

MOF Derived Catalysts for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cell

NOAMAN Khan^{1,a*}, SAIM Saher^{3,b}, XUAN Shi^{2,c}, MUHAMMAD Noman^{1,d},
MUJAHID Wasim Durani^{2,e}, ASAD Ali^{1,f}

¹Materials for Energy Storage and Conversion, U.S.-Pakistan Center for Advanced Studies in Energy (USPCAS-E), University of Engineering and Technology (UET) Peshawar, 25000, Khyber Pakhtunkhwa, Pakistan

²Fuel Cell Laboratory, The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA

³Department of Mechanical Engineering, CECOS University of Information Technology and Emerging Sciences, Peshawar, Khyber Pakhtunkhwa, Pakistan

^ankhan29@asu.edu, ^bs.saher@uetpeshawar.edu.pk, ^cShi.Xuan@asu.edu,

^dmuhammad.noman@uetpeshawar.edu.pk, ^emdurani@asu.edu, ^fasadali3201@gmail.com

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Abstract. Highly porous ZIF-67 (Zeolitic imidazole framework) has a conductive crystalline metal organic framework (MOF) structure which was served as a precursor and template for the preparation of nitrogen-doped carbon nanotubes (NCNTs) electrocatalysts. As a first step, the chloroplatinic acid, a platinum (Pt) precursor was infiltrated in ZIF-67 with a precise amount to obtain 0.12 mg.cm⁻² Pt loading. Later, the infiltrated structure was calcined at 700 °C in Ar:H₂ (90:10 vol%) gas mixture. Multi-walled nitrogen-doped carbon nanotubes were grown on the surface of ZIF-67 crystals following thermal activation at 700 °C. The resulting PtCo-NCNTs electrocatalysts were deposited on Nafion-212 solid electrolyte membrane by spray technique to study the oxygen reduction reaction (ORR) in the presence of H₂/O₂ gases in a temperature range of 50-70°C. The present study elucidates the performance of nitrogen-doped carbon nanotubes ORR electrocatalysts derived from ZIF-67 and the effects of membrane electrode assembly (MEA) steaming on the performance of proton exchange membrane fuel cell (PEMFC) employing PtCo-NCNTs as ORR electrocatalysts. We observed that the peak power density at 70 °C was 450 mW/cm² for steamed membrane electrode assembly (MEA) compared to 392 mW/cm² for an identical MEA without steaming.

Introduction

Proton exchange membrane fuel cell (PEMFC) is an interesting alternative energy source for future generations due to its high efficiency and environment-friendly operation. It converts chemical energy stored in hydrogen and oxygen to electricity, producing water as a byproduct. In recent times, conventional power sources such as fossil fuels have raised serious concerns due to rapid depletion, global warming and climate change. PEMFC has many advantages such as high power density, compact size, and low operating temperature in addition to its environment-friendly power generation [1, 2]. However, the large scale commercialization is primarily hindered by the high cost of platinum based electrocatalysts [1-4]. Platinum is an expensive and rare noble metal with 90% supply from South Africa and Russia. Platinum must be significantly reduced or replaced altogether with low cost alternatives to promote PEMFC commercialization. In PEMFC, two reactions occur simultaneously at the cell anode and cathode called hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), respectively and are facilitated by platinum based electrocatalysts. ORR is inherently sluggish due to slow kinetics, requiring a high platinum loading at the cathode [5, 6]. Commercial catalysts employ platinum particles supported on high surface area inert carbon black support such as Vulcan XC-72. Despite many advantages, Pt/C suffers long

term durability issues resulting from the weak interaction between Pt and carbon black support. The Pt particles erodes in PEMFC acidic environment and agglomerates, which decreases the active surface area and hence performance [7-9]. A great deal of work has been dedicated to reduce platinum loading by improving Pt utilization and catalytic activity [10-12]. The performance and utilization of Pt nanoparticles strongly depends upon the structural and electronic properties of catalyst support material. Novel catalyst support materials with desirable properties can significantly reduce Pt loading without suffering performance. Nitrogen-doped carbon nanotubes (NCNTs) have been utilized as Pt catalyst supports and demonstrated a higher catalytic activity than commercial Pt/C owing to its superior electronic and structural properties [13, 14]. Metal-free NCNTs are catalytically activity towards ORR attributed to pyrrolic and pyridinic configuration of nitrogen in graphitic CNT structure [15]. Nitrogen doping also induces defects into CNT structure which increase edge plane exposure and result in higher catalytic activity [16]. Higgins and coworkers showed that nitrogen-doped carbon nanotubes support for Pt catalysts synthesized from nitrogen-rich ethylenediamine (ED) precursor performs much better than pyridine (Py-CNTs) precursor with lesser nitrogen content [17]. Chen and coworkers compared un-doped CNTs with nitrogen-doped carbon nanotubes (CNx) and found that the structure and surface property of CNx leads to a higher dispersion of Pt on CNx compared to CNTs [18]. Another method of reducing Pt loading is to alloy it with other metals such as Co, La, Ni and Pd, to name a few [19-21]. Recently, metal organic frameworks (MOFs) have attracted attention as a precursor for synthesis of novel nano-carbon electrocatalysts for fuel cells due to advantages such as low cost, tunable pore sizes, high thermal stability and desirable electrochemical properties [22, 23]. MOF-derived nano-carbon composites are microporous and poor graphitic degree unfavorable for ion and electron conduction [24]. Zeolitic imidazole frameworks (ZIF) is a subclass of MOFs rich in carbon and nitrogen with imidazole structure and Co/Fe metal centers [25]. Xia and coworkers used ZIF-67 to synthesize metal-free nitrogen-doped carbon nanotube frameworks electrocatalysts with higher catalytic activity resulting from robust structure of the NCNTFs [26]. ZIF-67 derived NCNTs have been reported for super-capacitor electrode materials but rarely for fuel cells [27]. In addition to electrocatalysts, membrane electrode assembly optimization directly affects fuel cell performance. MEA conditioning procedures have been reported in literature [28, 29]. Zhiani and coworkers have reported three different on-line activation processes on membrane electrode assembly to achieve high cell performance. They demonstrated that steaming of MEA before conditioning procedures enhances cell performance by decreasing Ohmic resistance and mass and charge transport limitations [29]. Qi and coworker reported that steaming or boiling the catalyst-coated membrane (CCM) in water increases catalyst utilization and performance [30]. Here, we report highly active nitrogen-doped carbon nanotubes derived from ZIF-67 to be used as an active support for nano-sized Pt particles alloyed with Cobalt (Co) and use steaming as a pre-conditioning procedure for the MEA. Single fuel cell tests showed a very high performance improvement due to the robust structure of NCNTs enhancing Pt utilization, synergetic effect resulting from catalytically active NCNTs catalyst support and MEA optimization through steaming.

Experimental

Preparation of ZIF-67. 8.73 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to a mixture of 100 ml of ethanol and 100 ml of methanol and stirred for few minutes. In another beaker, 9.85 g of 2-methylimidazole was added to a mixture of 100ml of ethanol and 100 ml of methanol. The two solutions were mixed under continuous stirring and kept at room temperature for 24 hours in a closed container. ZIF-67 particles precipitated and were collected by centrifuging, washed in ethanol and methanol three times and fully dried at 80°C to get powder ZIF-67.

Synthesis of PtCo-NCNTs. The NCNTs were prepared by thermal treatment of crystalline ZIF-67 particles reported in published literature [31]. First, ZIF-67 particles were soaked in Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) solution (5 wt. % in DI water) and the resulting mixture was dried for 3 hours to ensure complete drying. The powder was collected and heated in a tube furnace for 1.25 hours at 350°C then the temperature was increased to 700°C at a constant rate of 2°C per minute and

calcined for 3 hours under Ar:H₂ (90:10 vol. %) environment. After calcination, the resulting powder was cooled under natural conditions and treated with 0.5 M sulfuric acid solution for 5 hours to remove excess Cobalt. The PtCo-NCNTs electrocatalysts obtained were thoroughly washed with DI water to remove any traces of impurities and vacuum dried at 70 °C.

Material Characterization. The morphology of ZIF-67 and PtCo-NCNTs were studied using Field-Emission Scanning Electron Microscope (HITACHI S-4700 FESEM). Powder X-ray Diffraction (XRD) peaks were collected using SIEMENS D5000 X-ray Diffractometer (Cu α , $\lambda = 0.156$ nm, 40 kV and 35 mA). For elemental analysis, Energy-dispersive X-ray Spectroscopy (EDS) was employed.

Electrochemical Single Cell Measurements.

Catalyst-Coated Membranes. Membrane electrode assembly (MEA) was prepared by micro spray technique using PtCo-NCNTs as cathode and commercial Pt/C as anode electrocatalysts. The cathode catalyst ink was prepared by dispersing PtCo-NCNTs in Nafion solution (5 wt. %) and isopropyl alcohol (IPA). For anode electrocatalysts, catalyst ink with commercial Pt/C (Tanaka TTK, Japan) catalyst was prepared. The catalyst ink was sprayed on a Nafion-212 ion exchange membrane to fabricate catalyst-coated membranes (CCM) with an active area of 5 cm². The catalyst loadings were calculated by weighing the nafion-212 membrane, before and after the each electrocatalysts were sprayed. The catalyst loadings at anode and cathode were 0.2 mg/cm² Pt and 0.12 mg/cm² Pt, respectively.

Gas Diffusion Layer. The gas diffusion layer (GDL) was fabricated using Teflonized carbon paper (with an area of 10 x 10. cm). 0.5 g of carbon particles (70% Pure black carbon and 30% VGCF) were dispersed in a mixture of DI water and sodium dodecyl sulfate (SDS) and magnetic-stirred for 15 minutes followed by sonicating. To improve the integrity and dispersion of GDL, Teflon was added to the mixture and stirred continuously before coating the slurry on carbon paper. The carbon paste was coated on the carbon paper using Easycoater and allowed to dry overnight followed by heat treatment at 350 °C for 1 h. After heat treatment, the GDL was placed in warm DI water and dried.

Membrane Electrode Assembly Fabrication and Performance Evaluation. The MEAs were fabricated by placing gas diffusion layers (GDLs) on each side of the CCM and assembled in PEMFC test cell. The cell was tightened by applying a constant torque on bolts oppositely placed to each other on the cell. Fuel cell tests were carried out in Greenlight test station (G50 Fuel Cell Test Station, Hydrogenics, Canada) at 50 °C, 60 °C, and 70 °C with H₂/O₂ at normal pressures by galvanostatic polarization. The relative humidity was held constant at 100%.

Pre-Conditioning and Conditioning of the MEA. The pre-conditioning was performed as reported in literature [29, 30]. Catalyst-coated membrane was first placed in a pressure cooker with steam for 10 minutes to hydrate Nafion within the catalyst layer. After assembly, the cell was connected to a steam injector. The steam was injected for 2 hours to the anode and cathode sides at a constant flow rate of 300 ml/min. Both steamed and un-steamed MEAs were conditioned at constant voltage of 0.6V for 8 hours. The cell performance with both MEAs was evaluated in single cell tests in Greenlight test station at different temperatures (50 °C, 60 °C, 70 °C.)

Results and Discussion

The surface morphology and physical dimensions were studied under field-emission scanning electron microscope (FESEM). The crystalline structure of ZIF-67 is shown in Fig. 1(a) showing different sizes with the largest ones close to 2 μ m. Fig. 1(b) shows carbon nanotubes densely formed at the surface of ZIF-67 crystals following pyrolysis at 700 °C. ZIF-67 leftovers from pyrolysis are visible within hair-like PtCo-NCNTs. The incorporation of Pt from chloroplatinic acid did not change the initial ZIF-67 structure. It can be seen that the surface morphology of NCNTs is rough and disordered, resulting from defects induced by the incorporation of nitrogen. The incorporation of nitrogen into CNT structure disrupted the ordered planar hexagonal structure of carbon atoms in CNTs and resulted in the rough surface of the NCNTs [32]. The presence of

uniformly distributed nitrogen on the surface of NCNTs also facilitated dispersion of Pt by providing nucleation sites. The NCNTs were well intertwined to provide a continuous conducting network as catalyst support. NCNTs without Pt are widely reported in published literature synthesized by different techniques [33-36]. This method, however, used a simple and low cost method to obtain nitrogen-rich NCNTs with a high BET surface area of 500 m²/g and nitrogen doping close to 2.4%. XRD peaks for PtCo-NCNTs are shown in Fig. 2. The XRD peak at 2 θ value of \sim 26.4 showed the presence of graphitic carbon, confirming the presence of the CNTs. The Pt/Co alloy formed is also evident from the peaks and expected to enhance the electrochemical properties towards ORR [37]. Using Scherer equation, the average crystallite size for Pt was calculated to be approximately 10 nm.

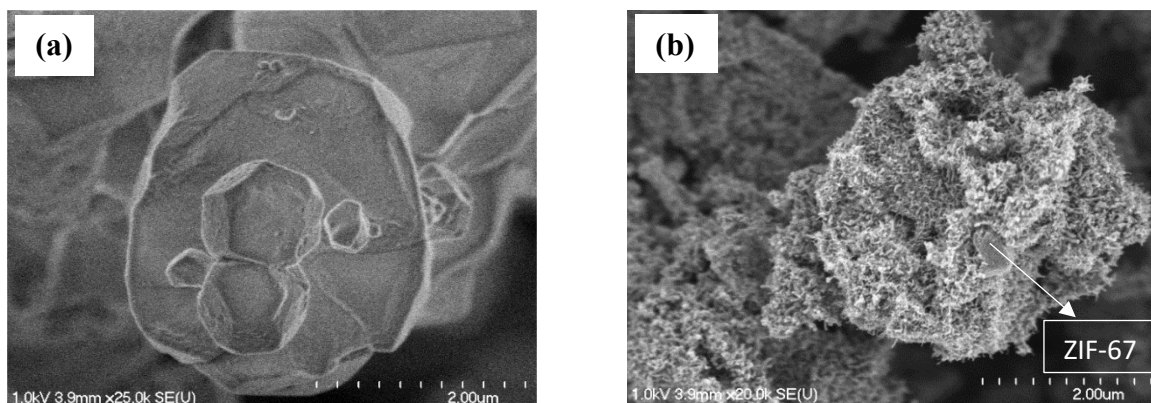


Fig. 1. SEM images of (a) ZIF-67 and (b) Nitrogen-doped carbon nanotubes (PtCo-NCNTs)

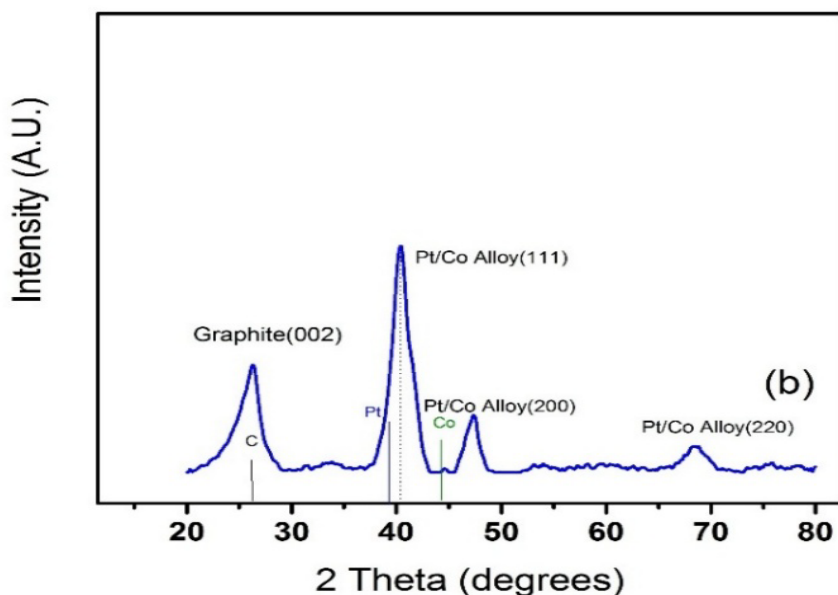


Fig. 2. XRD plot of PtCo-NCNTs confirming the presence of Pt/Co alloy and graphitic carbon NCNTs

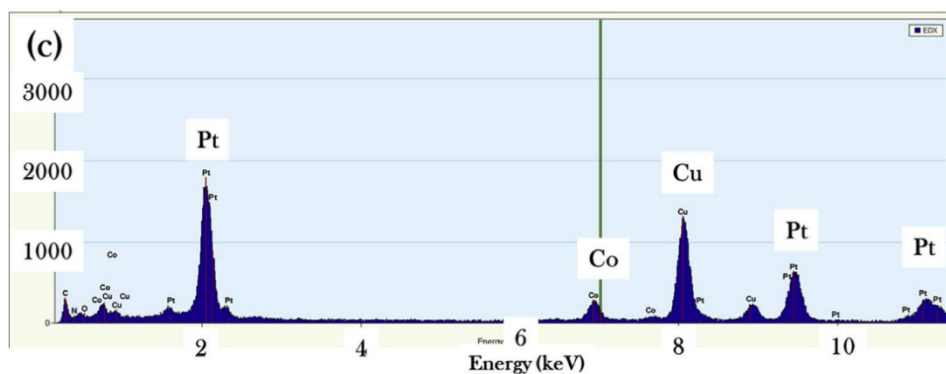


Fig. 3. EDS PtCo-NCNTs

Fig. 3 shows EDS analysis for PtCo-NCNTs. The specific metals were identified in EDS and predominantly consisted of Pt but Co was also present in Pt/NCNTs. Fig. 4(a) shows the performance of the MEA with PtCo-NCNTs as the cathode and commercial Pt/C as anode electrocatalysts. Pt loadings at cathode and anode were 0.12 mg/cm^2 Pt and 0.2 mg/cm^2 Pt, respectively. The I/C (ionomer to catalyst ratio) was 0.85:1 in the catalyst-coated membrane. High peak power density of 392 mW/cm^2 was seen at 70°C with H_2 and O_2 at 100% RH at an ultra-low Pt loading. Fig. 4(b) shows the single cell performance of an identical MEA treated with steam. The loadings and testing conditions for the steamed MEA were identical to the previous one. Ionic conductor such as Nafion was added to the catalyst layer to make it active in three-dimensions. In order for Nafion to conduct protons (H^+) efficiently, it must be sufficiently hydrated. The electrodes were dried completely before they were used in the cell, which reduced water content within catalyst-coated membranes. When the MEA was steam-treated, the Nafion was hydrated throughout the catalyst layer, increasing proton (H^+) conductivity and hence the performance. The highest power density for MEA with steaming was close to 450 mW/cm^2 at 70°C . In general, the power density increases with temperature below the boiling point of water, which is critical to H^+ conduction through Nafion electrolyte membrane. These results confirmed steaming as an efficient procedure for reducing MEA resistance and to improve power density without increasing the catalyst loading.

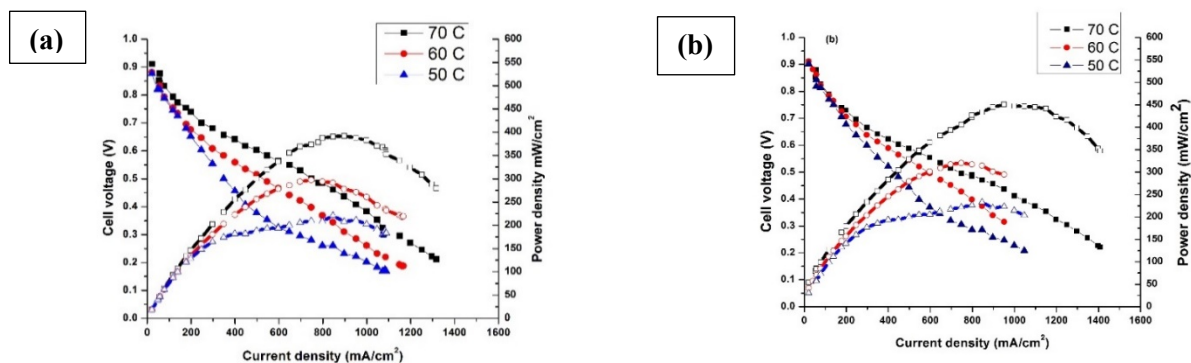


Fig. 4. Cell voltages and power densities as a function of current density measured in single fuel cell tests. (a) shows cell performance of MEA without steam treatment. (b) shows the current density vs power density for a steam-treated MEA under identical conditions and catalyst loadings

Conclusions

Highly active nitrogen-doped carbon nanotubes were synthesized from a low cost ZIF-67 precursor and used as a catalyst support for Pt/Co alloy in proton exchange membrane fuel cell. Only ZIF-67 was the source of C, Co and N in the electrocatalysts. The synergetic effect due to catalytically active NCNTs support structures for Pt nanoparticles enhanced the performance of PtCo-NCNTs electrocatalysts. A simple steaming procedure was employed to ensure efficient hydration of Nafion within catalyst-coated membrane and proved to greatly improve fuel cell performance from 392 to 450 mW/cm^2 . This work established MOFs as a new platform for the synthesis of novel nano-carbon ORR electrocatalysts for PEMFC as well as a variety of other energy storage and conversion applications.

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