An electrochemical energy conversion realized through Ag@Pt/rGO nano-catalyst enhancing activity of the ORR process in a PEMFC

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Abstract

Core-Shell structures of Ag@Pt nanoparticles (NPs) were dispersed upon reduced graphene oxide (rGO) support containing different Ag:Pt mass ratios synthesized through the ultrasonic treatment method. These were applied to an oxygen reduction reaction (ORR) process in a Proton Exchange Membrane Fuel Cell (PEMFC). The morphology of as-prepared catalysts were characterized through High Resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and induced coupled plasma atomic emission spectroscopy (ICP-OES) analyses. The ORR activities and stabilities of catalysts were studied through electrochemical measurements of Cyclic Voltammetry (CV) and single cell tests, respectively. Results revealed that, the prepared Ag@Pt/rGO catalysts possessed a Core-Shell nanostructure and the one with the Ag:Pt mass ratio of 1:3 displayed the largest electrochemical surface area of 77.6 m² g⁻¹. Moreover, this material provided the highest stability compared to other synthesized electrodes containing different Ag:Pt mass ratios as well as; the obtained commercial Pt/C electrode. The maximum power density for the MEA prepared with this electrocatalyst determined to be 55% higher than that of the commercial Pt/C evaluated through single cell techniques. Thus, the understudied material seemed to be a very promising cathode for being utilized in PEM fuel cells.
**Keywords:** Core-Shell; Electrocatalyst; Oxygen Reduction; PEMFC; Reduced Graphene Oxide

1 Introduction

In order to obtain a clean and environmentally-friendly power source, PEMFCs contemplated as the promoted versus other green devices, due to their advantages of possessing: i) a low working temperature of 80°C, ii) a good energy efficiency, iii) a high power density per unit volume, iv) immobilized electrolyte as well as; vi) near zero emission [1–5]. In light of the increased demands towards commercialization of PEM fuel cells, considerable attention was focused upon decreasing the cost while increasing the durability of such systems [5]. Platinum supported on electrically conductive carbon was the most widespread electrocatalyst used in such devices. Nevertheless, to reach sufficient current densities in particular; for sluggish reaction kinetics of oxygen reduction reaction (ORR) at the cathode side, high loadings of Pt were utilized to reach appropriate levels of performance [6–9]. Meanwhile; Pt’s high cost led to many efforts made towards using it more effectively for example; alloying Platinum with transition metals [10–14] or employing its synergetic chemical coupling with co-catalysts or support [15]. Nonetheless, the catalytic activities and long term stabilities of these materials used for the ORR taking place through the PEM fuel cells were still insufficient [16,17]. Core-Shell nanoparticles on the other hand are considered innovative structures in which the Pt species (i.e.; as the shell part) represented a more efficient material (compared to that of the core one) for the PEM fuel cells. Such electrode structures provided remarkable properties when utilized in the aforementioned fuel cells. These included; i) enhanced catalytic activities attributed to the ligand performances leading to changes in the d-band position hence; improving the charge transfer, ii) providing higher activation energies, iii) possessing better adsorption behaviors in particular; for the oxygen reduction reaction and iv) consuming lower amounts of the Pt leading to the overall cost reductions [18–28]. It was noteworthy to mention
that, in such oxygen reduction reactions the catalysis occurred as a surface phenomenon [29]. Furthermore, the Pt might have interacted electronically with the metal core increasing the activity and durability of this material for the ORR. This would have taken place, through reducing of the Pt–Pt bond distance at the interface and near-interface layers of the core as well as the Pt shell. This attributed to enhancement of the Pt’s 3d-orbital vacancies [30,31]. In this venue therefore; many researches involved with preparation of the Core-Shell structured catalysts some of which included; Co@Pt structure prepared by reduction method and subsequent electroless deposition [32], Ru@Pt structure [33] and Pd@Pt electrocatalysts prepared by a replacement and electroless deposition [34].

On the other hands, 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 the Pt species, silver was decided to be a promising metal for platinum core–shell structure. In other words, in view of the facts that; the Ag was a transition metal possessing face-centered cubic (fcc) crystals and had a lattice spacing being a little bit larger than that of the platinum[35], it was selected. Furthermore, these similarities in the lattice spacing paved down the road for growth of the Pt (shell) upon the Ag (core) [36,37]. In the past few years thus; Ag@Pt core–shell structures were investigated in PEMFCs [38–40]. Yu et al. [38] applied the Ag@Pt core–shell structure with different Ag:Pt mass ratios with total metal loading of 40% supported on multi-wall carbon nanotubes (MWCNT). Their results demonstrated that, the ECSA of Ag@Pt at optimum mass ratio was 70.63 m² g⁻¹. Then, their group upgraded the carbon base MWCNT through adding the MnO₂ to the Ag@Pt/MWCNT electrocatalysts such that, their findings ended up in an optimum activity with the electrochemical area of 85.83 m² g⁻¹. This material possessed a composition of Ag10%@Pt10%/MWCNTs-a-MnO₂ 20% and applied to the ORR[38]. In another research, Koh et al. [40] applied dilute aqueous solution of PtCl₄ (0.1 g L⁻¹) blended with a commercial Ag nanocatalyst with no extra chemical agents added and
set the mass ratio of Pt:Ag at about 1:19 to create a thin monolayer of Pt-shell over the silver nanoparticles followed by sonication. Their results demonstrated a good progress in durability and activity of the electrocatalyst[40].

In addition, one way to enhance the electrochemical (active) surface area (ECSA) per unit mass of an electrode, often involves reducing the size of particles [9] as well as; constructing Core-Shell or hollow structures [10–12]. Other routes include modifying the surface electronic states of the catalysts to tune materials’ catalytic properties and seek enhancement in both activity and durability. Examples of these include alloying with another metal [13,14]. Ultimately, in order to boost the performance and promote utilization of the Pt in a Core-Shell catalyst, support materials with particular capabilities were decided to be investigated. These abilities included; i) enhancing availability of the 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) possessing a suitable capability for the water transport property of a Core-Shell structure towards the cathode side of a PEM fuel cell [41–43]. On the other hand, carbon black are commonly used as a carbon type support for the fuel cell electrocatalysts. Nonetheless, it faced corrosion when coupled in a Core-Shell structure with Pt as the dissolution-aggregation problems were observed by other researchers [44,45]. To resolve this issue, carbon nanotubes [46,47] mesoporous carbon [48], carbon nanofibers [49] and graphene [50,51] were suggested to replace the carbon black. Moreover, in recent years, graphene was recognized as a possible catalyst support due to its high electronic and thermal conductivity, stable physical and mechanical properties and larger surface area compared with other sp2 bonded carbon materials [52,53]. In particular, graphene oxide (GO) was consisted as of sheet-like graphene frameworks with carbonyl (C=O), hydroxyl (-OH), carboxyl (-COOH) and phenol groups. Through a chemical or physical reduction of GO however; it transformed into a graphene-like semi-metal [54]. This made it a rather attractive support for the Pt Core-Shell catalyst utilized in a PEM fuel cell.
To the best of these authors’ knowledge to date there existed no studies demonstrating the graphene support for Ag@Pt Core-Shell structure applied to PEM fuel cells. In this venue, the current research reported a novel nano-catalyst structure, a silver-platinum Core-Shell supported upon the rGO to improve the durability, electrical conductivity and activity of catalyst for the ORR in a PEMFC. For this purpose, a specific Pt:Ag mass ratio was supported upon the rGO utilizing a reducing-agent as well as the ultrasonic treatment method. As the silver nanoparticles were loaded onto the graphene oxide surface, the GO substrate reduced while simultaneously the Ag nanoparticles grew upon it. Then, the Pt nanoparticles loaded upon surface of the rGO already supporting the silver species. Configuration of the Core-Shell structure verified through the HRTEM, XRD, and electrochemical techniques. Moreover; the best performing material in terms of the Pt:Ag mass ratio was determined. This catalyst system investigated from both the activity and stability point of views for an ORR medium taking place in a PEMFC while compared with performance of a commercial Pt/C material.

2 Experimental

2.1 Materials synthesis

2.1.1 Chemicals and reagents

Graphite flakes provided by the Sigma Aldrich Co. while concentrated sulfuric acid (H₂SO₄, 95%), potassium permanganate, hydrochloric acid (HCl), hydrogen peroxide aqueous solution (H₂O₂, 30%), HNO₃, AgNO₃, Sodium Citrate, NaBH₄, H₂PtCl₆.6H₂O, NaOH and 2-propanol were all obtained from the Merck Chemical Inc. (Darmstadt, Germany). These chemicals utilized without further purification. Nafion® 115 membranes from DuPont® was pretreated with hydrogen peroxide, distilled water, and dilute H₂SO₄. In all preparation procedures and analyzes, Deionized (DI) water through a Millipore system (Milli-Q®) was consumed.
2.1.2 Preparation of GO

Graphene oxide (GO) used in this study was synthesized through the Hummers and Offeman’s method [55] in the following manner. Initially, 2 g of graphite flakes and 2 g of NaNO₃ were mixed in 50 mL of H₂SO₄ (98%) in a 1,000 mL volumetric flask. This kept in an ice bath with continuous stirring at 0 to 5°C for 2 h. Then 6 g of potassium permanganate added to this mixture very slowly. The addition rate adjusted to keep the reaction temperature lower than 20°C. Next, the mixture stirred at 35°C until it became brownish. Then it was kept under stirring overnight at room temperature. This was followed by the slow addition of 100 mL of DI water under vigorous stirring at 98°C leading to a change in color to brown. Then solution diluted by adding additional 200 ml of DI water under stirring. Finally, the above resulting mixture treated with 10mL of H₂O₂ to end the reaction indicated through appearance of a yellow color. Next, for purification, the mixture washed through rinsing and centrifugation first with 10% HCl and then DI water several times. After filtrations and dryings took place under vacuum and the graphene oxide (GO) was ultimately generated.

2.1.3 Preparation of rGO Supported Ag Nanoparticles

The reduced GO supported Ag nanoparticles prepared through a colloidal method utilizing the NaBH₄ as a reducing agent. Analogous to Yu et al.’s [38] procedure, the graphene oxide powder functionalized by introducing surface oxide groups onto it. In a typical one, an Ag@Pt/rGO with a nominal Ag:Pt mass ratio of 1:1 (i.e.; the quantity of metal accounted for 10% of the total mass of the electrocatalyst) was prepared. The graphene oxide powder was added to a mixture of 370mL of 1 mM aqueous solution of AgNO₃ and 1.6mL of 38.8mM aqueous sodium citrate solution (which acted as a stabilizer) under continuous stirring. Then 37mL of 22.4mM aqueous NaBH₄ solution was added dropwise under rigorous stirring to the flask containing graphene oxide material till a yellow Ag hydrosol formed. As mentioned earlier, the GO reduced to rGO while Ag nanoparticles were grown simultaneously upon it.
Next, the mixture was stirred over night at room temperature to break down the residual NaBH₄ [38]. Due to presence of oxygen groups on graphene oxide, its surface became active and capable of absorbing Ag⁺. Therefore, the Core-Shell structure formation of the Ag@Pt electrocatalyst was more effortlessly achieved.

### 2.1.4 Preparation of Ag@Pt/rGO electrocatalyst

Ag@Pt electrocatalyst was supported on the synthesized rGO via the ultrasonic method through the following steps. Initially, Reduced GO supported Ag nanoparticles added to DI water and 2-propanol in an ultrasonic bath for 60min. Then a 0.03M solution of H₂PtCl₆·6H₂O was dispersed in this suspension at different mass ratios of Ag:Pt to obtain a total metal loading of 10wt% under constant stirring and ultrasonic conditions. This was performed for an hour while a few drops of a 1.0 M NaOH solution used for adjusting the pH at around 10. Finally, the electrocatalyst filtered and washed with DI water and acetone for several times. This material dried overnight at 80°C.

### 2.2 Physical characterization

Powder X-ray diffraction measurements (XRD) were performed using an XPERT MPD Phillips diffractometer with a Co X-ray radiation source and Ni filter by continuous mode at 40 kV and 30mA. The XRD patterns were obtained with a scanning rate of 1°C min⁻¹ and a step size in the 2θ scan of 0.02° over a range of 10-100°.

For evaluations of the bulk Pt and Ag contents of the synthesized electrocatalysts, Inductively Coupled Plasma (ICP-OES, Varian Vista-PRO, Australia) analysis of the dissolved materials was carried out. In this venue, 5mg of each synthesized material initially dissolved in a mixture of the HCl and HNO₃ in a 3:1 mass ratio and then refluxed at 120°C for 8h. Next, the Pt and Ag atomic ratios determined through the ICP technique using respective standard solutions with an error of around 2–4%.
The morphologies of Ag@Pt/rGO electrocatalyst were further investigated through high resolution-transmission electron microscopy (HRTEM) using a Philips Model CM200. Samples for these evaluations were prepared by dispersing $1.0 \times 10^{-3}$ g of nanoparticles in 30.0mL of ethanol using a sonication bath. Then a few drops of it were placed upon a cupper grid. Finally, this grid was dried at 80°C for 12h under vacuum to have it ready for the HRTEM observations.

### 2.3 Electrochemical characterization

Cyclic voltammetry (CVs) measurements for determination of electrocatalytic activity of the Ag@Pt/rGO material with different mass ratios (of the Ag to Pt) were performed with an EG&G Princeton Applied Research Model 273A instrument. All electrochemical experiments were carried out in a well-established three-electrode cell assembled with the: i) catalyst-ink coated glassy carbon (GC) disk (of 0.0314cm² area) as the working electrode, ii) Platinum wire (of 1.0 cm² area) as the counter electrode and iii) Ag/AgCl as the reference electrode. As a first step in electrode drawing up, the glassy carbon electrode polished with 0.1µm diamond solution until a mirror finish obtained. The surfaces of all electrodes were cleaned by potential cycling in N2, purged for 30min while immersed in de-aerated 0.5M H₂SO₄ electrolyte solution. Next, a 5mg sample of the Ag@Pt/rGO electrocatalyst was added to a 3ml mixture of 2-propanol and DI water. Then it was placed in a sonication bath medium for 20min. Next, 8µL of this catalyst suspension was transferred dropwise onto a GC substrate with 0.1µgPt·cm⁻²-loading and was dried at room temperature overnight. Then, 3µL of 0.05wt.% Nafion® solution introduced onto the Ag@Pt/rGO electrocatalyst layer as an ionomer solution. Cyclic voltammograms procured in 0.5M H₂SO₄ with scan rate of 50mV/s under N2 atmosphere at 25°C. In order to make sure of the quality and durability of the synthesized materials, accelerated durability tests (ADT) were performed. This occurred through applying CV between -0.25 and 1.2V versus the Ag/AgCl reference electrode at a scan rate of 50mV s⁻¹ for
a particular number of cycles. This simulated the environment of the membrane interface at the cathode side.

Next, the linear sweep voltammograms (LSV) and electrochemical Impedance spectroscopy measurement (EIS) were acquired. These were performed through the electrochemical cell which was connected to a potentiostat–galvanostat (EG&G Model 273A) for the I–V polarization measurements as well as; to a frequency response detector (Model 1025) for electrochemical impedance spectroscopy. LSV was performed at a scan rate of 5mV s\(^{-1}\) in the potential range of 1 to \(-0.2\)V vs. the Ag/AgCl reference electrode being cathodic to the equilibrium potential of the oxygen electrode for the ORR measurements. To obtain charge transfer resistance (Rct), electrochemical impedance spectroscopy measurement were developed at 0.5V vs. the Ag/AgCl potential. The AC potential amplitude was 5mV while the frequency range was set at 10 kHz–0.01Hz.

2.4 Fuel Cell Tests

PEM fuel cell performance tests were carried out in a single fuel cell. Membrane electrode assembly (MEA) prepared initially by the spraying method. The prepared catalyst ink contained 2-propanol and distilled water (1:1 volume ratio) and a 15wt% Nafion solution (which was made from the 5% Aldrich’s stock solution). Then the mixture was treated for 20 min under ultrasonication to achieve a uniform dispersion. The resulting material was sprayed directly onto the gas diffusion layer (GDL) according to the following procedure. First, the GDL was prepared from a suspension consisting of 30wt% PTFE (which was prepared from a 6% solution by weight) and 70wt% carbon Vulcan. Hence, the loading in the carbon and PTFE composite was 1 mg cm\(^{-2}\). Next, proper amounts of the PTFE and Vulcan were added into a medium of isopropyl alcohol (IPA) - distilled water solution (in a 2:1 volume ratio) and sonicated for 30min. The suspension was painted onto a porous carbon paper and then was
dried at 80°C for 30 min. The electrodes were heated at 280°C for 30 min to remove the dispersing agent (from the PTFE) and then were sintered at 330°C for 30 min. The DuPont’s Nafion-115 was utilized as the proton electrolyte membrane. It was boiled-up in a 5vol% H₂O₂ solution for 1.5h followed by rinsing and washing in DI water. The resulting material was further boiled in a 0.5M H₂SO₄ for 1.5h followed by being washed with several portions of DI water. The synthesized catalyst mixed into the Nafion solution and a solution of IPA: water (of 2:1 volume ratio) while it was sonicated for 30min at room temperature in order to create a uniform reaction layer. The mixture was spread onto the Nafion-115 membrane and sintered in a furnace at 350°C for 30 min. Ultimately; the MEA was assembled with the GDL for the electrochemical tests in a 6.25cm² Paxi-tech single fuel cell [57]. Accordingly, both anode and cathode contained platinum loadings of 0.5mg cm⁻² (MEA-1) and 1:3 mass ratio of Ag@Pt/rGO (MEA-2) all with Nafion loading of 0.9 mg cm⁻².

The electrochemical performance of the MEAs was determined by obtaining polarization curves. The current-voltage characteristics of different MEAs were acquired with feeding H₂ and O₂ onto the anode and cathode electrodes; respectively. Measurements performed at 80°C and 1.5bars as well as 90% relative humidity (RH).

3 Results and Discussion

3.1 Physical measurements

The composition of the synthesized catalysts and the actual Pt and Ag loadings determined through the ICP-OES of Ag@Pt supported on rGO nanocomposite tabulated in Table 1. These results indicated that, the actual and nominal atomic ratios of the Ag and Pt in the synthesized electrocatalysts were of the same order. This meant that, the Pt and Ag completely deposited upon the rGO.

The HRTEM images of the synthesized electrocatalyst of (1:3) Ag@Pt/rGO displayed in Figures 1 (a) and (b) at low and high magnifications, respectively. The particle size,
morphology and dispersion status of this material further analyzed in these images. It was revealed that, the uniform distribution of high amount of Ag@Pt nanoparticles upon the rGO possessed rather spherical or elliptical shapes. According to this figure, the Ag@Pt nanoparticles for 1:3 ratios formed with particle size diameters in 7.5 to 16 nm range at an average diameter of 9.2 nm. The electrical conductivity of the rGO was determined to be 3.8 $\text{E}^{11}$[S m$^{-1}$]. This was found to be in agreement with works of other researchers [56,58] for such materials. Due to these small sizes and well distribution of nanoparticles on the graphene surfaces as well as, good electrical conductivity of the reduced graphene oxide support, the synthesized electrocatalysts were expected to demonstrate good catalytic activities and stabilities. Moreover, Figure 1b, a high-resolution view of an HRTEM micrograph emphasized the Core-Shell structure of the Ag@Pt nanoparticles synthesized.

The XRD patterns of the prepared Core-Shell catalytic samples as well as the Ag/rGO material (for which the preparation procedure was provided in section 2.1.3 above) were demonstrated in Figure 2. One observed through these patterns that, the synthesized Ag@Pt/rGO catalysts represented polycrystalline Pt diffractions. The most intense peak of the GO was displayed at around 2θ of 11° corresponding to the water bound intercalated oxidized graphite and oxygen functionality groups that made the GO disappeared. Moreover, in this venue, a new peak rose at around 2θ=26° which was observed in the as-prepared graphene supporting NPs. This was associated with carbon material corresponding to the (002) indicating that, the GO successfully reduced to the rGO. 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 observed. These were characteristics of the face-centered cubic (fcc) lattice of the Pt, attributed to the (111), (200), (220) and (311); respectively. In addition, the Ag peaks were displayed at 2θ=32.2°, 46.2°, 67.4° and 76.7°. These were attributed to (111), (200), (220) and (311); respectively. These emphasized the existence of the fcc cubic crystalline planes of the Ag species. Such peaks displayed (be it) rather weakly on the Ag/rGO spectrum in Figure 2.
Hence, the Ag/rGO spectra indicated that, the Ag was indeed present in the current electrocatalytic system. Nonetheless, the provided XRD spectra of the Ag@Pt/rGO did not reveal the existence of the lone Ag species. These were attributed to a couple of factors including the; i) Ag surface was covered up with the Pt species in the Core-Shell structure and ii) Ag’s amount (as depicted in the Ag/rGO spectra) was comparatively minute to that of the Pt material (even at 1:1 ratio of the Ag@Pt catalyst). Thus, the 2θ angles significantly shifted to lower and smaller negative values and crystallinity of the Ag was not distinct through the Ag@Pt supported upon the rGO spectra. In other words, the Ag surface in synthesized materials was mostly wrapped-up by the Pt species while the Core-Shell structure of nanoparticles was formed. The average crystallite size estimated by the Scherrer’s equation [59] for the diffraction peak due to the (111) was determined through the following (Equation 1) relationship:

\[ d = 0.9 \lambda (B_{2\theta} \cos \theta)^{-1} \]  

(Equation 1)

Where d is the average particle size (nm), B_{2\theta} is the full width of the diffraction peak at half maximum in radians of the plane reflection calculated by a Lorentzian function, \( \lambda \) is the X-ray wavelength (1.54 Å for Cu Kα radiation) and \( \theta \) is the angle stand at the position of the peak’s maximum. The average crystallite size of the Ag@Pt catalyst estimated and the results provided in Table 1. According to this table, the mean crystallite size of the Ag@Pt raised as its mass ratio of Pt:Ag was enhanced.

The lattice parameter (\( a_{fcc} \)) values were calculated utilizing the Vegard’s law [60] for the synthesized electrocatalysts and the outcomes were tabulated in Table 1. These results demonstrated that, the lattice parameter of the synthesized electrocatalysts was larger than that of the lattice constant of 3.92 Å of the Pt alone. Moreover, insertion of Ag with the lattice constant of 4.08 Å caused the Pt’s lattice to expand. These results emphasized that, the Ag surface was mostly intricate by the Pt hence, a Core-Shell structure of synthesized
electrocatalyst was created. These outcomes superlatively confirmed the previously discussed XRD and HRTEM results in this paper.

At this point, one needs to distinguish between Core-shell structures as opposed to alloy formations with regards to the prepared electrocatalyst in this research. This is considered as a two-folded concept. First, evidences for verifying a Core-Shell structure are needed. Then a discussion upon the obtained results ought to be followed in order to distinguish between the alloy and Core-Shell structures. To begin with, through the open literature; it is well-accepted that three evidences including the; XRD, HRTEM and lattice parameter evaluations sufficiently may verify the existence of Core-Shell structures [32,39,61,62]. In addition, the most important one of such evaluations is known to be the HRTEM analysis [40]. In this venue, the conclusion drawn through the current research regarding formation of the Core-Shell structure clearly fulfilled all three aforementioned criteria. Then to discuss the observed behavior of the prepared material, one should exercise care to make sure no alloy instead of a Core-Shell structure is formed. In this research, this scientific curiosity was overcome through the following arguments. If an alloyed structure (being an intertwined mixture of the two metals) of Ag and Pt was formed in the current research, its corresponding XRD peaks characterized through the 2θ angles for the synthesized electrocatalyst would have provided two distinct groups of peaks relating to both the Pt and Ag elements or peaks locating between those of alloying species. However, this was not the case in this study. Here no Ag peak observed through the XRD spectrum since this species acted as the core part being placed within the Pt shell. Furthermore, the 2θ peak corresponding to the Pt species slightly shifted to a lower value near the one relating to that of the Pt element. Moreover, as a second rationale towards not having an alloy of Pt-Ag, one’s attention is called to the obtained HRTEM image of the present research. Here, a clear display of two contrasting darker and lighter regions corresponding to Ag and Pt species; respectively are observed. Once again, if the synthesized material was an alloy of the Pt and Ag, all active site spots displayed in the obtained HRTEM
micrograph were dark due to presence of both metallic elements. All these rationales provided and emphasized upon elsewhere in the open literature as well, further supporting the conclusion of formation of Core-Shell [63,64] structure reached at in the present work. Moreover, the carbonyl and carboxylic as oxygenated groups upon the GO surface were in charge of adsorption of Ag ions from the solution through electrostatic interactions and the addition of reducing agent caused reduction of such ions [65,66]. Moreover, the stronger interaction between the Ag and Pt compared with that between either metal and the carbon based surface of the support (i.e.; rGO) as well as; the face centered cubic structure of both Pt and Ag crystallites all were in favor of the growth of Pt on the Ag surface rather than the reverse of it. All these were sufficient rationales for coverage of the Ag nano particles by the Pt hence, formation of a Core–Shell structure in synthesized electrocatalysts [67]. Ultimately, the aforementioned form of structure reasoned-out was mainly accounted responsible for the behaviors displayed in the present research.

3.2 Electrochemical measurements

The electrochemical surface area (ECSA) provided an extent of the number of electrochemically active sites accessible per unit mass of the electrocatalyst [68]. ECSA is calculated through Eq. (2) [19], essentially attributed to the charges of H₂ adsorption/desorption peaks after deducting the charge from the double layer area in cyclic voltammograms (CVs) [69]. In other words;

\[
\text{ECSA}_H (\text{cm}^2 \text{g}_{\text{Pt}}^{-1}) = Q_H (\mu \text{C cm}^2) \cdot (210 (\mu \text{C cm}^2_{\text{Pt}}) \cdot L_{\text{Pt}} (\text{g}_{\text{Pt}} \text{ cm}^2))^{-1}
\]

(Equation 2)

Where \(Q_H\) is the average integrated area depicting the total charge with regards to the hydrogen adsorption/desorption on the Pt surface obtained from the CV method. Moreover, \(L_{\text{Pt}}\) represents the platinum loading on the electrode and the constant value of 210µC cm² is determined by the charge required to oxidize a monolayer of H₂ on a smooth platinum surface [70].
The ECSA is considered as a significantly important parameter for the comparison of activities of different electrocatalysts. Furthermore, a fuel cell catalyst possessing a high activity is believed to have a high ECSA value. It seems worthy of mentioning that, the ECSA is calculated according to the charges of the H$_2$ adsorption/desorption peaks. This parameter evaluation is also based upon the CO$_{ad}$ oxidation charges which was determined in a previously published work of these authors [71]. The results of the ECSA determinations of Ag@Pt materials understudied in this research summarized at Table 2. These indicated that; the ECSA of (1:3) Ag@Pt/rGO catalyst was 77.6 (m$^2$ gPt$^{-1}$) taken to be the best Ag:Pt mass ratio prepared in this work. In other words, it was much larger than that of the commercial Pt/C as well as; being noticeably bigger than those of other synthesized electrocatalysts of different Pt:Ag mass ratios prepared in this research. In addition, as expected the catalytic activity of the Core-Shell structure catalysts prepared was indeed higher than that of the commercial one. This was attributed to the comparatively extended bonding distances and the resulting modified charge transfer behavior from the Ag to Pt as well as; more uniformly dispersed particles which were formed upon the rGO supports.

The cyclic Voltammetry analyses of the prepared electrocatalysts with different mass ratios (of Pt :Ag) as well as; a commercial Pt/C (of 10wt.% metal content purchased from the Electrochem Inc.) and the synthesized Ag/rGO (with 10wt% Ag content) were performed in a 0.5M H$_2$SO$_4$ solution under N$_2$ atmosphere at 25°C. Results demonstrated in Figure 3. For the potential range of -0.2 to 1.1V, hydrogen adsorption/desorption peaks of the Pt species acquired at -0.2 to 0V while oxidation and reduction of the Pt metal obtained at 0.5 to 1.1V. In addition, Figure 3 included a voltammogram of lone Ag/rGO species providing a better background comparison for the materials understudied. Obviously, insertion of the Ag onto the Pt lattice enhanced the extent of the Pt’s active sites exposed towards the hydrogen stream (in the ORR) at the shell part of this structure. Thus, characteristic hydrogen adsorption/desorption peaks of the electrocatalyst’s Core-Shell structure were pronounced. On
the other hand, increasing of the incorporated amounts of the Ag onto the Pt lattice from 2.5 to 5%, transformed the crystalline structure of the Pt as well as lowered availability of the Pt active sites. Consequently, when the Ag content grew; the characteristic hydrogen adsorption/desorption peaks became ill explained. Nonetheless, well-established features of the double layer charging and the Pt oxidation/reduction peaks demonstrated through obtained voltammograms along with the prevalent characteristics of the Pt nanoparticles observed in this research well emphasized the previously revealed results by other researchers [72].

Figure 4 depicted the oxygen reduction reaction (ORR) results in O₂ saturated solution by linear sweep voltammetric (LSV) scans at a rotation rate of 1,600 rpm and a sweep rate of 5mV s⁻¹ in a 0.5 M H₂SO₄ solution. This indeed provided the Ag/rGO as a contrast material better reflecting performance improvement of the ORR due to utilization of the Ag@Pt/rGO nano-catalyst synthesized in this research. This took place in a potential range of 1 to –0.2V vs. the Ag/AgCl reference electrode for different Ag:Pt ratios as well as, the commercial Pt/C electrocatalysts. As is shown in this figure, the electrochemical reaction seemed to be under both kinetic and diffusion control regimes in the range of 0.3–0.7V vs. the Ag/AgCl. Moreover, the diffusion limiting currents were obtained in the potential region below 0.3V. One notices that in comparison to the Pt/C electrocatalyst, the ORR polarization curve of (1:3) Ag@Pt/rGO material exhibited higher onset of the reduction potential. This behavior indicated that, the Core-Shell structure in synthesized electrocatalysts affected activity of the ORR reaction. On the other hand, the limiting current due to the Pt/C electrocatalyst revealed to be 3.84mA cm⁻² (based upon the geometric area) in the ORR. This parameter was enhanced to 5mA cm⁻² for the (1:3) Ag@Pt/rGO material. These values indicated that, the diffusion-limiting currents strongly affected by the Core-Shell structure as well as the supporting materials for the Pt catalyst. Moreover, information provided in Table 2 further emphasized that; the onset of the reduction potential value for the synthesized catalyst of the (1:3) Ag@Pt/rGO shifted 125mV compared to that of the virgin Pt/C material. This was occurred
due to the surface oxide formed followed by its reduction under the aforementioned potential range.

In addition, the enhancement of the open circuit potential of the (1:3) Ag@Pt/rGO catalyst under oxygen-saturated condition compared to that of the virgin commercial Pt/C material was observed. This attributed to the improved oxygen adsorption upon the synthesized electrocatalyst which was also seen by other researchers as well [73]. However, the stronger adsorption energy of the oxygenated Pt species upon the surface of the pure Pt (i.e.; the Pt/C) compared to that of the Ag@Pt/rGO catalyst may have led to desorption of the oxygenated Pt species more readily occurring from the Ag@Pt/rGO material [74]. According to Yu et al.’s [39] work on the Ag@Pt Core-Shell structured surface for oxygen electroreduction catalysts, the formed surface complexes were observed to catalyze the reaction through a dominating 4e⁻ reduction pathway from O₂ to water or the 2e⁻ pathway when it was reduced to H₂O₂. Fortunately, the reduction pathway of 4e⁻ is favored for the ORR because of its high catalytic efficiency for the PEMFC and the onset values of the electrode potentials for catalyzing the oxygen reduction demonstrated in this study. This was attributed to such surfaces being much more positive when the Core-Shell materials was utilized versus a lone Pt species. Hence, incorporating such positive catalytic surfaces as fuel cell cathodes is indeed recommended.

For a quantitative analysis of the catalyzed ORR by the synthesized electrocatalysts developed in this work, the kinetic current (J_k) was calculated from the measured current (J) and diffusion limited current (J_d) on a rotating disc electrode (RDE). For this purpose, the Koutecky–Levich (K-L) equation [75] was utilized:

\[ J^{-1} = J_k^{-1} + J_d^{-1} \]  

(Equation 3)

Where diffusion limited current, J_d, might be expressed through the following (Equation 4) relationship:

\[ J_d = 0.62 nF D^{0.66} \mu^{-0.16} w^{0.5} \]  

(Equation 4)
In which, \( n \) represents the overall transferred electron number, \( F \) is the Faraday’s constant (96,500 C mol\(^{-1}\)), \( C \) is the saturated concentration of oxygen in 0.5M H\(_2\)SO\(_4\) solution, \( \mu \) is the kinetic viscosity of saturated O\(_2\) electrolyte and \( w \) is the rotation rate. If one utilized Equation (3) and (4) to Plot \( j^{-1}(\text{mA}^{-1}\text{cm}^{2}) \) vs. \( w^{-0.5}(\text{ras}^{-0.5}\text{s}^{-0.5}) \), the overall electron transfer number \( (n) \) for the synthesized materials in the ORR might be determined.

The resulting Koutecky–Levich (K-L) behaviors of all prepared electrocatalysts at 0.3V vs. Ag/AgCl potential and the electron transfer number \( (n) \) in the overall reduction process were tabulated in Table 3. The \( n \) value for the (1:3) Ag@Pt/rGO electrocatalyst possessed a higher number compared with other synthesized mass ratios of the Ag@Pt catalysts as well as the commercial Pt/C material. This \( n \) value of about 4 emphasized that, the oxygen reduction on the surface of the Core-Shell structure nanoparticles derived the water direct formation via the 4e\(^-\) pathway of Equation (5) [76]:

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O} \quad \text{(Equation 5)}
\]

Moreover, this pathway for the (1:3) Ag@Pt/rGO provided the most efficiently promoted catalytic activity towards the ORR process. Nonetheless, it did not affect a typical ORR mechanism.

Next, the electrochemical impedance spectroscopy (EIS) technique was performed to measure the frequency dependence of the impedance of a PEM fuel cell. This took place through utilizing a small sinusoidal AC potential as a perturbation signal to the cell followed by evaluating the current response. This diagnostic investigation was done in order to obtain a better understanding of the effect of electrochemical behavior of the undertaken system analyzing the electron transfer kinetics hence; assessing the microscopic information about the fuel cell as well as providing a model for the understudied system with an appropriate equivalent circuit (EC). Moreover, this helped determining the electrochemical parameters of the system. The EIS was accomplished for the synthesized electrocatalysts and commercial Pt/C at a frequency range from 10 kHz to 0.01Hz. The \textit{in-situ} AC impedance spectra of a
PEM fuel cell was operated at the room temperature and ambient pressure of different synthesized catalysts at 0.5V vs. the Ag/AgCl electrode shown in Figure 5. There were two semicircles observed on these spectra. One at a high-frequency domain and the other at a low frequency one similar to what previously presented in another research for a PEM fuel cell [77]. These figures revealed that, based upon employing the Luggin capillary technique, the Ohmic resistance of the fuel cell was determined by the intercept of the high-frequency domain on the real axis. Nonetheless, this effect was insignificant compared to that of the charge-transfer ($R_{ct}$) indicated through the arc diameter. Moreover, the first semicircle demonstrated the fuel cell reaction kinetics supplied to the cathodic ORR processes while the second one represented the mass transfer process contributing to the diffusion of oxygen to the Pt active surfaces within the catalyst layers. Furthermore, all the Nyquist plots of the impedance spectra had nearly similar semi-circular shapes with different arc diameters. In addition, the proposed equivalent circuit was utilized to simulate the impedance data inserted in Figure 5. In this circuit, R is representing the high-frequency Ohmic resistance. In addition, due to the porous nature of the utilized electrodes, the double-layer capacitance was distributed between the Ohmic and Faradic processes while expressed as the constant-phase elements (CPE) in this equivalent circuit model [78]. $R_{ct}$ was the charge transfer resistance and the sum of the charge transfer- and diffusion- resistances provided the polarization resistance. The determined charge transfer resistances ($R_{ct}$) extracted by fitting the EIS plots using the Z-view software and summarized in Table 2. It was observed that, the $R_{ct}$ values increased in the order of (1:3), (1:9) and (1:1) Ag@Pt/rGO material being in good agreement with the CV analysis provided earlier in this paper. As shown in Table 2, the $R_{ct}$ value of the (1:3) Ag@Pt/rGO electrocatalyst was found to be the lowest and the resistance for the (1:1) Ag@Pt/rGO was too high in comparison with other Ag:Pt mass ratio electrodes synthesized in this work. When the amount of Ag increased from 1 to 2.5%, the $R_{ct}$ was enhanced however; further increment to about 5% in the catalyst caused the $R_{ct}$ to reduce significantly. Moreover,
the impedance arc diameter of the (1:3) Ag@Pt/rGO material was smaller than others; indicating a higher electrocatalytic activity for this electrode [3,71]. Thus, the experimentally determined best ratio of the Ag:Pt in this research was 1:3 also confirmed by other analyses such as the CV and LSV data provided earlier above.

On the other hand, the ECSA is considered to be an essential factor for characterizing a PEMFC catalyst undergoing an accelerated durability tests (ADT). As previously mentioned above, larger ECSA meant availability of more active sites for catalysis and the loss of ECSA led to the performance degradation of the PEMFCs[40]. For this purpose, the cyclic voltammetry performed in the potential range of -0.25 to 1.1V at the scan rate of 50mVs⁻¹ in N₂ purged 0.5M H₂SO₄ solution at the room temperature [79]. The degradations of the ECSA plotted in Figure 6 was normalized with respect to the initial amounts in a similar manner to previous studies performed [79,80]. Upon enhancement of the number of cycles as expected, the ECSA of the Pt/C and Ag@Pt/rGO catalysts was reduced. More importantly, one observed from this figure that, the durability of the commercial Pt/C material was considerably lower than that of the Core-Shell structure of Ag@Pt/rGO prepared in this work. In other words, after 2,000 cycles, only 12.7% of the initial ECSA of the Pt/C was remained whereas; for the prepared Core-Shell structured electrocatalysts of (1:3), (1:9) and (1:1) Ag@Pt/rGO; 72, 54 and 32% of the initial ECSA remained after that many cycles. It was also evident that, the commercial Pt/C electrocatalyst had a lower stability than the synthesized Core-Shell structured materials. This was due to a significant reduction of the Pt’s active surface area by the dissolution, aggregation and perhaps sintering of the Pt nanoparticles occurred. The main reason for this higher stability of prepared materials was indeed the Core-Shell preparation idea of them. Based upon the differences of the lattice parameters of the core and the shell (discussed above), an internal stress engendered into these materials. Furthermore, utilizing the same crystal structure of materials undertaken in this study, if the core lattice parameter was larger than that of the shell one, the chemical potential of the Pt on
the shell side become smaller than that of the virgin Pt. This meant that, the propensity for the catalyst degradation was reduced. Hence, its stability was enhanced. Thus, a major consequence of these obtained results is that, the (1:3) Ag@Pt/rGO catalyst represented a higher activity and durability amongst understudied materials in this work. This meant that, this catalyst might be considered as a rather auspicious cathode material for the oxygen reduction reaction in PEM fuel cells.

3.3 Performance of catalyst measured in PEM fuel cell tests

The single fuel cell tests were performed upon the prepared (1:3) Ag@Pt/rGO and Pt/C catalysts operated at 80°C and 1.5bars under 90% relative humidity (RH) with feed flow rates of 300ml min⁻¹ for the hydrogen and 500ml min⁻¹ for the pure oxygen. To record the polarization curves, the cell was retained at each current density for 5min [81]. In this venue, performances of the commercial Pt/C (MEA-1) and (1:3) Ag@Pt/rGO (MEA-2) catalysts as cathodes in an actual fuel cell reported. The polarization and power density curves of the MEA-1 and MEA-2 under similar conditions as the V- and P-I plots of PEMFCs were presented in Figure 7. As shown in this figure, due to mass transport limitations at the high current density area, the fuel cell performance rapidly were dropped to 246 and 405 mWcm⁻² for the MEA-1 and MEA-2, respectively. These values meant that, the mass transport losses of the MEA-2 were considerably lower than that of the MEA-1. This was attributed to the higher surface area as well as; better electrical and mechanical properties of the graphene leading to better mass transfer of Oxygen and water compared to that of the commercial Pt/C material. A similar conclusion was reached at by other researchers as well [82].

Once more, it was a foregone conclusion that, the performance of (1:3) Ag@Pt/rGO was better than that of the commercial Pt/C over the whole range of the current density investigated. Moreover, the maximum established power density of the Core-Shell synthesized electrocatalyst was 576 mWcm⁻² being 55% higher than that of the commercial
Pt/C. Furthermore, the open circuit voltage (OCV) of the MEA-2 was considerably higher than that of the MEA-1. In this regard, since the OCV associated with the concentration of fuel present at the cathode side, its higher value stated that a less fuel crossover occurred. Fuel crossover corresponded to diffusion of un-reacted fuel from the anode to the cathode across the Nafion membrane. Such fuel crossover led to major drawbacks in terms of creating a mixed potential effect as well as, poisoning of the Pt electrocatalyst at the cathode. This phenomenon remarkably reduced the cell performance and fuel utilization efficiency. Accordingly, MEA-2 substantially reduced the fuel crossover enhancing the efficiency and stability of the PEMFCs. In addition, the reduced graphene oxide enacting as the catalyst support positively affected the reduction of the fuel crossover across the membrane in the single cell tests undertaken. On the other hand, as demonstrated in Figure 7; the fuel cell performance in the ohmic and concentration resistance regions for the MEA-2 was superior compared to that of the MEA-1. Ultimately, these outcomes further confirmed and emphasized that, the respective electrocatalyst of the MEA-2 might be a propitious candidate as a cathode for the PEM fuel cell applications.

4 Conclusions

In this research, a facile synthesis of well dispersed Ag@Pt core–shell NPs supported upon reduced graphene oxide through ultrasonic treatment method with different Ag:Pt mass ratios were investigated. Initially, silver nanoparticles were decorated upon the graphene oxide utilizing the NaBH₄ as a reducing agent. Then Pt loading upon the surface of silver nanoparticles was accomplished ultrasonically. Next, physical and electrochemical characterization tests and performance evaluations of Ag@Pt/rGO Core-Shell electrocatalyst for the ORR in a PEM fuel cell were undertaken. The average size of the Ag@Pt nanoparticles were about 9.2-10.7nm for different synthesized materials with various mass ratios of Ag:Pt. This size enhanced through increasing amounts of the Ag species. The
HRTEM and XRD results emphasized the Core–Shell structure of the prepared electrocatalyst. According to obtained results determined through the CV techniques, the Ag@Pt/rGO material with Ag:Pt mass ratio of 1:3 possessed largest electrochemical surface area of 77.6m$^2$g$^{-1}$. Moreover, the resulting impedance arc diameter for this mass ratio turned out smaller compared with those of others. This revealed a higher electrocatalytic activity for this electrode determined through the EIS measurements. Furthermore, the Koutecky–Levich’s (K-L) analysis revealed that, the 4e$^-$ transfer pathway for this electrocatalyst provided the most efficiently promoted catalytic activity route towards the ORR process. It is considered noteworthy to mention that; the aforementioned mass ratio possessed the highest stability amongst all other synthesized Ag:Pt mass ratios as well as the commercial Pt/C electrocatalysts.

Ultimately, the performance of the optimal (1:3) Ag@Pt/rGO as a cathode inquired in a PEM single cell and compared to that of a commercial Pt/C material. The maximum power density of the MEA based upon the aforementioned electrocatalyst with Ag:Pt mass ratio of 1:3 was revealed 55% higher than that of the one prepared with a commercial Pt/C. In addition, the higher OCV value resulting from the MEA evaluations in single cell tests for this synthesized species led to less fuel crossover compared to a commercial Pt/C. This emphasized that, the former material performance was superior. Thus, due to all evidences obtained in this research, it seemed logical to conclude that, the (1:3) Ag@Pt/rGO electrocatalyst might be considered a desirable cathode candidate for a PEM fuel cell producing the sought electrochemical energy.

List of Symbols

- d: average particle size / nm
- $B_{2\theta}$: full width of the diffraction peak at half maximum / rad
- $\lambda$: X-ray wavelength / Å
- $\theta$: angle stand at the position / rad
\( a_{\text{fcc}} \) lattice parameter / Å
\( Q_H \) average integrated area / \( \mu \text{C cm}^{-2} \)
\( L_{\text{Pt}} \) platinum loading on the electrode / g Pt cm\(^{-2}\)
\( J_k \) kinetic current / A
\( J \) current / A
\( J_d \) diffusion limited current/ A
\( n \) overall transferred electron number
\( F \) Faraday’s constant
\( C \) saturated concentration of oxygen in 0.5M H\(_2\)SO\(_4\) solution / mol m\(^{-3}\)
\( \mu \) kinetic viscosity of saturated O\(_2\) electrolyte / m\(^2\) s\(^{-1}\)
\( w \) rotation rate / rad s\(^{-1}\)

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Figure 1. HRTEM micrographs of Ag@Pt/rGO (1:3) prepared in this research: (a) low and (b) high magnification

Figure 2. XRD patterns of GO, electrocalatlysts with different Ag:Pt mass ratios prepared in this research and the commercial Pt/C.

Figure 3. Cyclic voltammograms of electrocalatlysts synthesized with different Ag:Pt mass ratios supported on reduced graphene oxide and a commercial Pt/C in 0.5M H₂SO₄ with scan rate of 50mVs⁻¹ under N₂ atmosphere at 25°C

Figure 4. Polarization curves of the prepared electrocalatlysts with different Ag:Pt mass ratios supported on reduced graphene oxide and a Pt/C in oxygen saturated 0.5M H₂SO₄ with sweep rate of 5mVs⁻¹ and rotation speed of 1600rpm at 25°C

Figure 5. EIS Nyquist plots of electrocalatlysts with different prepared Ag:Pt atomic ratios supported on reduced graphene oxide and a commercial Pt/C in oxygen saturated 0.5M H₂SO₄ at 0.5V vs. Ag/AgCl. The frequencies ranged from 10 kHz to 0.01Hz, Schematic
representation of the equivalent circuit for corresponding EIS plots, driven by Z_{view} software for the (1:3) Ag@Pt/rGO was inserted. R_s: electrolyte resistance, R_{ct}: charge transfer resistance and CPE: constant-phase element

Figure 6. Normalized ECSAs of prepared electrocatalysts with different Ag:Pt mass ratios supported on reduced graphene oxide and a commercial Pt/C in 0.5M H_2SO_4 versus the cycle number

Figure 7. Polarization and power density curves of single PEMFCs with MEA-1 and MEA-2 prepared in this work. MEA active area: 6.25 cm^{2}, anode gas flow rate of 300mL min^{-1}, cathode gas flow rate of 500mL min^{-1} and a gas pressure at the back of the electrodes of 1.5atm
Figure 1. At (a) low and (b) high magnifications
Figure 2.
Figure 3.
Figure 4.

![Graph showing electrochemical performance of different catalysts. The x-axis represents E/V vs Ag/AgCl, and the y-axis represents I mA/cm². The graph compares Pt/C, Ag@Pt/rGO (1:9), Ag@Pt/rGO (1:3), and Ag@Pt/rGO (1:1) catalysts.]
Figure 5.
Figure 6.

![Graph showing normalized ECSA versus number of CV cycles for different samples: Pt/C, Ag@Pt/rGO (1:9), Ag@Pt/rGO (1:3), and Ag@Pt/rGO (1:1).]
Figure 7.
Table Captions

Table 1: Structural characteristics of electrocatalysts with different Ag:Pt mass ratios supported on reduced graphene Oxide and the commercial Pt/C determined in this work.

Table 2: Performance data of electrocatalysts with different Ag:Pt mass ratios and commercial Pt/C determined in this research.

Table 3: Koutecky–Levich data from $j^{-1}(\text{mA}^{-1}\text{cm}^2)$ vs. $w^{1/2}(\text{ras}^{-1/2}\text{s}^{1/2})$ of electrocatalyst with different Ag:Pt mass ratios made in this and commercial Pt/C.
### Tables

**Table 1:**

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<th>Particle size /nm, HRTEM</th>
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Table 2:

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