sub>2</sub> (90/10 %) environment. ZIF-67 served as single source for Co, C and N. The MEA with Pt-NCNFs nanocatalyst showed excellent PEMFC performance with a peak power density of 630 mW.cm<sup>-2</sup> using Nafion-212 membrane at 70 °C with H<sub>2</sub> and O<sub>2</sub> gases at ambient operating pressure. The fuel cell performance with low Pt loading towards ORR could be attributed to the synergistic effect from Pt, Co, Pt-Co alloy, nitrogen and carbon nanotubes framework. It was interesting that the composition of the nanocatalyst Pt-NCNTFs estimated using Vegard's law was 84 - 16 atomic wt. % Pt-Co alloy.

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