

Plasma modified carbon supported Pt and PtRu electrocatalyst materials for PEMFCs

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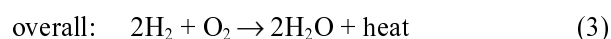
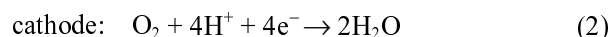
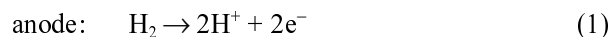
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In this study, Pt and PtRu supported on N₂ plasma treated carbon were prepared by a simple microwave-assisted solution method using ethylene glycol as both a reducing agent and the solvent. The N₂ plasma treatment of the carbon supporter provided C-N and C=N functional groups on the surface of the carbon support which are the active sites for hydrogen oxidation and oxygen reduction reactions. Moreover, by employing microwave heated polyol, Pt and PtRu solutions can be reduced by ethylene glycol and become Pt metal or PtRu alloy on the carbon support. Depending on these procedures and physical and electrochemical characterizations, Pt and PtRu supported on plasma treated carbon were obtained and their catalytic activity studied. X-ray diffraction patterns of the catalysts prepared indicated the crystallographic structure of Pt/C and PtRu/C. TEM images of the catalysts prepared showed the particle size of Pt/C catalysts to be about 1.67 nm and for the PtRu/C catalyst it was about 1.04 nm. The catalysts prepared were homogeneously distributed on the carbon supports. Among the catalysts prepared and commercial Pt catalysts, PtRu catalyst supported on plasma treated carbon showed the highest electrochemical activity.

Key words: Plasma, Pt, PtRu, Electrocatalyst, Carbon.

Introduction

In recent years, there has been a considerable interest in alternative energy sources due to the constant increase in the world petroleum price. Moreover, the pollution that is produced by the consumption of petroleum oil is a consequence effect that needs to be urgently considered. A proton exchange membrane fuel cell (PEMFC) is a power source with various applications such as for a back up power system, a stationary power system, and electrically powered vehicles. PEMFCs were introduced in order to reduce the consumption of petroleum oil and reduce the production of air pollution because a PEMFC is associated with zero emissions. Moreover, a PEMFC is the most appropriate energy source because it may be operated all the time with a supply of fuel. Hydrogen and oxygen gas are used as the fuel of a PEMFC. By feeding hydrogen and oxygen gas with the assistance of appropriate catalysts, the fuel cell can generate energy in an electric form without any air pollution. The reactions at the anode, cathode and overall of a PEMFC are:



The properties of the catalysts play an important role in fuel cell performance. In general, the catalyst is prepared as nanometer size particles of a noble metal such as Pt on a high surface area carbon support. Later on, due to the very high cost of Pt, a Pt alloy was introduced in order to reduce the amount of Pt and to enhance the performance of the catalysts [1, 2]. Carbon-supported materials also play an important role in the catalyst performance. The most commonly used carbon support is Vulcan XC-72 with a BET specific surface area of 250 m²g⁻¹ that was developed for PEMFC catalysts. The carbon support should have an excellent combination of electron conductivity, corrosion resistance, surface properties and low cost for fuel cell commercialization [3]. Therefore, several research groups have been using various carbon supported materials such as carbon nanotubes [4], graphitic carbon nanofibers [5], carbon nanohorns [6], carbon nanocoils [7], ordered uniform porous carbon networks [8], etc. in order to replace the commonly used Vulcan XC-72. However, a promising carbon support that could replace Vulcan XC-72 has not yet been discovered. In this study, plasma surface treatment technology [9] was introduced to treat the surface of carbon

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supports in order to obtain some functional groups on the surface which will decrease the average size and increase the dispersion of small Pt and PtRu particles. Carbon black N115 was selected to be the support material due to its low cost, good conductivity and acceptable high surface area and small particle size. The preparation of catalyst may be done by several methods. An impregnation method [10-14] was conducted by adding an equal volume of Pt solution to the carbon and the solution made alkaline by adding KOH solution to give a uniform distribution and homogeneous dispersion on the carbon support. Then the solution was calcined and pyrolyzed with a reducing gas at various temperatures for various times. A solution method [15] is always used with the basis of adding a reducing agent in order to reduce Pt^{4+} to Pt nanoparticles on the carbon support.

A microwave heated polyol [1, 16-19] which is a simple and convenient technique that can provide the nanosize and good dispersion of Pt and PtRu alloy supported on carbon was selected in this experiment. A microwave radiator was used as the source of energy for initiating the redox reaction and inducing the solvent molecule (ethylene glycol) to reduce Pt^{4+} to Pt and Ru^{3+} to Ru nanoparticles supported on carbon. However, various synthesis parameters can affect the size and dispersion of the supported Pt metal and PtRu alloy on carbon involving the amount of water in the substrate solution, the duration of the sample in the microwave radiator and the position of the sample in the microwave radiator. Furthermore, the good catalytic activity of catalysts depends on the small size (2-6 nm.) and good dispersion of the metal or alloy on the carbon support. Therefore, it is important to prepare catalysts by controlling these parameters to obtain high efficiency Pt/C and PtRu/C fuel cell catalysts.

Experiments

Plasma surface treatment of carbon support

Carbon black N115 (Thai carbon black public CO., LTD.) was pre-washed with 1 M H_2SO_4 to dematerialize the carbon impurities for 24 hours and washed in distilled water to remove the sulfuric acid and other impurities, and dried in an oven at 80 °C overnight. The cleaned carbon was exposed to the N_2 plasma with the following conditions:

Gas type: N_2
Power: 200W.
Pressure: 4.3×10^{-3} torr. (5.73×10^5 μPa)
Flow rate: 9.00sccm.

After being exposed to the N_2 plasma for 4 hours, the carbon supporter was kept dry in a dessicator.

Preparation of catalysts by a microwave radiation method

A microwave radiation method was used to prepare nanoparticle 20%wtPt/Cplasma and 20%wtPtRu/Cplasma with a good particle dispersion on the carbon surface.

The procedure is explained, as follows. First, 0.04 g of plasma-treated carbon was dispersed in 25 ml ethylene glycol (J.T. Baker, 99.9% purity). For the Pt/Cplasma preparations, 5 ml of 1 mM aqueous solution Pt was added and 0.75 ml of 0.05 M Pt solution ($\text{H}_2\text{Cl}_6\text{Pt}$, Sigma) and an equal volume of 0.05 M Ru solution ($\text{RuCl}_3 \cdot \text{XH}_2\text{O}$, Aldrich) were added for the preparation of PtRu/Cplasma catalysts. Then the solution was made alkaline with 0.75 ml of 0.44 M KOH (BDH, 85.0% purity). An hour of high frequency ultrasonic treatment was applied to obtain a good dispersion of carbon in the Pt or PtRu ethylene glycol solution. Then the mixture was put into a microwave radiator (SHARP Model: R-26 PS 800 W.) for 50 s and the resulting mixture was left to cool down to room temperature gradually. The product particles were collected by centrifugation which were then washed by methanol (J.T. Baker, 100.0% purity) and dried in an oven at 80 °C for 24 hours.

Physical characterization of catalysts

The phases and elemental composition of the catalysts prepared were determined by X-ray powder diffraction (XRD, Siemen D500/501, $\text{Cu K}\alpha$ ($\lambda 1.54$) Ni filter, $2\theta = 10$ - 60°). The Pt and PtRu dispersion on the carbon and their particle sizes were also determined using a transmission electron microscope (TEM) (JEOL JEM-2010).

Electrochemical characterization of catalysts

All of the prepared catalysts were electrochemically characterized by a cyclic voltammetry (CV) technique which was performed in a single cell with three different electrodes. A 5 mm dimension glassy carbon disk electrode (CH Instruments, Inc.) was used as the working electrode. Pt wire was used as the counter electrode. A standard Ag/AgCl 3 M KCl electrode was used as the reference electrode. The catalysts prepared were applied to the surface of glassy carbon disk electrodes in the form of a constant drop of ink. The ink was prepared by mixing 10 mg of catalyst with 100 mg of Nafion solution and 0.5 ml of deionized water. Then the mixture was ultrasonically blended for 15 minutes to obtain the ink catalyst. Fifty microlitres of ink catalysts was dropped on the surface of glassy carbon disk electrodes by a micropipette and dried in an oven at 60 °C for 30 minutes. 1 M H_2SO_4 was used as the electrolyte and the cyclic voltammogram was recorded by scanning the potential from 1.20 V to -0.20 V versus Ag/AgCl at a scan rate of 50 mV/s. The tenth cycle of each catalyst was recorded.

Results and Discussions

Physical characterization

The X-ray diffraction patterns of the catalysts prepared are shown in Fig. 1 indicating a typical crystallographic structure of Pt ((111) $2\theta = 39.673$, (200) $2\theta = 46.284$) and Ru ((100) $2\theta = 43.43$) according to JCPDS numbers 04-0802 and 06-0663. The width of the maximum peak indicates the mean particle size of the catalysts, the broader the peak the smaller particle size. As shown in Fig. 1,

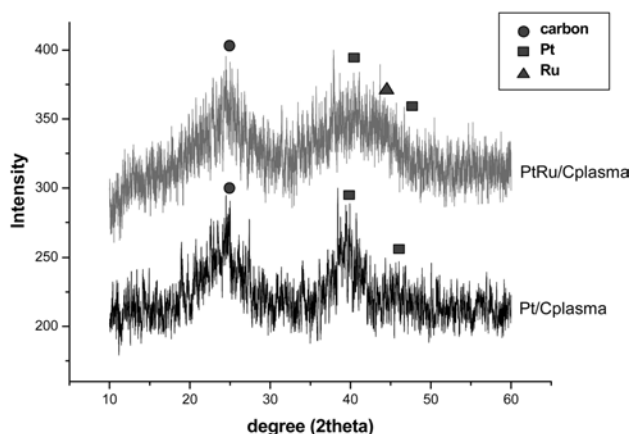


Fig. 1. X-ray diffraction patterns of Pt and PtRu supported on plasma treated carbon.

the PtRu supported on plasma treated carbon showed a broader peak than that from Pt supported on plasma treated carbon. Therefore, the mean particle size of the PtRu supported on plasma treated carbon tended to be smaller than the Pt supported on plasma treated carbon.

An indication of the catalyst particle size is provided by the TEM images. Fig. 2 shows the good dispersion and very small particle sizes of Pt and PtRu supported on plasma treated carbon catalysts compared to the Pt and PtRu supported on carbon catalysts. The reason for this is because the N_2 plasma surface treatment provides C-N and C = N functional groups on the surface of carbon support. These functional groups make partial interactions with the metal to support on each specific site of the

functional groups on the carbon support.

The very small and uniform dispersion in size of Pt and PtRu supported on plasma treated carbon catalysts are illustrated by histograms measured from TEM images as shown in Fig. 3. The mean particle size of the Pt supported on plasma treated carbon was 1.67 nm with a standard deviation of 0.42 while the mean particle size of the PtRu supported on plasma treated carbon was 1.04 nm with a standard deviation of 0.36.

Electrochemical characterization

Pt and PtRu supported on plasma treated carbon and Pt commercial catalysts (Fuel Cell Scientific; PTC-20) were tested by the cyclic voltammetry technique. The results were compared in terms of electrochemical activity in oxidation and reduction reactions. Cyclic voltammograms of Pt supported on plasma treated carbon catalyst, PtRu supported on plasma treated carbon catalyst, and Pt commercial catalysts are shown in Fig. 4. The voltammograms showed similar oxidation and reduction reaction peaks. In these voltammograms, the potential is referred to a Ag/AgCl 3 M KCl reference electrode in the same solution. Following the current starting from 150 to 780 mV is required for the oxygen reduction reaction and the current that flows at -200 mV is required for deposition of H-atoms on the surfaces of the catalysts. After the reversion of potential, Pt-H oxidation began in the region of -200 to 140 mV and around 650 mV is formation region of Pt-OH. The formations of the Pt-H and Pt-OH coverage are [20]:

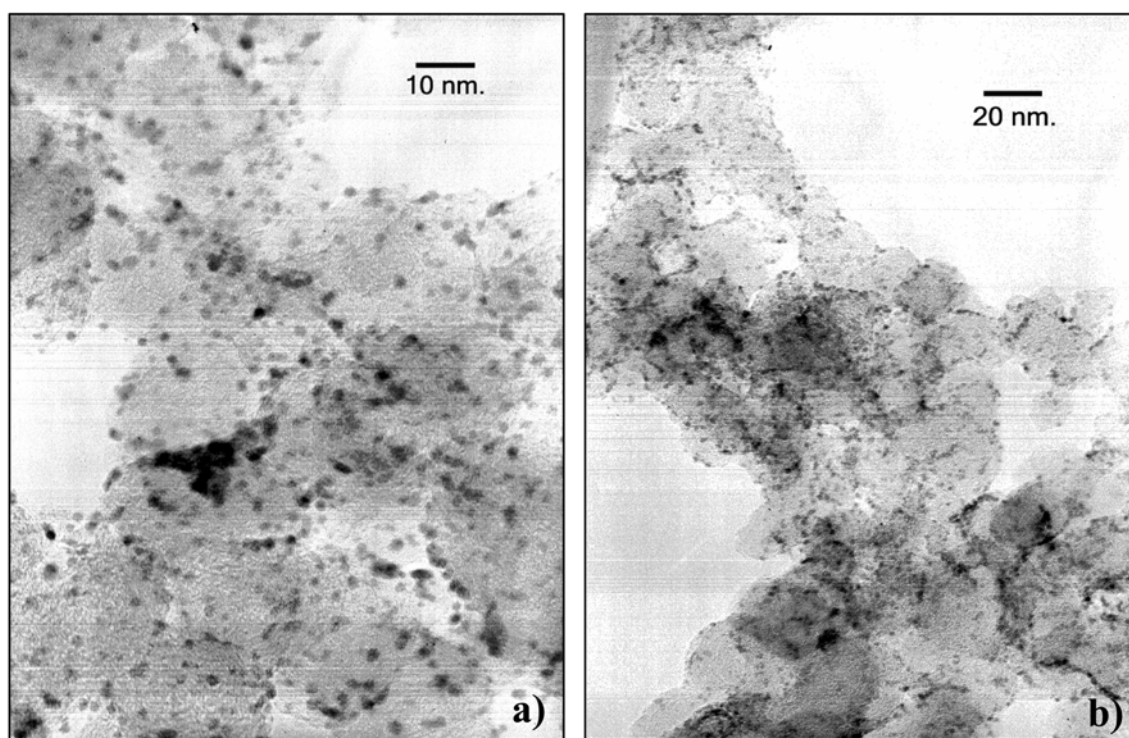
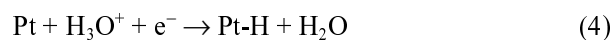


Fig. 2. TEM images of a) Pt/Cplasma and b) PtRu/Cplasma.

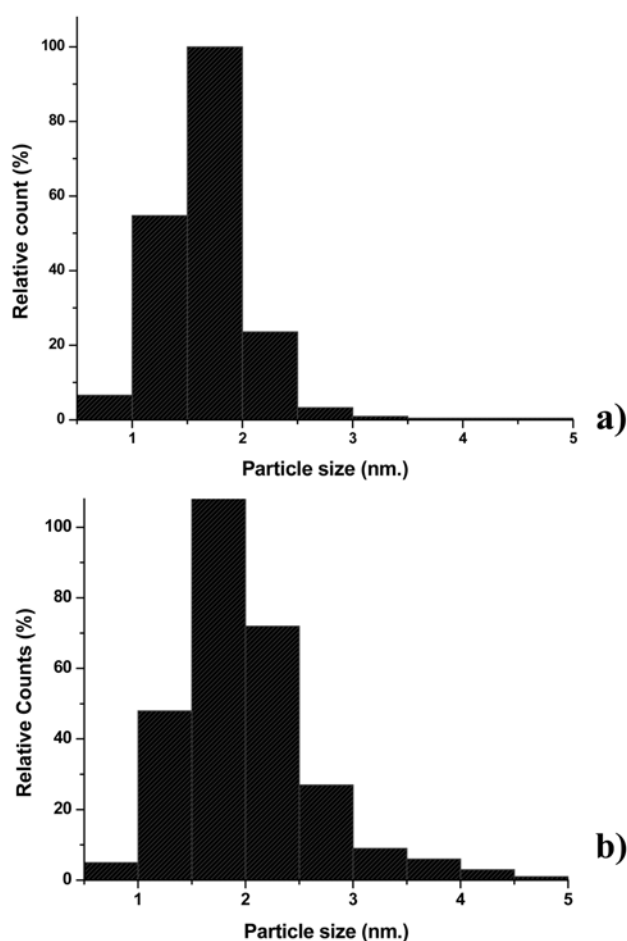


Fig. 3. Histograms of particle size distributions of prepared catalysts; a) Pt/C plasma, and b) PtRu/C plasma.

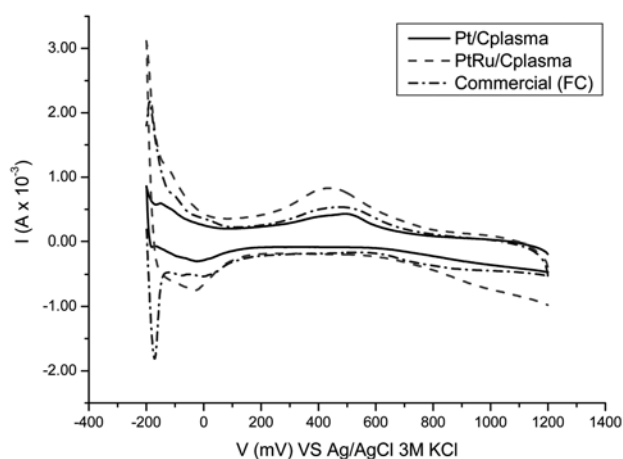
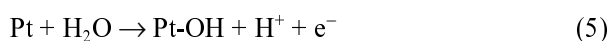


Fig. 4. Cyclic voltammogram of prepared catalysts and Pt commercial catalyst.



The results from cyclic voltammograms of prepared catalysts and the commercial catalyst show that the PtRu catalyst supported on plasma-treated carbon displayed the highest electrochemical activity in both oxidation

and reduction reactions. While the Pt catalyst supported on plasma-treated carbon and the Pt commercial catalyst showed a similarity in electrochemical activity. It may be suggested that the presence of Ru nanoparticles on the carbon support provided a higher catalytic activity in the redox reaction of H^+ and H_2 . Moreover, the plasma treatment provided the C-N and C = N functional groups which were the active sites of the Pt and PtRu catalysts for H_2 oxidation.

Conclusions

Well dispersed Pt and PtRu catalysts supported on plasma-treated carbon with a mean particle size 1.67 nm and 1.04 nm of Pt and PtRu particles, respectively, can be obtained using N_2 plasma treated carbon supports and an assisted microwave radiation method for catalyst preparation. The powder X-ray diffraction patterns of these catalysts indicated the crystallographic structure of the Pt metal and PtRu alloy supported on carbon N115. TEM images showed a uniform dispersion of catalyst nanoparticles on the carbon supports. Moreover, measurements from TEM images confirmed the nanosize of Pt and PtRu particles. Cyclic voltammograms of the prepared catalysts and a Pt commercial catalyst indicated that the PtRu catalyst supported on plasma treated carbon showed the highest electrochemical activity. The presence of PtRu nanoparticles on the N_2 plasma treated carbon which contained C-N and C = N group provided the active sites for hydrogen oxidation and oxygen reduction reactions.

Acknowledgements

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