

Investigating Electrochemical Behaviors of Ag@Pt Core–Shell Nanoparticles Supported Upon Different Carbon Materials Acting as PEMFC’s Cathodes

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Core-Shell structures of Ag@Pt Nanoparticles (NPs) dispersed on different carbon base supports such as Graphene Oxide (GO), Multiwall Carbon Nanotubes (MWCNT) and Carbon black (CB) Vulcan applied to the oxygen reduction reaction (ORR) in a Proton Exchange Membrane Fuel Cell (PEMFC). Electrocatalysts synthesized through the ultrasonic treatment method. The morphology of as prepared materials characterized through the High Resolution Transmission Electron Microscopy (HRTEM) and X-ray diffraction (XRD) analyses. The ORR activities and stabilities of electrocatalysts studied through electrochemical measurements of Cyclic Voltammetry (CV) and single cell tests, respectively. Results revealed all prepared carbon based electrocatalysts displayed Core-Shell nanostructures moreover; the Ag@Pt/rGO with Ag:Pt mass ratio of 1:3 possessed the largest electrochemical surface area of 77.6 m²/g amongst all synthesized materials. The maximum power density of the membrane electrode assembly (MEA) prepared with Ag@Pt/rGO determined to be 55% higher than that of the commercial Pt/C species. In addition, this was considerably higher than corresponding values of other mentioned synthesized electrocatalysts in this research. These results evaluated through single cell techniques. The understudied core-shell material based upon the rGO considered as a very promising cathode for utilizing in PEMFCs.

1. Introduction

In order to obtain a clean and environmentally green power source, an electrically produced energy considered promising (Chen and Zhu, 2017). Amongst clean power sources such as wind, hydrothermal, solar and geothermal energies, fuel cells and specially PEMFCs provided significant follow-ups. In other words, the PEMFCs considered the most propitious alternative energy devices among stationary and mobile systems (Saebea et al., 2017). A good deal of research focused upon reducing cost of the ORR through applying Pt while enhancing durability of such systems. On one hand, Pt species supported upon electrically conductive carbon considered as one of the most widely used in PEMFCs. On the other hand, to reach sufficient current densities, high loading weights of Pt utilized to attain appropriate levels of performance (Gasteiger et al., 2005). Pt's high cost led to many efforts made toward using it more effectively for example, alloying it with transition metals (Kim et al., 2004) and developing non-platinum electrocatalysts (Meng and Shen 2006). However, the ORR catalytic activities and long-term stability of these catalysts still were insufficient.

Core-shell nanoparticles considered innovative structures for utilization in PEM fuel cells. This attributed to their remarkable properties including; i) enhanced catalytic activities due to the ligand performances leading to changes in the d-band position hence; improving the charge transfer, ii) providing higher activation energies and iii) possessing better adsorption behaviors in particular; for the ORR (Di Noto and Negro, 2010). In addition, for the Core-Shell materials like Ag@Pt; the shell layer (i.e.; Pt) mainly imposed to and reacted with the gas stream. Therefore, lower amounts of the Pt required. This led to a cost reduction of the PEM fuel cells (Kristian and Wang, 2008). In this direction thus; many researches involved with preparation of the Core-Shell structured catalysts some of which included; Ni@Pt nanoparticles synthesized by a polyol method (Bhlapibul et al., 2012), Cu@Pt structure developed by a partial replacement method (Wei et al., 2008) and Pd@Pt electrocatalyst prepared by electroless deposition (Wongkaew et al., 2016). On the other hand, durability of synthesized

electrocatalyst considered as one of the principal factors for deciding upon an appropriate metal playing the role of the core in this structure. Therefore, based upon possessing similar crystal structure and lattice parameter as that of the Pt species, Silver chosen to be a promising partner for the platinum Core–Shell structure.

In order to boost the performance and promote utilization of the Pt in a core-shell catalyst, support materials needed further investigations. These hinged upon; i) enhancing the availability of catalyst surface area for electron transfer, ii) providing preferable mass transport to the catalyst, iii) promoting transfer of electrons to the current collector and ultimately iv) reflecting the capability of the water transport property of a Core-Shell structure for the cathode side of the PEM fuel cell (Gasteiger et al., 2005). Carbon black, carbon nanotubes (Yu et al., 2012), mesoporous carbon (Shao et al. 2010) and graphene (Şanlı et al., 2016) based materials commonly used as supports for synthesized electrocatalyst. Hence, in the current research, Ag@Pt core-shell nanoparticle (NP) structures dispersed upon different carbon-based supports such as; Graphene Oxide (GO), Multiwall Carbon Nanotubes (MWCNT) and Carbon Black (CB) Vulcan applied to the ORR and utilized in a PEMFC. These synthesized by the ultrasonic treatment method. Moreover, in previous investigations of these authors (Esfandiari et al., 2017) and (Esfandiari et al., 2018) the Ag@Pt Core-Shell electrocatalyst understudied with Ag: Pt mass ratio of 1:3 revealed to possess the largest electrochemical surface area and highest stability amongst all other synthesized Ag: Pt ratios. Thus, this ratio utilized in the present study as well.

2. Materials and method

Carbon base materials including; Carbon Black, MWCNT and GO (each separately) added (under continued stirring) to a mixture of 370 mL of 1 mM aqueous solution of AgNO_3 and 1.6 mL of 38.8 mM aqueous sodium citrate solution (acting as a stabilizer). Then 37 mL of 22.4 mM aqueous NaBH_4 solution added dropwise under rigorous stirring to the flask containing carbon materials till a yellow Ag hydrosol formed. Next, this mixture stirred over night at room temperature to break down the residual NaBH_4 . Carbon supported Ag nanoparticles added to deionized (DI) water and 2-propanol in an ultrasonic bath for 60 min. Then, a 0.03 M of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ dispersed in this suspension at 1:3 mass ratios of Ag: Pt to obtain a total metal loading of 10 wt%, under constant stirring and ultrasonic conditions for an hour while a few drops of 1.0 M of NaOH added to adjust the pH of the solution at around 10. Finally, obtained electrocatalyst filtered and washed with DI water and acetone for several times then dried overnight at 80 °C.

The XRD performed using a XPERT MPD Phillips diffractometer with a Co X-ray radiation source. The resulting patterns obtained with a scanning rate of 1 °/min and a step size in the 2θ scan of 0.02° over the range of 10-100°. The morphologies of Ag@Pt electrocatalyst further investigated through HRTEM using a Philips Model CM200. Samples for evaluations prepared by dispersing 0.001 g of nanoparticles in 30.0 mL of ethanol using sonication bath and then dropping on the copper grid. The resultant dried at 80 °C for 12 h under vacuum.

Cyclic voltammetry (CV) measurements made for determination of electrocatalytic activity of the Ag@Pt electrocatalysts with different supports through an EG&G Princeton Applied Research Model 273A instrument. All electrochemical experiments carried out in a well-established three-electrode cell assembled with catalyst ink coated on a glassy carbon (GC) disk (of 0.0314 cm² area) as the working electrode, Platinum wire (of 1.0 cm² area) as the counter electrodes and Ag/AgCl as the reference electrode. As the first step in electrode drawing up, glassy carbon electrode polished with 0.1 µm diamond solution until a mirror finish obtained and the surface of all electrodes cleaned by potential cycling in N₂, purged for 30 min and immersed in de-aerated 0.5 M H₂SO₄ electrolyte solution.

Prepared PEM fuel cells evaluated in single fuel cell tests. MEA prepared initially by spraying method. The catalyst ink gathered with catalyst, 2-propanol: distilled water (1:1 volume ratio), and a 15 wt% Nafion solution. Each MEA consisted of a Nafion®-115 membrane sandwiched between anode and cathode electrodes with the same platinum and Nafion loadings of 0.5 and 0.9 mg/cm², respectively on each electrode. Nafion-115 pre-treated in a boiling 5 vol% H₂O₂ solution for ample time. The resultant washed with DI water and placed in boiling 0.5 M H₂SO₄ solution for ample duration. Finally, this rinsed with DI water. The synthesized catalyst mixed into the Nafion solution and isopropyl alcohol (IPA) to water (2:1 volume ratio) and sonicated for 30 min in order to create a uniform reaction layer. One spread out this onto the Nafion-115 membrane. Ultimately; the MEA assembled with the gas diffusion layer (GDL) for the electrochemical tests in a 6.25 cm² Paxi-tech single fuel cell (Gharibi et al., 2015). Accordingly, both anode and cathode contained platinum loading of 0.5 mg/cm² (MEA-Pt) and Ag@Pt with different supports all with Nafion loadings of 0.9 mg/cm². The electrochemical performance of the MEAs determined by obtaining polarization curves. The current-voltage characteristics of the different MEAs acquired with feeding H₂ and O₂ onto the anode and cathode electrodes, respectively. Measurements made at 80 °C and 1.5 bars as well as 90 % relative humidity (RH).

3. Results and discussion

The HRTEM images of the synthesized electrocatalyst of Ag@Pt supported on rGO, MWCNT and CB displayed in Figures 1 (a), (b) and (c) all at resolution of 10nm. The particle size, morphology and dispersion status of the Ag@Pt NP analysed from these images. These revealed that, the uniform distribution of high number of Ag@Pt nanoparticles upon the supports possessed rather spherical or elliptical shapes. According to these figures, the average diameters of the Ag@Pt nanoparticles dispersed upon different carbonaceous species determined and tabulated in Table.1. One observed that, the smallest size belonged to the rGO base electrocatalyst. Due to this small size and a well distribution of the NPs upon the graphene surfaces as well as good electrical conductivity of this support, the related synthesized material expected to demonstrate good catalytic activity and stability.

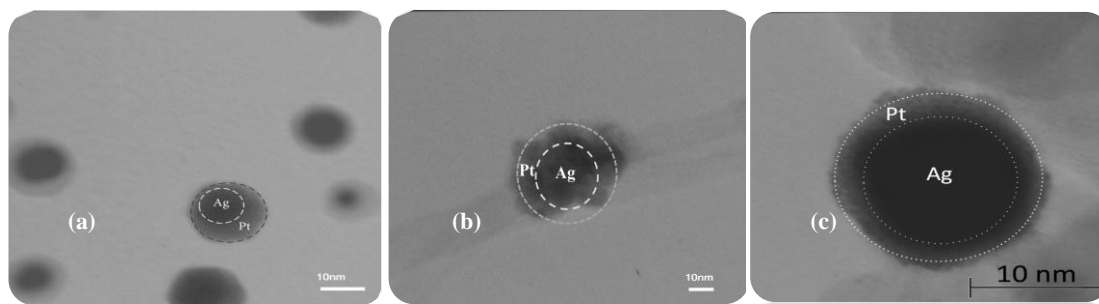


Figure 1: TEM micrographs of Ag@Pt (1:3) prepared on: (a) rGO, (b) MWCNT and (c) CB

The XRD patterns of the prepared samples demonstrated in Figure 2. According to Figure 2 the peak at around $2\theta = 25^\circ$ observed in association with carbon material corresponding to the (002). This peak indicated that the GO successfully reduced to Graphene. For the Pt supported upon carbon materials, the four diffraction peaks at 2θ values of 38.9° , 46.5° , 67.5° and 81.4° were characteristics of the face centered cubic (fcc) lattice of the Pt, attributed to: (111), (200), (220) and (311); respectively. On the other hand, the corresponding Ag peaks at $2\theta = 32.2^\circ$, 46.2° , 67.4° and 76.7° attributed to (111), (200), (220) and (311) respectively indicating the fcc structure of the cubic crystalline planes of Ag did not appear in this XRD spectrum since the surface of this element covered up with the Pt species. The peaks corresponding to the 2θ characteristic diffraction angles for the synthesized electrocatalyst located between those of the Pt and Ag. The 2θ angles significantly shifted to lower and smaller negative values and the crystallinity of Ag was not clear in the Ag@Pt structure. Therefore, the Ag surface in synthesized materials mostly wrapped-up by the Pt species and the Core-Shell structure of nanoparticles formed. The average crystallite size estimated for the diffraction plane of (111) peak provided in Table 1. Lattice parameter (a_{fcc}) values calculated for the synthesized electrocatalysts and the outcomes tabulate in Table 1. These results indicated that, the lattice parameter of the synthesized electrocatalysts was larger than that of the lattice constant of 3.92 \AA of the Pt species alone.

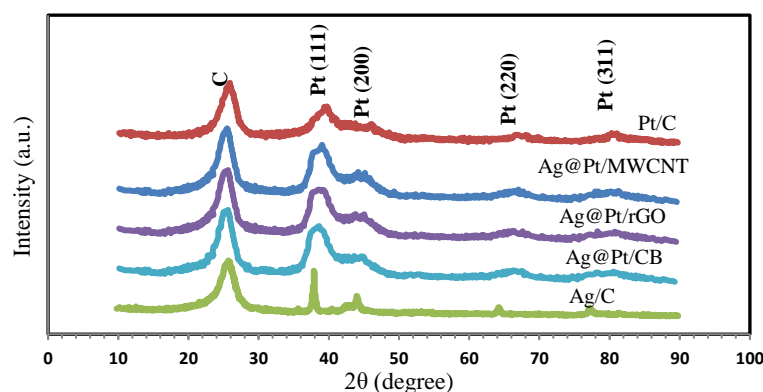


Figure 2: XRD patterns of electrocatalysts with different carbon base supports as well as the commercial Pt/C and Ag/C species.

Table 1: Structural characteristics of differently carbon based electrocatalysts prepared in this research

Electro-catalyst	Particle size (nm), XRD	Particle size (nm), TEM	Lattice parameter (nm)	ECSA ($\text{m}^2/\text{g}_{\text{Pt}}$)
Ag@Pt/rGO	10.3	9.2	0.3938	77.6
Ag@Pt/MWCNT	12.7	13.5	0.3945	71.8
Ag@Pt/CB	13.7	14.1	0.3955	67.8

The Cyclic Voltammetry analyses of prepared electrocatalysts with different supports as well as; a commercial Pt/C (of 10 wt% metal contents purchased from the Electrochem Inc.) performed in a 0.5M H_2SO_4 solution under N_2 atmosphere at 25 °C. Results demonstrated in Fig 3. For the potential range of -0.2 to 1.1 V hydrogen adsorption/desorption peaks of the Pt species acquired at -0.2 to 0 V while oxidation and reduction of the Pt metal obtained at 0.5 to 1.2 V. The electrochemical surface area (ECSA) considered as a significant parameter for the comparison of catalytic activities of different electrocatalysts. Furthermore, a high ECSA value well accepted to be very desirable for a fuel cell catalyst providing high activity. Results of the ECSA determinations for the Ag@Pt materials understudied in this research summarized in Table 1. These indicated that; the ECSA of Ag@Pt/rGO catalyst was 77.6 ($\text{m}^2/\text{g}_{\text{Pt}}$) (due to Ag:Pt of 1:3) taken to be the best Ag:Pt mass ratio prepared in this work. This attributed to the comparatively extended bonding distances and the modified charge transfer from Ag to Pt as well as; more uniformly dispersed particles formed upon the rGO support.

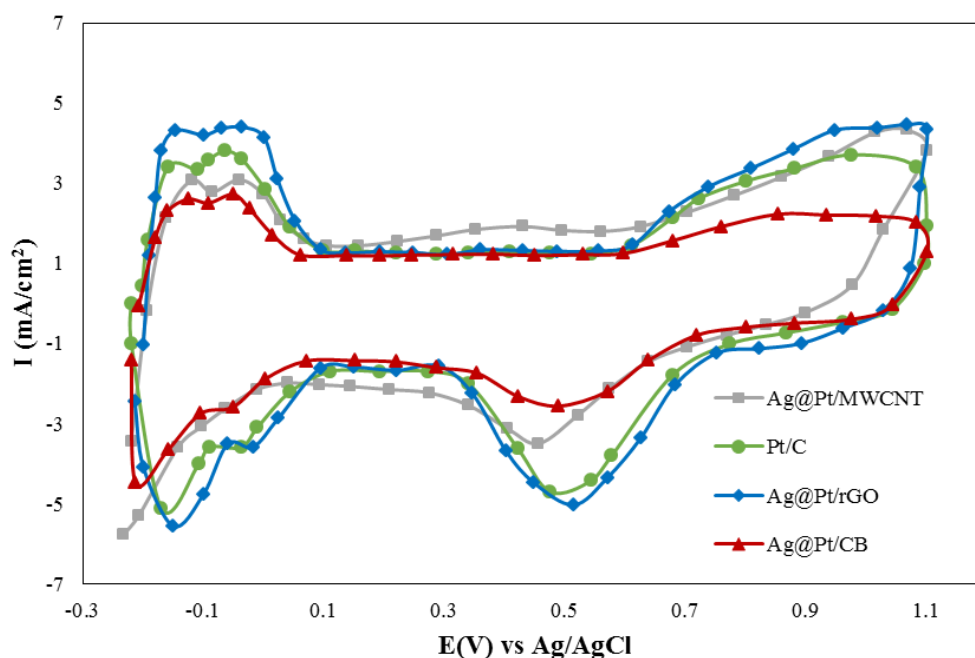


Figure 3: Cyclic voltammograms of electrocatalysts synthesized with different carbon supports

On the other hand, the loss of ECSA led to the performance degradation of PEMFCs. The degradations of the ECSA plotted in Figure 4 normalized with respect to the initial value. One observed from this figure that, the durability of the Pt/C material was considerably lower than that of the Core-Shell structures of Ag@Pt prepared in this work. After 2,000 cycles, only 12.7 % of the initial ECSA of Pt/C remained however; for Core-Shell structured electrocatalysts of reduced Graphene Oxide, MWCNT and Carbon Black Vulcan; 72, 68 and 65 % of the initial ECSA remained after that many cycles. The main reason for this higher stability of synthesized materials was indeed the Core-Shell preparation idea of them. Based upon the differences of the lattice parameters of the core and shell of the synthesized electrocatalysts; an internal stress was engendered into these materials. Furthermore, with the same crystal structure of materials in this study, if the core lattice parameter was larger than that of the shell material the chemical potential of the Pt on the shell side became smaller than that of the virgin Pt and this meant the stability enhanced. Thus, as a major consequence of these results, the Ag@Pt/rGO catalyst represented a higher activity and durability amongst understudied catalysts in this work.

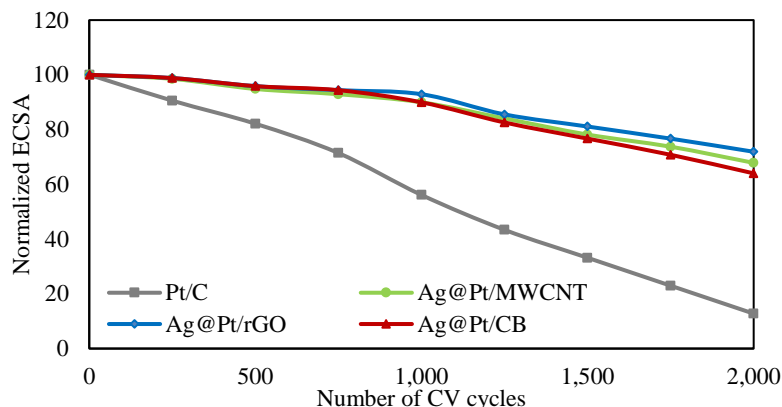


Figure 4: Normalized ECSAs of prepared electrocatalysts with different supports and a commercial Pt/C versus the cycle number

Finally, the single fuel cell test performed upon the prepared Ag@Pt/rGO, Ag@Pt/MWCNT, Ag@Pt/CB and Pt/C as electrocatalysts. For recording the polarization curves, the cell retained at each current density for 5 min. Performance of the commercial Pt/C and synthesized catalysts as a cathode in an actual fuel cell reported in Figure 5. These data represented the polarization and power density curves of these materials under similar conditions as the cell voltage vs. current density (“V-I”) and power density vs. current density (“P-I”) plots of PEMFCs. As shown, the performance of Ag@Pt/rGO was better than other ones and commercial Pt/C. As seen, the MEA-rGO had a better performance over the whole current density region. The maximum established power density of the Core-Shell synthesized electrocatalyst based upon rGO, MWCNT and CB determined as 576.0, 545.2 and 478.9 mW/cm² being 55, 47 and 30 % higher than that of the commercial Pt/C, respectively. Moreover, the catalyst based upon the Graphene Oxide support utilized in this work essentially acted positively towards reducing the fuel crossover through the membrane in the single cell tests performed.

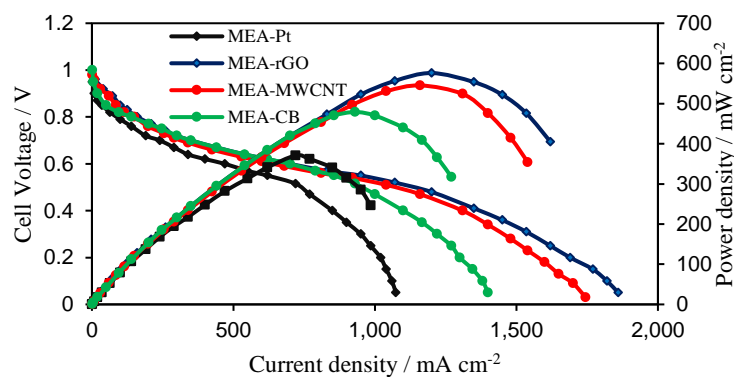


Figure 5: Polarization and power density curves of single PEMFCs with MEA-Pt and prepared electrocatalysts in this work

4. Conclusions

In this research a facile synthesis of well dispersed Ag@Pt Core-Shell NPs supported upon different carbon base supports such as; graphene oxide (GO), multiwall carbon nanotubes (MWCNT) and carbon black Vulcan applied to the ORR in a PEMFC. Initially, silver nanoparticles loaded upon the carbon base by the NaBH₄ as a reducing agent. Then Pt loading upon the surface of silver nanoparticles accomplished ultrasonically. Physical and electrochemical characterization tests and performance evaluation of Core-Shell electrocatalysts for the ORR in a PEM fuel cell performed. The average size of the Ag@Pt nanoparticles was about 9.2-14.1 nm for different synthesized materials. The HRTEM and XRD results revealed and emphasized the Core-Shell structure of the prepared electrocatalysts. According to obtained results, the Ag@Pt/rGO Core-Shell electrocatalyst possessed the largest electrochemical surface area of 77.6 m²/g and highest stability amongst all other synthesized as well as the commercial Pt/C materials. Respected values determined through the CV techniques. Ultimately, the performance of the synthesized materials as a cathode inquired in a PEM single cell

and compared to that of the commercial Pt/C material. The maximum power density of the MEA of the synthesized electrocatalyst with rGO support excelled and revealed to be 55 % higher than that the commercial Pt/C. Finally, it considered a foregone conclusion that, the Ag@Pt/rGO electrocatalyst behaved as a very promising cathode for utilizing in PEM fuel cells.

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