Evolution and degradation phenomena of electrode for proton exchange membrane fuel cells (PEMFCs)

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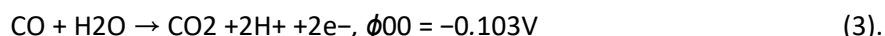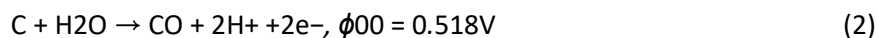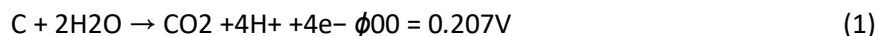
Abstract

Electrode degradation is the main problem of the lifetime for proton exchange membrane fuel cell performance. The operating conditions with different parameters, as high and low flow rates, high and low pressures for hydrogen and oxygen and the aggressive operating which the results show the distribution of the catalyst in the cathode by scanning electron microscopic (SEM) and degradation, especially in the catalyst. This shows the detachment of catalyst from the support as shown by X-ray diffraction (XRD) peaks and transmission electron microscopy (TEM). The XRD showed the decrease in intensity peaks after operating, which increase in the degradation of cathode as crystallinities phases, and increasing the particle size of catalyst from 4.14 to 5.57 nm for more than 100 h operating in a single cell of 25 cm2 with different operating conditions as shown by the TEM.

Keywords: Electrode fabrication, degradation; characterisation.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is one of the most popular types of fuel cell system because of their important characteristics, such as easy to transportation, friendly and zero pollution. Electrodes for PEMFCs are the sites of reactions, where the oxidation and reduction processes occur, which delivered the electrons that produce electrical energy from the chemical reactants. The lifetimes of electrodes depend on the catalyst degradation included the carbon support catalyst, operating conditions, fabrication method, etc., these parameters related to the electrode performance. Therefore, better optimisation for these parameters leads to good performance and a long catalyst lifetime. Catalyst degradation is an important problem that affects the lifetime of PEMFCs. Many researchers have studied the PEMFCs degradation and the lifetimes of the catalysts. Chen, Gasteiger, Hayakawa, Tada and Shao-Horna (2010) reported the degradation of the anode and cathodes in the catalyst layer, especially the active surface area, in addition to a decrease in the thickness of the Nafion® membrane. The electrochemical measurements showed a $\approx 75\%$ Pt surface area loss and a $\approx 40\%$ specific activity loss for a membrane electrode assembly (MEA) cathode with acid-treated Pt_3Co. Furthermore, Co dissolution from acid-treated Pt_xCo particles leads to an increased thickness of the Pt-enriched surface layer, and the development of core/shell Pt_xCo particles was largely responsible for the reduction in the specific activity of the Pt_xCo nanoparticles after potential cycling. The Pt weight loss associated with the formation of Pt crystallites near the cathode/membrane interface contributed significantly to the measured electrochemical surface area loss (Jao, Ke, Chi, Jung & Chan, 2010). The MEA degradation contains three steps in one cycle after the experimental process. The first step is to apply an open circuit voltage for 30 second under 100% R.H. and then to apply 0.6 V for 150 second under 100% R.H. The final step is to apply 0.6 V for 120 second under 0% R.H. The results showed that catalyst degradation is the main reason for the decay in the MEA. After 280 cycles, the MEA begins to exhibit creep deformation due to the R.H. cycle. The electrochemical surface area and the high-frequency resistance were used to estimate approximately the degree of the MEA degradation. Luo, Li, Tang, Pan and Ruan (2006) determined that the decay of the catalyst is more serious than that of PEM, and the Pt nanoparticles exhibited serious physical aggregation after 200 hours without a change in the crystal lattice. The oxygen reduction potential of the Pt/C catalyst considerably decreased from $V = 0.48$ V versus SCE to $V = 0.4$ V. The loss of the Pt particles is more rapid than that of the carbon supports in the catalyst layer, which is most likely due to the fact that the platinum is absent as metal particles when the contact carbon layer has been corroded. Maass, Finster Walder, Frank, Hartmann and Merten (2008) reported that the carbon can react with water vapour to oxidise to CO and CO_2 if the voltage E > 0.207 V, as shown in the following equations:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-\ \phi_{00} = 0.207V \tag{1}$$

$$C + H_2O \rightarrow CO + 2H^+ + 2e^-,\ \phi_{00} = 0.518V \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-,\ \phi_{00} = -0.103V \tag{3}.$$

Moreover, in the presence of platinum, carbon monoxide could not be detected because it is adsorbed onto the metal surface at potentials below 0.55 V. At higher potentials, CO is oxidised to CO_2 according to the reaction: $Pt–CO_{ad} + Pt–OH_{ad} \rightarrow Pt_2 + CO_2 + H^+ + e^-$ (4) (Huang, Tan, Lin & Tan, 2003). Note that the decrease in the Nafion crystallinity depends strongly on the operation conditions, for example, the humidification temperature. With a decrease in the $H_2 = O_2$ humidification temperatures, the intensity of the characteristic XRD peak of the Nafion membrane decays significantly. It is also noted that at low humidification temperatures, the platinum (111) peak remains relatively strong and sharp. All of these results reveal that the humidification temperature can alter the degree of crystallinity of the Nafion® membrane and of the platinum particles. Platinum accelerates the adjustment of the thermodynamic equilibrium of monoxide and dioxide de Carbone, and it also affects the catalyst by water vapour, humidity and the electrode operating conditions. The various pressures ratio of air/H_2, and a flow rate of air/H_2 = 1.2/0.6 L/min at room temperature ($\approx 30°C$), which demonstrated that the increasing pressure ratio of air/hydrogen increased the current density, power density and the

performance of other electrode parameters. The results for an air/H_2 pressure ratio of equal to 3/2, the power density is 35.48 mW/cm^2 and a current density is 99.96 mA/cm^2 compared to the results for the low-pressure ratio (Rachid, Wan Daud, Abdellah & Yarmo, 2015). All these parameters affect the electrode microstructure degradation in terms of the catalyst support and the MEA. This paper studies the electrode evolution as fabrication and degradation of the electrode (cathode) using the scanning electron microscopic (SEM), transmission electron microscopy (TEM) and XRD after operating separately with various operating conditions, such as various air and hydrogen pressures, humidifier temperatures and flow rates of air and hydrogen (Rachid et al., 2015).

2. Experimental

2.1. Electrode fabrication

Carbon cloth 'A' with thickness 350 μm supplied from (E-TEK, Inc.) as the substrate, platinum-supported carbon 20 wt% Pt/C (Fluka, Chemie AG), activated carbon black (Ajax Chemicals, Sydney, Australia), 20 wt% Pt/C Teflon (PTFE) 60 wt% (Aldrich Chemical, Inc.), and 5 wt% Nafion® were used.

The electrode generally consists of three layers, namely, a backing layer (carbon cloth and Teflon), a diffusion layer (carbon black/Teflon) and a catalyst layer (Pt/C/Teflon/Nafion®).

2.2. Catalyst layer

Platinum-supported carbon black, 20 wt% Pt/C and 30 wt% Teflon were used, as reported in a previous work (Chebbi, Beicha, Daud & Zaamouche, 2009), with modification in the heat treatment of the electrode. A homogenous suspension was prepared by mixing and ultrasonication in a beaker containing 20 wt% platinum-supported carbon black and 30 wt% Teflon with isopropyl alcohol and water as the solvents in an appropriate ratio. This mixing requires 30 min at room temperature in an ultrasonicator until a homogenous solution is obtained. Ultrasonication was performed at 15 wt%. The ink was applied onto the diffusion layer (PTFE/C) into two or three microlayers, using a spraying method and casting, and it was then dried at 100°C for one hour to remove the solvents (water and alcohol). Finally, the electrode was baked at 260°C for 1 h in an oven to remove the residual surfactant in the catalyst layer, and it was then sintered at 350°C for 1 h. The loading for the anode and cathode was 0.3 mg$_{Pt}$/cm^2. The second layer for the catalyst layer is an electrolyte layer (Nafion®); this layer was coated using the manual brush method, and the weight of the Nafion® was 0.8–0.9 mg/cm^2.

2.3. Operating cathode in a single cell of 25 cm^2

The MEA is fixed at a 25 cm^2 single cell supply from ElectroChem, equipped with two graphite plates with a ribbed channel for the distribution of reactant gases behind the porous gas-diffusion electrodes, a gasket containing the gas inlet and outlet, and a copper plate used as the current collector from the fuel cell positioned behind each of the graphite plates. The single cell is connected to a GasHub, Ltd., test station, which is equipped with two humidifiers for oxygen and hydrogen that can operate at various humidifier temperatures, and with two flow controllers for hydrogen and air. This test station was connected to the digital voltlab computer to obtain a single cell output voltage versus current density and power density.

3. Results and discussion

The electrode prepared with the loading 0.3 mg$_{Pt}$/cm^2 using 20 wt% Pt/C is passed to SEM analysis to identify the surface of the electrode. Figure 1a shows the gas diffusion layer (GDL) that can observe the distribution of Teflon (PTFE) all over the layer bond with carbon black as binded, and Figure 1b shows the catalyst distribution as sligh particles, with some agglomeration mentioned by yellow circles that

can affect the performance, this layer prepared without Nafion® solution. Figure 2a shows the surface of catalyst layer coated with Nafion® solution, whereas Figure 2b shows the SEM for cross-section MEA.
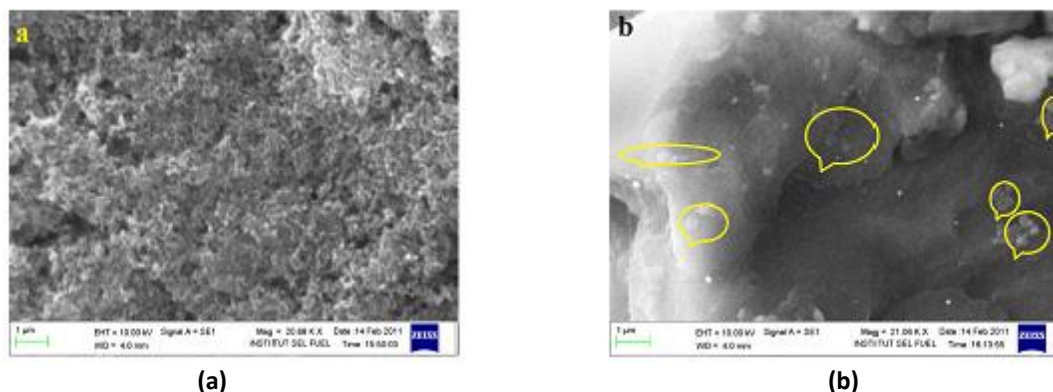

(a)   (b)

Figure 1. (a) SEM GDL. (b) SEM of catalyst layer (Pt/PTFE/C)

The electrode prepared with 0.3 mg_{Pt}/cm^2 was operated in a single cell of 25 cm^2 with aggressive conditions of the parameters, such as pressures, humidifier temperatures and flow rate of air/hydrogen. The values of parameters were measured during the operation and the on/off switch of the single cell.

The electrode prepared with 0.3 mg_{Pt}/cm^2 was operated in a single 25cm^2 cell with various conditions of the parameters such as the humidifier temperature, air/hydrogen pressures and air/hydrogen flow rates. The values of parameters were measured during operation, and the on/off switch of the single cell was connected to the test station.
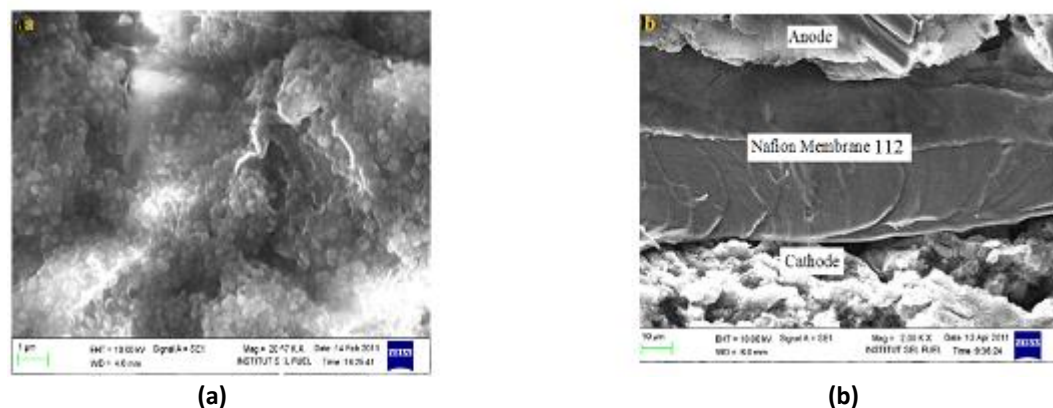

(a)   (b)

Figure 2. (a) SEM of catalyst layer with Nafion solution using brush method. (b) SEM of cross section MEA

3.1. Transmission electron microscopy analysis

TEM is a technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through to provide an image of the specimen for analysis. The change in the catalyst particle size was characterised via TEM and energy dispersive X-ray (EDX) analysis using a Philips CM 120 microscope/EDX analyser equipped with a LaB6 filament. To prepare the sample, a small drop of the solution was placed on a Au grid, and the solvent was evaporated. The cycled catalysts were recovered by ultrasonication of the electrode in ethanol. TEM observations allow the determination of the mean size of the platinum particles and the evaluation of the corrosion and degradation of the catalyst and carbon support. However, great care has to be taken when counting the particles. In our case, only isolated-like particles with sizes less than 6 nm were taken into account; 22

and 12 particles were counted after and before the test, respectively, and were used for statistical analysis. For the determination of the particle size, it was reasonably assumed in a first approximation that platinum particles were spherical in shape. The average particle sizes were calculated using the following equation: $\overline{d} = \sum n_i\, d_i/n$. The electrode before testing (E_{bT}) and the electrode after testing (E_{CaT}) are shown in Figure 3a and b. The Pt nanoparticles, which are visible as darker grey/black dots on a brighter grey carbon background, are all round in shape and exhibit a narrow size distribution. Furthermore, the Pt distribution on the support is very homogeneous before testing (Fig. 3a). The distinctive shapes of the carbon support in Figure 3a and b are completely different as a result of carbon corrosion after testing (operation); the particles in image a are considered fresh, exhibiting little oxidation and agglomeration support. Furthermore, the Pt particles in Figure 3a can appear as concentrated and attached to the carbon, which results in a large surface area for catalysis. Conversely, the Pt after testing (shown in Fig. 3b) contains few Pt particles and few catalyst particles, which can be explained by catalyst detachment (dissolution) from the carbon support and movement towards the membrane electrolyte as well as dissolution of species at high voltages (0.75 V) and under the harsh conditions imposed for the electrode operation (Nguyen & White, 1993).
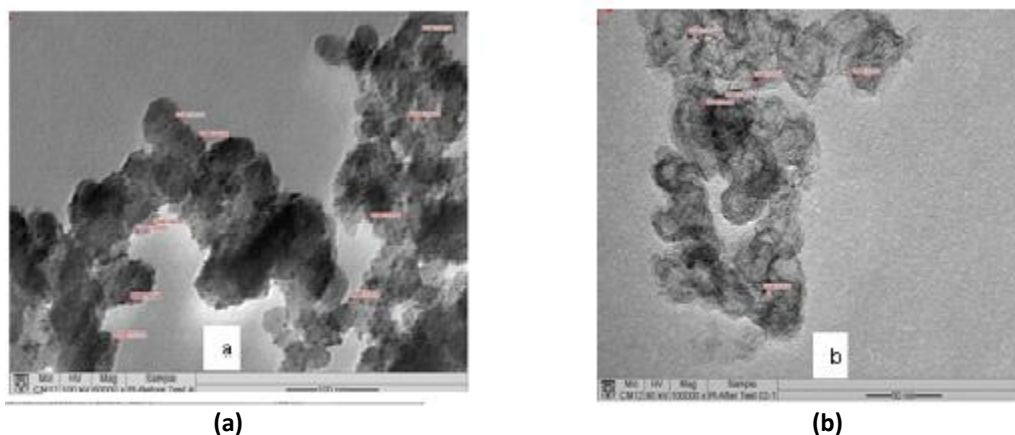
**Figure 3. (a) TEM of the 20 wt% Pt/C electrode before operating E_{bT}.
(b) TEM of the 20 wt% Pt/C electrode after operating E_{Cat}**

The Pt/C catalyst has a mean particle size close to 4.0 nm. The effect of aggressive operating conditions was studied. Clearly, the mean particle size has increased compared to that of the Pt before testing (from 4.14 ± 0.9 to 5.57 nm) for the fresh catalyst with a carbon support compared to the catalyst after operating; see Figure 3b., which is similar to results of Ferreira et al. (2005) who found the increase in sizes from 4.9 to 5.6 nm after electrochemical treatment. The particle sizes change due to changes in the environment during sonication, operation, repeated on/off fuel cell procedures and aggressive conditions such as hot gas due to increasing humidifier temperature and the presence of water in the air gas in the cell; all these parameters result in changes in the particle size of the Pt catalyst and the carbon support.

3.2. X-Ray diffraction analysis

The analysis was performed using Bruker AXS Brand machine Model D8. The anode was used $K\alpha 1$ as a source of energy with wavelength of 1.54060 KV. The scan type 2Th/T starts from 5 and ends by 80, with a step size of 0.025 and timing for one step is 0.1 s. The XRD machine operates with generator 40 Kv, 40 mA, UKM Applied Physics Department, Malaysia. The deconvolution peaks interpretation using a Free software Fitik® is used to deconvolute the diffraction peaks. The functions are used for the deconvolution of Pearson VII-type functions. Bragg's law equation allows the determination of the lattice parameter and the position of the vertex of the diffraction peak. The XRD for Pt/C 20 wt% raw

material powder without any treatment was shown in Figure 4 (peak no. 01). The crystallite size shown the best crystallite size between 35° and 40° (2Ɵ), and the crystallinity phase considers optimal for this structure Pt/C, which the crystallinity size is about 81.3 Å. The second point for this XRD scan, the crystallinity size is in the area 45°–48° (2Ɵ is about 101.1 Å) given by the software, so the crystallinity phase decreases in Pt/C 20 wt% with increasing the crystallinity size from 81.3 to 90 Å for the first scan 2Ɵ = 35°–40°. The second scan points the crystallinity size from 101.1 Å at 2Ɵ = 45°–48° in Pt/C 20 wt% and the raw material powder to 150 Å in E_{Cat}.
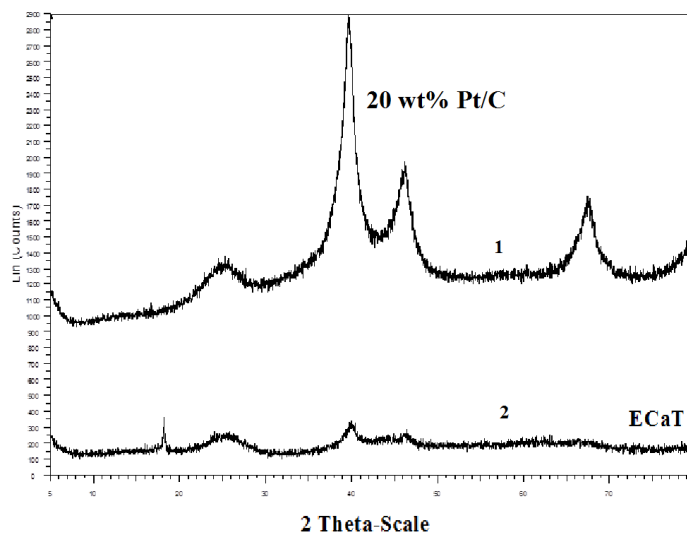

Figure 4. XRD for catalyst 20 wt% Pt/C before operation and catalyst (cathode) after operation E $_{Cat}$ loaded 0.3 mg$_{Pt}$/cm²

The crystallite size decreases as phase crystalline decreases. For catalyst and carbon support, the changes are clear. The crystallinity size decreases from 183.7 Å at 2Ɵ 22°–27° the crystallite size varies from 324 Å in Pt/C 20 wt% to 637 Å Ecat, which increases the amorphous phase and decreases the crystalline phase, which shown the detachment and degradation of the catalyst to the support.

4. Conclusion

Electrode for PEMFC can be efficient with optimising the preparation methods. The SEM analysis shows the better distribution of Teflon (PTFE) all over the layer bond with carbon black as binded and the catalyst distribution as sligh particles located on the front of the layer for better sites reaction. The XRD showed the decrease in intensity peaks after operating the cathode in a single cell of 25 cm², which increase in the degradation of cathode as crystallinities phases. The TEM showed the increase of the particle size from 4.14 to 5.57 nm of Pt and also the detachment from the support. Catalyst along with the dissolution/redeposition and mechanism, the particle sizes of cathode Pt catalysts after test markedly have increased. The size of the cathode catalyst within, utilisation and agglomeration of catalyst are the main factors of the performance decay of PEMFC.

Acknowledgment

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