Investigating a New Electrocatalyst for Polymer Electrolyte Membrane Fuel Cells and the Effect of Carbon Additives in the Reaction Layer

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Abstract

In this study gas diffusion electrodes for Oxygen Reduction Reaction (ORR) was prepared for Polymer Electrolyte Membrane Fuel Cells (PEMFCs) using a new electrocatalyst. For this purpose, the Pt/ZnO electrocatalyst was synthesized, and graphite and Vulcan XC-72 was used as the additive in cathode catalyst layer. This approach was designed to investigate the effect of electrical conductivity and surface area in the reaction layer. Electrochemical methods, such as linear sweep voltammetry and impedance analysis, were applied to investigate the actual role of graphite and Vulcan XC-72 in the electrocatalyst and forms a conductive and porous layer, facilitating an efficient mass transport. The network structure of the catalyst layer and its performance depends on the amount of the carbon additives. It was found that the addition of graphite and Vulcan XC-72 into the catalyst layer enhanced the performance at the high current density region, probably due to an increase in the gas diffusion rate. The amount of carbon additives varied from 10 wt.% to 50 wt.% with respect to the weight of the Pt/ZnO catalyst layer used. The Pt/ZnO electrocatalyst by only 10 wt. % addition of Vulcan XC-72 shows much higher reduction current. This suggests an excellent catalytic activity for oxygen reduction in comparison with Pt/ZnO electrocatalyst with graphite additive. Hence Vulcan XC-72 additive acts better than graphite additive due to its high surface area and pore structure.

Keywords: Additive, Catalytic Activity, Electrocatalyst, Gas Diffusion Electrode, Polymer Electrolyte Membrane Fuel Cell

1. Introduction

Nowadays there has been an increasing interest in Polymer Electrolyte Membrane Fuel Cells (PEMFCs) due to their high power density, high efficiency, clean utilization and zero emission¹⁻⁴. The main challenges for their commercialization include the slow kinetics of the Oxygen Reduction Reaction (ORR) on the cathode and the cost of the electro catalyst (Pt) involved⁵⁻¹⁰. For improving cathode performance, one of the best ways is to utilize supported Pt catalysts with a higher surface area for a great dispersion of nano sized catalysts, an appropriate pore structure and strong interaction between the catalyst nanoparticles and the support¹¹. Platinum on carbon (Pt/C) catalysts are commonly used in electro-chemical power sources¹².

Among the various kinds of carbons, graphite with a layered and planar structure is the most stable form of carbon under standard conditions. Graphite is an electric conductor. It can conduct electricity because of the wide electron delocalization within the carbon layers. These valence electrons can move easily to conduct electricity¹³.

Carbon blacks are currently the most frequently used carbon supports, because of their graphite features and mesoporous structures. In the preparation of commercial electrocatalysts and particularly in PMFCs, Vulcan XC-72(R) is routinely used as electrocatalyst support, due to its good agreement between electrical conductivity and high surface area. It has a specific surface area around¹⁴ 250 m² g⁻¹. One major problem in catalyst is carbon corrosion and the existence of platinum on carbon enhances the rate of carbon corrosion^{15–18}; therefore, in this study non-carbon substrate has been used to decrease carbon corrosion. Interactions between the catalyst and the support enhance catalyst efficiency and reduce catalyst loss; furthermore, they control charge transfer. The support can help enhance the catalyst performance, although the kind of support material is very important for specific performance, life and cost of the catalyst as well as the overall fuel cell¹⁶.

Over the past decade, the use of the metal oxides substrate for preparation of fuel cell electro catalyst has been investigated. For instance, TiO_2^{19-23} , SiO_2^{24} , NbO_2^{25} , $\text{SnO}_2^{26,27}$ and $\text{WO}_x^{22,28-31}$ have been studied for preparation cathode catalyst in fuel cell systems and to improve the catalytic activity.

Camacho et al. prepared a series of oxide-carbon composites with TiO_2 , SnO_2 and ZnO oxides and a selective platinum deposition onto the oxide sites to generate Pt/ TiO_2 -C, Pt/ SnO_2 -C and Pt/ZnO-C. They found that the Pt/oxide-carbon materials exhibited higher ORR activity than Pt/C catalyst did³².

In this study the use of ZnO as a substrate has attracted interest because of its important properties. ZnO is a well-known semiconductor material with direct band gap (3.37 ev or 375nm), good transparency and high electron mobility (>100 $cm^2/v.s$). Its critical features including chemical stability towards air, inexpensiveness, relative abundance, excellent electrical properties, the specific morphology (nanorod), higher surface area, (23 m².g⁻¹), and high dispersion in solution³³⁻³⁸ have made ZnO very attractive. Therefore, Pt/ZnO electrocatalyst was prepared as a new electrocatalyst for the ORR in PEMFCs by combined procedures of impregnation and seeding method. Then, because of their properties Vulcan XC-72 and graphite inserted in reaction layer to change surface area and conduction respectively and the effects of different amounts of these additions were studied.

Sang-Min park et al³⁹ added Vapor–Grown Carbon Fiber (VGCF) to the anode of catalyst layer of a Direct Methanol Fuel Cell (DMFC) and the amount of VGCF changed up to 6 wt.%. The electrode with 2 wt. % VGCF loading indicated the best cell performance. Nishicawa et al⁴⁰ suggested novel gas diffusion electrodes for PEMFC. They investigated the impact of carbon black addition in reaction layer and found that Uncatalyzed Carbon Black (U-CB) into cathode catalyst layer improved the performance of electrodes.

In the present study, initially Gas Diffusion Electrodes (GDEs) were fabricated by addition of Vulcan and graphite to reaction layer and then mutual effects of these additions were investigated.

2. Experimental Method

2.1 Synthesis of Nano ZnO Powder

All chemicals were purchased from Merck and utilized as received. The preparation of nano ZnO powder is described below: First, 1.0 mmol Zn $(CH_3COO)_2.2H_2O$ was poured in an agate mortar. Then, 4 mmol NaOH was added to the sample and ground for 60 min at room temperature. Lastly, the white mixture was poured in a beaker and washed fully with de-ionized water and ethanol for numerous times and dried at room temperature³³.

2.2 Electro Catalyst Preparation

At first the 0.00193 MPt solution was prepared by H₂PtCl₂ (Fluka) and then the solution pH was adjusted with 1 M NaOH, as required, to the desired value. The Zinc oxide slurry was obtained by dispersing of 2.26 mg of Zinc oxide in de-ionized water, sonicating for 10 min and mixing approximately 10% (v/v) of the Pt solution with the Zinc oxide slurry and sonicating for 30 min. The seeded electro catalyst was prepared by the reduction of the prior solution with 0.1 M NaBH, separated by centrifugation and dried in an oven. Thereafter, the obtained powder was dispersed in de-ionized water, and sonicated for 30 min. Then the Pt solution (90%) that was remaining was added to the Zinc oxide substrate. To obtain the catalyst powder, the mixture was again reduced with 0.1 M NaBH, The electro catalyst solution washed thoroughly with deionized water, separated by centrifugation and dried in an oven for 7 hours at 110 °C⁴¹.

2.3 Preparation of Gas Diffusion Electrodes

For preparation of the electrode, the carbon paper was used as gas diffusion layer. The catalyst ink was prepared by sonicating an adequate amount of electrocatalyst with 1.0 ml of 2-propanol, 1ml de-ionized water and 30 wt. % of polytetrafluoroethylene (PTFE) solution, at room temperature for 30 min to create a highly dispersed material. After evaporating the solvents, a homogeneous paste was gained which spread homogeneously over the carbon paper (0.64cm²) and dried at 200°c for 60 min. The total loading of Pt was controlled about 0.35 mg cm⁻². This electrode is labeled Pt/ZnO. The electrodes were fabricated at different amounts of Vulcan XC-72 and graphite addition in catalyst layer⁴¹.

2.4 Physical Characterization of Electrocatalyst

XRD is often used to identify what elements a heterogeneous mixture is composed of, the crystalline structure of those elements, as well as the crystallite size or grain size. The X-ray diffraction equipment usually controls the position of the X-ray beam (incident ray) and the position of the detector (reflected ray) and records the observed intensity at the detector. In this way, a plot called a diffractogram is obtained with the angle in 2θ on the x-axis versus intensity which is plotted on the y-axis. The resulting diffractogram can then be compared to diffraction data in a well-known database to determine what species or molecules exist in a sample. With techniques such as Rietveld refinement, the diffractogram can also provide lattice structural information⁴². Through a Cu Ka source radiation in an equinox diffractometer, the X-ray diffractograms were recorded. The diffractometer was run in the step scan mode by a 0.03 step and in the range of 5-118° (2θ) . The high tension generator, Equinox3000 was set at 40 Kv and 30 mA.

2.5 Electrochemical Measurements of Electrocatalyst

The electrochemical experiments were carried out at 27°C with a potentiostat (Zahner). A conventional threeelectrode cell was used in Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS). A platinum electrode was utilized as the counter electrode; an Ag/AgCl electrode was used as the reference electrode. However, all reported potentials are given with respect to Ag/AgCl electrode. The amount of synthesized electrocatalyst powder that was coated on Carbon paper was used as the working electrode. The LSV assessments were conducted in a 0.5 M H_2SO_4 aqueous solution electrolyte saturated with O_2 . The potential range was 0.8 to -0.2 V vs. Ag/AgCl and the scan rate was 1 mV/s.

Electrochemical Impedance Spectroscopy (EIS) is a frequency-domain method that provides a quantitative evaluation of resistance against the ORR. Impedance analysis was studied at 0.5 V vs. Ag/AgCl potential for obtaining electronic resistance. The AC potential amplitude and the frequency range were 10 mV and 10 mHz to 100 KHz, respectively. The Nyquist diagrams were recorded from Impedance analyzer to obtain charge transfer resistance⁴³.

3. Results and Discussion

3.1 XRD Analysis of Pt/ZnO Electrocatalyst

Figure 1 shows the X-ray diffraction pattern of Pt on zinc oxide substrate nano powder. This XRD patterns analysis reveals the characteristic (111), (200), (220) and (311) reflections of face centered cubic crystalline Pt at 2θ values of 39.6°, 46.1°, 67.2° and 81.8°, respectively as reported elsewhere. Main ZnO hexagonal wurtzite structure (JCPDS 36-1451) can be seen in XRD pattern and (100), (002), (101), (102), (110), (103) and (112) reflection of zinc oxide are located at 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, and 68.13°, respectively, as reported in a published article³³. Therefore this analysis confirms that the fabricated product has a high-quality wurtzite ZnO structure⁴⁴.

3.2 Study of Pt/ZnO Electrocatalyst for ORR

In this investigation, ZnO nano powder was employed as the support to deposit platinum by means of a combined procedure of impregnation and seeding. The synthesized Pt/ZnO electrocatalyst was used as the ORR electrocatalyst in PEMFC. The catalytic activity for oxygen reduction was studied in the electrochemical half cell.

3.2.1 E/I Response

The oxygen reduction reaction on the Pt/ZnO catalyst was studied in oxygen-saturated 0.5 M H_2SO_4 solution at a scan rate of 1 mV/s. As can be seen in Figure 2 although the Pt/ZnO electrocatalyst doesn't show high reduction current, zinc oxide nanoparticles can be used

as a substrate for platinum. This is due to the low conductivity of ZnO, because ZnO is a semiconductor.

3.2.2 Electrochemical Impedance Spectroscopy (EIS) Studies of the Pt/ZnO Electrocatalyst

Electrochemical Impedance Spectroscopy (EIS) is a method that provides much more information about the system. Figure 3 shows Nyquist plot of Pt/ZnO electrocatalyst that has a semicircle form. The diameter of this semicircle indicates charge transfer resistance. As can be seen the Pt/ZnO electrocatalyst displays high charge transfer resistance which can be improved by adding carbon to the reaction layer.

3.2.3 Study of ZnO Substrate in Comparison of Carbon

Due to the problem of carbon corrosion, which is endured by all carbon supports, further investigation for noncarbonaceous supports is required. Recently, scientists have focused on nanostructured supports because they faciliate rapid electron transfer with a high electrocatalytic activity¹⁶. The high electron movement, high thermal conductivity, broad and direct band gap, great exciton binding energy, cost-effective, non-toxic and easily available make ZnO suitable for a broad range of devices, involving transparent thin-film transistors, solar cells, photo detectors, light-emitting diodes and laser diodes that work in the blue and ultraviolet areas of the spectrum⁴⁴. It could be assumed that ZnO can act as a good substrate for cathode catalyst in PEMFC.

3.3 Optimization of Pt/ZnO Electrocatalyst Performance at a Range of Graphite Concentration

By changing the substrate from carbon to zinc oxide, efficiency was reduced but it can be optimized by adding a range of graphite concentration.

3.3.1 Kinetics of Oxygen Reduction Reaction

The kinetics of oxygen reduction reaction on the Pt/ ZnO electrocatalyst was studied in oxygen-saturated 0.5 M H_2SO_4 solution and at 27°C in a three electrode cell. The potential was varied from 0.80 to -0.20 V vs Ag/ AgCl, with a scan rate of 1 mV/s. Using the same catalyst loading under the same conditions for: 1) Pt/ZnO, 2) Pt/ZnO+10%G, 3) Pt/ZnO +20%G, 4) Pt/ZnO+30%G, 5) Pt/ZnO+40%G, and 6) Pt/ZnO+50%G electrodes. In accordance with the voltammogram (Figure 4), the oxygen reduction peak began at potential of + 0.56 V vs Ag/ AgCl. Specifically the curve includes three areas. The first area started from +0.8 to +0.56 V vs Ag/AgCl is a kinetics-control area; the current density was not affected by the rate of mass transfer. The second area is an intermediate region of mixed control from +0.56 to -0.20 V vs Ag/AgCl, where the current is partly restricted with mass transport and the kinetics of electron transfer. The last region, which started from -0.20 V vs Ag/AgCl, is a diffusion-controlled area. As shown in Figure 4, the ORR current is increasing with decreasing the potential for all of them. However, the slope of the polarization curves for the electrodes with 40% and 50% graphite was larger than the others. The last current density for the electrode with 50% graphite in reaction layer is 180 mA/cm², whereas for the electrode with no graphite it is 95 mA/cm². The polarization curves show that the efficiency can be increased by adding graphite in the reaction layer which can be ascribed to the high electrical conductivity of graphite. Hence, the best result related to the electrode containing 50% graphite.

3.3.2 Exchange Current Density

Tafel plots in LSV measurements used to determine the exchange current density (i_0) . The values of exchange current density of electrodes in high current density area are listed in Table 1 as can be observed by adding graphite to the reaction layer of gas diffusion electrode; the exchange current density was improved. The highest value was related to the electrode with 50% graphite.

3.3.3 E/I Response

The current densities at 700, 500, 300 mV are shown in Figure 5. 700mV is a measure of the kinetics, while the measure of the ohmic drop is 500mV and 300mV is a measure of the concentration polarization. The electrode with 50% graphite shows better performance and has a good kinetics.

3.3.4 Electrochemical Impedance Spectroscopy (EIS) Studies of the Electrodes

The Nyquist plots of EIS measurements are shown in Figure 6. As can be seen, all plots have a semi-circle form. The diameter of these semi-circles displays the charge transfer resistance indicating catalytic activity for ORR.



Figure 1. XRD patterns of ZnO powder prepared by solid-state reaction at room temperature.



Figure 2. Linear potential sweep curve of ORR on Pt/ZnO electrocatalyst for oxygen reduction in O_2 saturated 0.5 M H₂SO₄ solution at Potential scan rate of 1 mV/s and 27°C.



Figure 3. Nyquist plot of Pt/ZnO electrocatalyst from 100kHz to 10mHz, in O2-saturated 0.5 M H2SO4 solution at 0.5V vs Ag/AgCl electrode and 27°C.



Figure 4. Polarization curves of Pt/ZnO and different electrodes with graphite additive for oxygen reduction recorded in O_2 -saturated 0.5 M H₂SO₄ solution at 27°C, Potential scan rate: 1 mV/s.



Figure 5. Current-voltage curves for Pt/ZnO electrocatalyst with various amounts of graphite additive.



Figure 6. Nyquist diagrams of Pt/ZnO electrocatalyst with various amounts of graphite additive from 100 kHz to 10 mHz, in O2-saturated 0.5 M H2SO4 solution at 0.5V vs Ag/AgCl electrode and 27°C.



Figure 7. Polarization curves of Pt/ZnO and different electrodes with Vulcan XC-72 additive recorded in O_2 -saturated 0.5 M H₂SO₄ solution at 27°C, Potential scan rate: 1 mV/s.



Figure 8. Current-voltage curves for Pt/ZnO electrocatalyst with various amounts of Vulcan XC-72 additive.



Figure 9. Nyquist diagrams of Pt/ZnO electrocatalyst with various amounts of Vulcan XC-72 additive from 100kHz to 10 mHz, in O_2 -saturated 0.5 M H₂SO₄ solution at 0.5V vs Ag/AgCl electrode and 27°C





Figure 10. Comparison of polarization curves between Pt/ZnO, Pt/ZnO+50%G and Pt/ZnO+10%V recorded in O_2 -saturated 0.5 M H₂SO₄ solution at 27°C, Potential scan rate: 1 mV/s.



Figure 11. Comparison of nyquist diagrams between Pt/ZnO+50%G and Pt/ZnO+10%V electrodes from 100kHz to 10 mHz, in O_2 -saturated 0.5 M H₂SO₄ solution at 0.5V vs Ag/AgCl electrode and 27°C.

 Table 1.
 Values of exchange current density and current density of Pt/ZnO electrocatalyst with various amounts of graphite additive

Electrocatalysts	Exchange current density; i ₀ (mA/cm ²)	Current density in 300 mV (mA/cm²)	Current density in 500 mV (mA/cm²)	Current density in 700 mV (mA/cm²)
Pt/zno	20.17	43.3	14	0.9
Pt/zno +10%G	36.53	77.6	40.4	9.65
Pt/zno +20%G	33.78	68.3	34.9	7.47
Pt/zno +30%G	39.21	93.4	50.3	13.7
Pt/zno +40%G	41.35	107	55.3	13.5
Pt/zno +50%G	42.92	109	55.6	13.8

Electrocatalysts	Exchange current density; i ₀ (mA/cm ²)	Current density in 300 mV (mA/cm²)	Current density in 500 mV (mA/cm²)	Current density in 700 mV (mA/cm²)
Pt/ZnO	20.17	43.3	14	0.9
Pt/ZnO +10%V	54.84	130	71.6	20.8
Pt/ZnO+20% V	40.61	118	67	23.5
Pt/ZnO+30% V	52.3	127	67.4	16.6
Pt/ZnO+40% V	37.8	108	58.3	17.4
Pt/ZnO+50% V	47.71	102	53.3	13.6

Table 2.Values of exchange current density and current density of Pt/ZnO electrocatalyst with various amountsof Vulcan XC-72 additive

As shown in Figure 6, however the electrode with no graphite has a high charge transfer resistance, by adding graphite charge transfer resistance decreased and the diameter of semicircles got smaller. Therefore the electrode with 50% graphite has the lowest charge transfer resistance.

3.4 Optimization of Pt/ZnO Electrocatalyst Performance at a Range of Vulcan XC-72 Concentration

After studying graphite addition, Vulcan XC-72 was selected as an additive to the catalyst layer and was investigated for oxygen reduction reaction and 1) Pt/ZnO, 2) Pt/ZnO +10%V, 3) Pt/ZnO +20%V, 4) Pt/ZnO +30%V, 5) Pt/ZnO +40%V, 6) Pt/ZnO +50%V electrodes were prepared.

3.4.1 Kinetics of Oxygen Reduction Reaction

Linear Sweep Voltammetry (LSV) measurements were conducted to investigate the influence of adding Vulcan XC-72 on the oxygen reduction reaction. Figure 7 illustrates polarization plots for ORR of the supported cathode catalysts with a scan rate of 1 mV s⁻¹. As shown in Figure 7, the ORR current is increasing with decreasing the potential for all of them. In the range of kinetics, results are closer together and in the concentration range the results are far from each other. The last current density for the electrode with 10% Vulcan XC-72 is 202 mA/cm² and this electrode displayed the highest current density between the others. As a result, the existence of carbon Vulcan in the reaction layer improves catalytic activity for ORR which could be attributed to high surface area of Vulcan XC-72.

3.4.2 Exchange Current Density

The exchange current density (i_0) of prepared electrodes was obtained from LSV measurements. As listed in Table 2 compared to the cathode catalyst layer without Vulcan XC-72 additive, there is a remarkable increase of exchange current density for the cathode catalyst layer with Vulcan XC-72 additive. Thus, it can be assumed that the pore structure of the reaction layer was considered to vary significantly by the Vulcan XC-72.

3.4.3 E/I Response

Figure 8 illustrates current-voltage curves, as can be seen in the range of kinetics, results are closer together and in the concentration range the results are far from each other. By inserting Vulcan XC-72 in the reaction layer, the current density significantly increased in all three regions in comparison with no Vulcan XC-72 additive in reaction layer.

3.4.4 Electrochemical Impedance Spectroscopy (EIS) Studies of the Electrodes

The Electrochemical Impedance Spectroscopy (EIS) measurement for the samples was conducted to identify charge transfer resistance. Figure 9 illustrates the impedance spectra measured Pt/ZnO electrocatalyst at a range of Vulcan XC-72 concentration. It was found that the electrode with 10% Vulcan XC-72 exhibited the lowest charge transfer resistance. This result confirms the results of LSV measurements. Also, decreasing charge transfer resistance for the electrodes with the amount of Vulcan XC-72 implies that the dissolved oxygen reactant can diffuse onto the Pt catalyst layer.

3.5 Comparison of the Effects of Graphite and Vulcan XC-72 Additive

Two types of carbon were added into the catalyst layer to study the effects of additives on catalyst performance. As shown in Figure 10 both of additives (graphite and Vulcan XC-72) increase catalytic activity of Pt/ZnO electrocatalyst. The Pt/ZnO electrocatalyst with Vulcane XC-72 additive demonstrates much higher reduction current i.e an outstanding catalytic activity for ORR in comparison with Pt/ZnO electrocatalyst with graphite additive. The improved activity of Pt/ZnO with Vulcan XC-72 in the electrochemical half cell may be attributed to the interaction between support, platium and additive which may lead to a significant activity for ORR as compared to that of Pt/ZnO without additive. The EIS of optimum electrodes with graphite and Vulcan XC-72 additives and without additive are shown in Figure 11. As can be seen, by inserting additives, charge transfer resistance was reduced. Therefore, the presence of additive in the reaction layer affected the pore structure and conductivity of catalyst. The diameter of semicircle which related to the Pt/ZnO electrocatalyst with Vulcan XC-72 additive is smaller than the diameter of semicircle which related to the Pt/ZnO electrocatalyst with graphite additive.

Hence, Vulcan XC-72 additive acts better than graphite additive due to its high surface area and pore structure.

4. Conclusion

A comparative study of carbon additives on electrochemical activity improvement of Pt/ZnO electrocatalyst for PEMFC was carried out. The catalyst layer with graphite additive had a better performance than the electrode catalyst layer without graphite additive. This is most likely because of an electrical conductivity of graphite. The catalyst layer with vulcan XC-72 additive showed the greatest performance most likely due to a higher surface area and a greater porosity. It was found that the optimum content of Vulcan XC-72 in the reaction layer of the electrode was 10%. Decreasing charge transfer resistance for the electrode with the amount of Vulcan XC-72 indicates that the existence of the Vulcan influenced the surface area and porosity catalyst layer that provides proton moves easily within the catalyst layer. Therefore, adding Vulcan XC-72 to the catalyst layer enhanced the continuity of electric conducting networks and developed the Pt utilization as a result of its high surface area.

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