Performance evaluation of platinum-based catalysts for the development of proton exchange membrane fuel cells

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Platinum-based catalysts are considered the most efficient catalysts for triggering electrochemical reactions in proton exchange membrane (PEM) fuel cells. In the present study, commercial catalysts containing 10% and 30% Pt supported on Vulcan XC-72 carbon were studied to assess their performance in PEM fuel cells. Both catalysts consisted of Pt particles of almost the same size. The utility of these catalysts in PEM fuel cells was studied by finding the real surface area and rate of electro-oxidation of methanol in 0.5 M H_2SO_4 by using cyclic voltammetry. The methanol oxidation reaction was used for characterization of catalysts of PEM fuel cells due to the liquid nature of methanol and the close resemblance of basic electrochemical features of direct methanol fuel cells and PEM fuel cells. Comparison of the data of real surface area and rate of electro-oxidation of methanol showed that 30% Pt catalyst having higher Pt loading is more suitable for PEM fuel cells as compared with 10% Pt catalyst. The PEM fuel cell components were designed and fabricated for testing of membrane electrode assemblies (MEAs). The importance of an additional gas diffusion layer in the form of carbon paper was also emphasized for improving gas diffusion and electrical contact of electrodes of MEAs with the flow field area of monopolar/bipolar plates of PEM fuel cells. The MEAs prepared from 10% and 30% Pt catalysts with Pt loading of 0.5 mg cm^{-2} gave the maximum power density of 119 and 185 mW cm^{-2}, respectively. It was concluded that nanosize carbon supported Pt catalysts having higher Pt loading are more suitable catalysts for preparing high performance MEAs of PEM fuel cells and the cyclic voltammetric data of real surface area and rate of methanol oxidation may be utilized to assess the performance of a given catalyst prior to its use in the preparation of MEAs of PEM fuel cells.

Key Words: Methanol, catalysts, cyclic voltammetry, PEM fuel cell, membrane electrode assembly, gas diffusion layer.

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Introduction

Polymer electrolyte membrane (PEM) fuel cells are costly electrochemical energy conversion devices but they are receiving increasing attention due to their environmentally friendly characteristics.[1−5] The PEM fuel cell produces electricity as long as the fuel (usually hydrogen) and oxidant (usually oxygen) are supplied continuously to the respective anode and cathode. Pure water is the only by-product of PEM fuel cells. The efficiency of energy conversion in PEM fuel cells is dependent on the catalytic activities of the catalysts used in the cathode and anode of membrane electrode assemblies (MEAs). MEAs are considered the heart of PEM fuel cells without which they cannot produce electricity. Nafion® membrane is commonly used as a proton exchange membrane in PEM fuel cells. The most commonly used catalysts in PEM fuel cells are platinum-based metals supported on high surface area carbon.[6−10] Platinum-based catalysts are costly materials and hence it is desired to evaluate their performance by using alternate methods so as to avoid wastage of MEAs. X-ray diffractometry (XRD), transmission electron microscopy (TEM), and cyclic voltammetry are the most common techniques used in this respect.[9−14]

Cyclic voltammetry is a highly versatile electrochemical technique for finding different kinetic parameters of electrochemical systems.[15−21] Oxygen reduction, hydrogen evolution, and methanol oxidation reactions are commonly studied to find the catalytic activities of catalysts.[11,22−25] The cyclic voltammetric study of methanol oxidation reaction is advantageous over other reactions on the basis of the fact that methanol is liquid in nature and hence its handing is easy during electrochemical measurements. Moreover, there is a close resemblance of methanol oxidation in direct methanol fuel cells (DMFCs) and hydrogen oxidation in PEM fuel cells. In both cases, protons are electrochemically generated at the anode and they pass through the proton exchange membrane towards the cathode. Nafion® membrane is commonly used as a proton exchange membrane in both DMFC and PEM fuel cells.[26]

The present study was conducted in connection with the development of a PEM fuel cell. The main objectives were to fabricate PEM fuel cell components and to investigate the comparative performance of commercially available 10% and 30% Pt catalysts supported on Vulcan XC-72 carbon in the PEM fuel cell. Cyclic voltammetry was used to assess the catalysts by finding the real surface area and rate of the methanol oxidation reaction. The fabrication of MEAs and PEM fuel cell components and the effect of an additional gas diffusion layer on the overall performance of the PEM fuel cell are also discussed.

Experimental

Equipment

The model 173 potentiostat/galvanostat equipped with model 179 digital coulometer, model 175 universal programmer, model 178 electrometer probe, and RE 0089 x-y recorder, all from EG&G Princeton Applied Research (PAR), USA, were used for cyclic voltammetric measurements. A Philips X-ray diffractometer was used for finding particle sizes of catalysts. An Ultrasonic Cleaner, Model 08894-26, Cole-Parmer, USA, was used to prepare a homogeneous suspension of catalysts for the preparation of MEAs. The Fortune Presses Model TP 400, Netherlands, was used for hot pressing of MEAs. The Fuel Cell Test Station, PS-DR (^{TM}), ElectroChem, Inc., USA, was used to test the performance of MEAs in the PEM fuel cell using hydrogen as fuel and oxygen as oxidant. The gases were supplied to the PEM fuel cell at a flow rate of 500 cm^3 per minute.

Preparation of working electrodes for cyclic voltammetric measurements

Two different commercial catalysts containing 10% and 30% Pt supported on Vulcan XC-72 carbon were used in the preparation of working electrodes. Since Pt metal is costly and there are numerous well-developed methods for preparation of Pt-based catalysts in the literature,[27−32] as-received commercial catalysts were utilized in the present comparative study. The 10% Pt catalyst was obtained from ElectroChem Inc, USA, while the 30% Pt catalyst was obtained from GasHub Technology Pte Ltd, Singapore. The catalysts were pasted onto the surface of graphite rod (Ø = 1.0 cm) for making the working electrode.[19,24,33] The graphite rod was insulated from the sides using epoxy resin. The 8 mg mL^{-1} suspension of catalyst was prepared in deionized water and 30 μL of the suspension was pipetted out and spread over the tip of the graphite rod followed by the application of 20 μL of Nafion® solution (5 wt.%). The catalyst layer was allowed to dry at room temperature.

Nature of the electrochemical cell

The electrochemical cell consisted of a beaker-type cell equipped with a working electrode, Ag/AgCl (Sat. KCl) as the reference electrode, and Pt-gauze as the counter electrode. As it is customary to quote the electrode potentials with respect to the reversible hydrogen electrode (RHE) for quick reference, all potentials are referred to RHE in the present study. Furthermore, 0.5 M H_2SO_4 was used as a supporting electrolyte. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. All experiments were carried out at room temperature.

Preparation of MEAs of PEM fuel cell

The MEAs were prepared for testing of performances of catalysts in the PEM fuel cell. For this purpose 2.5 mL of suspension containing 0.0833 g of catalyst and 0.71 mL of Nafion solution was prepared in a test tube. The suspension was ultrasonically homogenized to make catalyst slurry. The slurry was applied to one side of the 3.5 × 3.5 cm^2 Teflon® treated Toray carbon papers by using a micropipette and then it was spread over the carbon paper by brushing. The coated electrode was allowed to dry at room temperature. More slurry was applied onto the carbon paper after slight drying of the previous layer. This process was repeated until the desired catalyst loading was achieved on the carbon paper. These catalyst-coated 3.5 × 3.5 cm^2 Teflon® treated Toray carbon papers were used as cathodes and anodes of MEAs.

Nafion® 115 membrane was used as proton exchange membrane in the preparation of MEAs. The 6.5 × 5.5 cm^2 pieces of Nafion® 115 membrane were protonated by treating them successively at 80 °C for 1 h with deionized water, 3% H_2O_2, deionized water, 0.5 M H_2SO_4, and finally soaking in deionized water.[34−36] A transparency sheet was placed on the smooth stainless steel plate and one electrode was placed over it, with the coated surface up, and then Nafion® 115 membrane was placed over it in such a way that the electrode remained at the center of the membrane. The second electrode with the coated surface down was placed over the membrane at the center. A transparency sheet and then the stainless steel plate were placed over the sandwich to prevent the displacement of the electrode during hot pressing. The hot pressing was done at 40 kN for 100 s at 120 °C.

Designing and fabrication of a PEM fuel cell

The PEM fuel cell was designed and fabricated for testing of MEAs. Diagrams of the monopolar plate, back plate, and end plate are shown in Figures 1-3, respectively. Brief descriptions of the monopolar plate, back plate, and end plate are given in the following subsections.
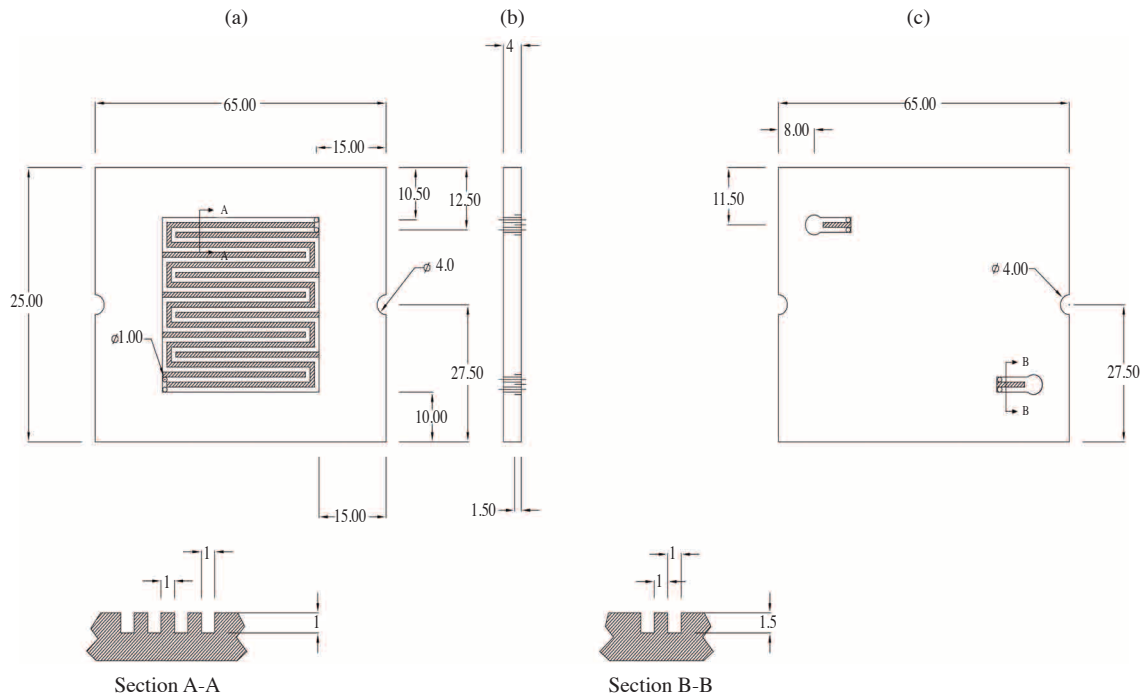
Figure 1. Diagram of monopolar plate: (a) front view (b) side view (c) back view. All dimensions are in mm.
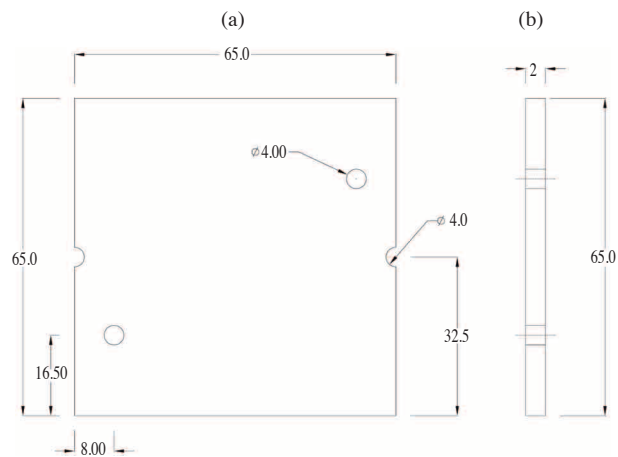
Figure 2. Diagram of back plate of monopolar plate used for hiding the gas entrance and exit channels present on the backside of monopolar plate. All dimensions are in mm.
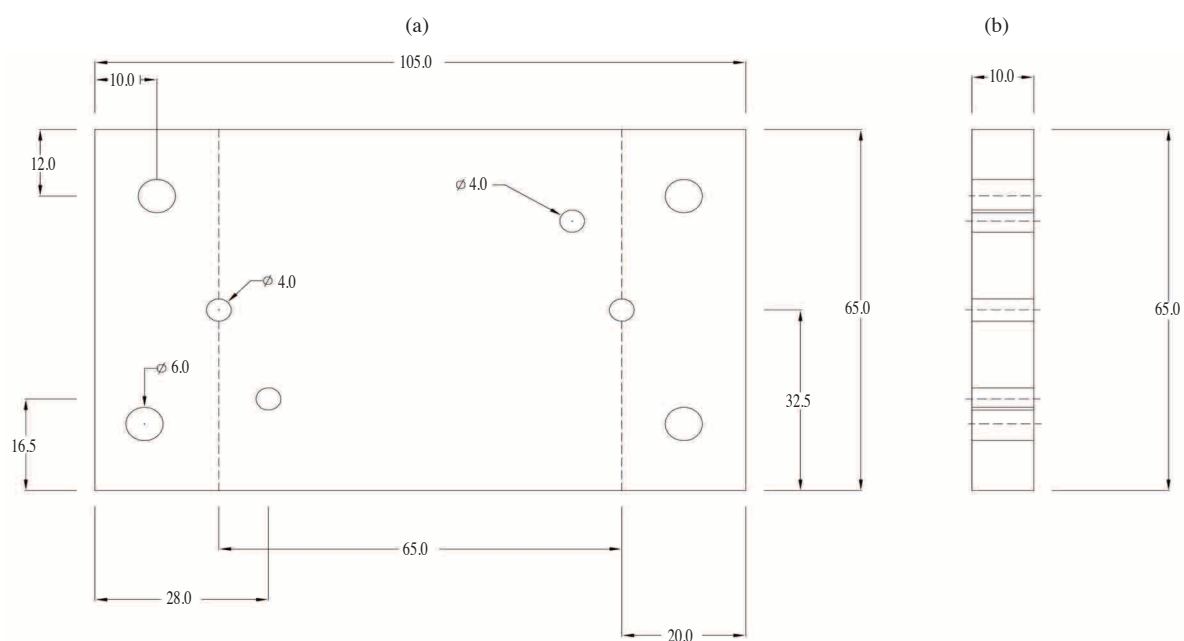
Figure 3. Diagram of end plate: (a) front view (b) side view. All dimensions are in mm.

Monopolar plate

The monopolar plate acts as flow field plate for a single cell PEM fuel cell. It was fabricated from a commercial 4-mm thick graphite plate (FU-4369 grade). The area of the monopolar plate was 65×55 mm^2. The 2 channel serpentine flow field patterns with a total of 18 channels were made on one side of the monopolar plate for effective distribution of reactant gas (hydrogen or oxygen) over the electrode (anode or cathode) of the membrane electrode assembly during operation of the PEM fuel cell. Such flow field configurations are most commonly used for testing of MEAs of small active areas.[1,37] The holes of 1-mm diameter were drilled at the start and end of both channels for the entrance and exit of reactant gases. On the backside of the monopolar plate, 2 channels were made that meet with 4 mm holes (Figure 1). The 4 mm holes on the backside were of 1.5 mm depth.

Back plate for the monopolar plate

A back plate was fabricated to hide the channels present on the backside of the monopolar plate. For this purpose a 2-mm thick graphite plate of 65×65 mm^2 area was used; 4 mm holes at 2 corners of back plate (Figure 2) were made for the entrance and exit of gases. These 2 mm holes exactly match the 4-mm holes on the backside of the monopolar plate. The back plate is attached to the backside of the monopolar plate by using some sort of epoxy and silver paste, for making a complete monopolar plate with hidden channels for the entrance and exit of reactant gases.

End plate

An aluminum plate of 105×65 mm^2 area was used as the end plate. The 4 holes located at the corner of the end plate (Figure 3) are used for tightening of the whole assembly by nuts and bolts. The 2 holes at the corner of the center area of the end plate match the two 4 mm holes on the monopolar and back plate plates. These holes are used for the entrance and exit of reactant gases. The other 2 holes are used for the alignment of PEM fuel cell components during the assembling process.

The assembled PEM fuel cell is shown in Figure 4. Silicon gaskets were used between the MEA and monopolar plate as well as between the monopolar plate and end plate to prevent the leakage of gases. Conducting metal plates made of nickel, copper, gold etc. may be used for current collection but in the present case no special current collectors were used. For current/voltage readings flexible wires were inserted into holes drilled on the sides of each monopolar plate.
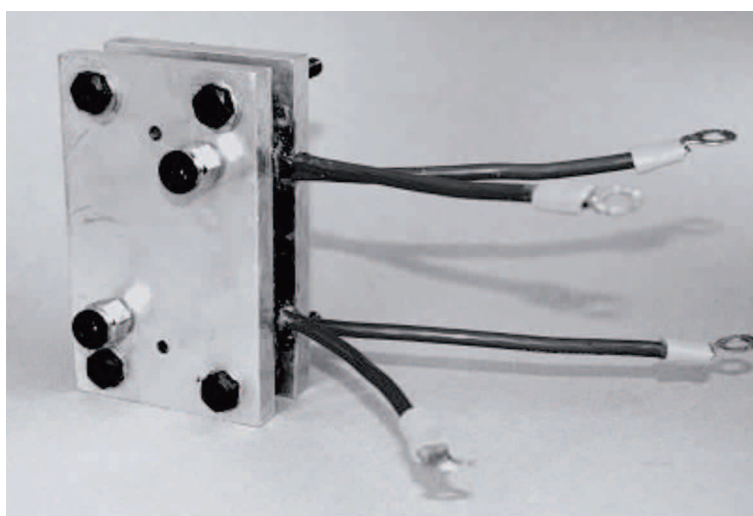

Figure 4. Assembled PEM fuel cell.

Results and discussion

Particle size measurements from XRD

Particle size of a catalyst is an important physical property that may affect the performance of a given catalyst and hence it was desired to have data of particle sizes of both catalysts. Particle size was evaluated from XRD data by using the Scherer equation:[12-14]

$$D = \frac{0.9\lambda}{\beta_{1/2}\cos\theta} \qquad (1)$$

where D is the average particle size, θ is the Bragg angle, λ is the wavelength of X-rays used, and $\beta_{1/2}$ is the width of a peak at half height (in radians 2 θ). The X-ray diffraction patterns of catalysts recorded by using Cu Kα radiation (λ=1.5406 Å) are shown in Figure 5. The particle sizes of catalysts were calculated from the analysis of the (111) diffraction peak of Pt. The data in Table 1 indicate that both catalysts consisted of

nano-size Pt particles. Since the particle sizes of both catalysts are in the same range, one cannot predict the relative contribution of these catalysts in PEM fuel cells on the basis of XRD data only.
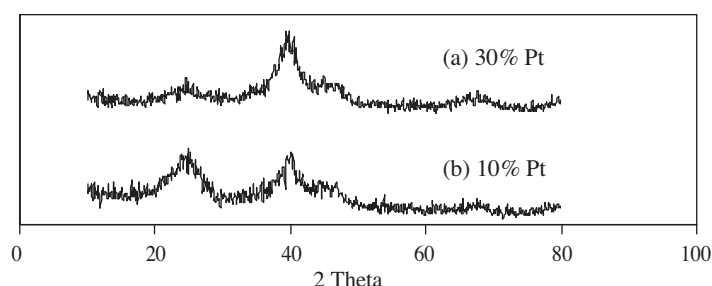

Figure 5. X-rays diffraction patterns of carbon supported (a) 30% Pt and (b) 10% Pt catalysts.

Table 1. Data of particle size of carbon supported catalysts obtained from XRD.

Catalyst type	Peak width (2θ in degree)	Peak position (2θ in degree)	Particle size (nm)
10% Pt	3.2	40.1	2.64
30% Pt	3.1	39.9	2.73

Real surface area measurements from cyclic voltammetry

The real surface area is an area of a catalyst that is actually available for electrochemical reaction. It may be evaluated from cyclic voltammetry by determining the charge transferred during adsorption of hydrogen on the surface of the platinum catalyst (Q_{Pt-H}). The real surface area of platinum-based catalysts (S_{Pt-H}) may be calculated by using the following relation:[19−21,24,25]

$$S_{Pt-H} = \frac{Q_{Pt-H}\mu C}{210\mu C cm^{-2}} \tag{2}$$

where 210 μC cm^{-2} is the charge transferred during monolayer hydrogen adsorption (Pt:H = 1:1) on an ideal surface of a polycrystalline platinum electrode having a roughness factor of 1. The value of Q $_{Pt-H}$ was evaluated from the hydrogen adsorption region obtained in the cathodic sweep in the potential range 0.4 to 0.05 V at a scan rate of 50 mV s^{-1} in 0.5 M H$_2$SO$_4$ as shown in Figure 6. A detailed description of the evaluation of Q $_{Pt-H}$ from the cyclic voltammogram is given elsewhere.[24] Knowing the real surface area of a catalyst, one may calculate the roughness factor (RF) by taking the ratio of real surface area to usual geometric area (or apparent area) of an electrode exposed to the working solution.[19−20]

$$RF = \frac{\text{Real surface area}}{\text{Apparent surface area}} \tag{3}$$

The comparison of data of real surface area and the roughness factor of different catalysts is given in Table 2. The real surface area of the 30% Pt catalyst is 3 times higher as compared with the 10% Pt catalyst due to the presence of 3 times more Pt loading in the 30% Pt catalyst. The appearance of well-defined hydrogen

adsorption-desorption peaks during the recording of cyclic voltammograms of both catalysts indicates that both catalysts may be utilized in the PEM fuel cell. However, 3 times more 10% Pt catalyst should be used to get the same performance as that of the 30% Pt catalyst. In the PEM fuel cell, the higher loading of the 10% Pt catalyst may make the catalyst layer thicker, which may lower the performance of MEAs as discussed in later sections.
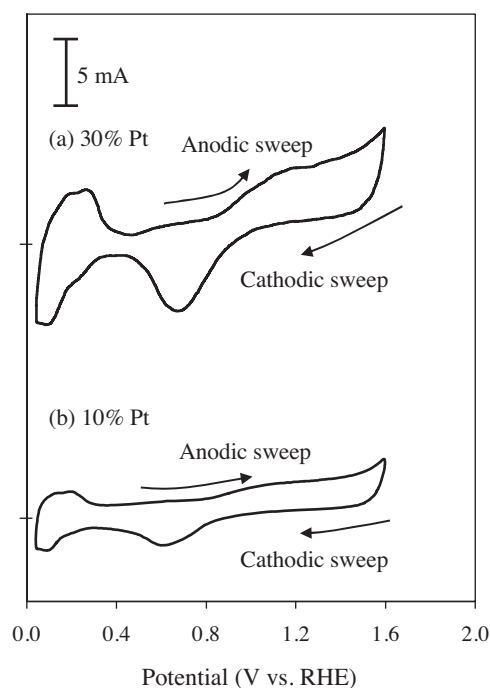

Figure 6. Comparison of hydrogen adsorption-desorption regions of cyclic voltammograms obtained at 50 mV s^{-1} scan rate in 0.5 M H$_2$SO$_4$ on (a) 30% Pt catalyst and (b) 10% Pt catalyst.

Table 2. Cyclic voltammetric data of real surface area and rate of electro-oxidation of 0.2 M CH$_3$OH in 0.5 M H$_2$SO$_4$ on 10% and 30% Pt catalysts.

Catalyst type	Real surface area (cm^2)	Roughness factor	I$_p$ (mA)	k (E$_p$) (cm s^{-1})
10% Pt	24.51	31.22	5.51	2.67×10^{-4}
30% Pt	70.69	90.05	18.1	8.77×10^{-4}

Evaluation of rate of electro-oxidation of methanol on catalysts

The methanol oxidation reaction was selected to assess the performance of a given catalyst in the PEM fuel cell firstly due to ease in handling of liquid methanol during electrochemical measurements and secondly to the existence of close similarities in basic electrochemical features of the direct methanol fuel cell and PEM fuel cell.[19,26] Cyclic voltammograms of electro-oxidation of 0.2 M CH$_3$OH in 0.5 M H$_2$SO$_4$ at 50 mV s^{-1} obtained

on the 10% and 30% Pt catalysts are shown in Figure 7. Only anodic peaks for methanol oxidation are observed in both anodic and cathodic sweeps, which have been attributed to the highest catalytic activity of Pt-based catalysts for methanol oxidation. A detailed discussion on the nature of the different peaks observed during the electro-oxidation of methanol is given elsewhere.[25] In the present work, the kinetic data evaluated from the analysis of methanol oxidation peak observed in the anodic sweep were used to assess the relative performance of a given catalyst in the PEM fuel cell. The rate of electro-oxidation of methanol was evaluated from peak current data using following relationship between the rate of reaction at peak potential and peak current at a given concentration of methanol:[33]

$$k(E_p) = \frac{I_p}{0.227nFAC} \tag{4}$$

where I_p is the peak current (in amperes), n is the total number of electrons transferred in the overall reaction (in this case 6), F is Faraday's constant (96487 C mol^{-1}), A is the apparent surface area of the electrode (in cm^2), and C is the bulk concentration of the reactant (in mol cm^{-3}). The comparison of kinetic data of electro-oxidation of methanol given in Table 2 indicates that utilization of 30% Pt catalyst in the preparation of membrane electrode assemblies may be more suitable for getting higher power density from the PEM fuel cell. Moreover, the presence of 90% carbon in 10% Pt catalyst did not contribute significantly towards the enhancement of catalytic activity of catalysts. It only minimized the loading of precious metal in a given catalyst.

Testing of MEAs in PEM fuel cell

The MEAs prepared from 10% and 30% Pt catalysts were tested in PEM fuel cell fixture (Figure 4) using hydrogen as fuel and oxygen as oxidant. Three different MEAs were prepared, designated as MEA1, MEA2, and MEA3. The MEA1 and MEA2 contained the same amount of 30% Pt and 10% Pt catalysts, respectively, while MEA3 was prepared by using 3 times more 10% Pt catalyst for maintaining the same Pt loading per cm^2 of an electrode as in MEA1, i.e. 0.5 mg Pt cm^{-2}. Details of Pt loading in each MEA are given in Table 3.

Table 3. Performance data of a 10% and 30% Pt catalysts obtained by testing of MEAs in a PEM fuel cell.

Type of MEA	Catalyst loading (mg cm^{-2})	Pt loading (mg cm^{-2})	Maximum power density (mW cm^{-2})
MEA1 (30% Pt)	1.67	0.50	185
MEA2 (10% Pt)	1.67	0.17	113
MEA3 (10% Pt)	5.00	0.50	119

The plots of cell potential (V) versus current density (mA cm^{-2}) of the PEM fuel cell with MEA1, MEA2, and MEA3 are shown in Figure 8. The cell potential at higher current density region dropped significantly in MEA2 and MEA3 as compared with MEA1. This fall of cell potential in the higher current density region is more obvious in Figure 9, where the power density (mW cm^{-2}) is plotted against current density (mA cm^{-2}). The power density is the product of cell potential and current density; hence a peak shape is observed at higher current density where the cell potential dropped sufficiently to lower values (0.3 to 0.45 V). The
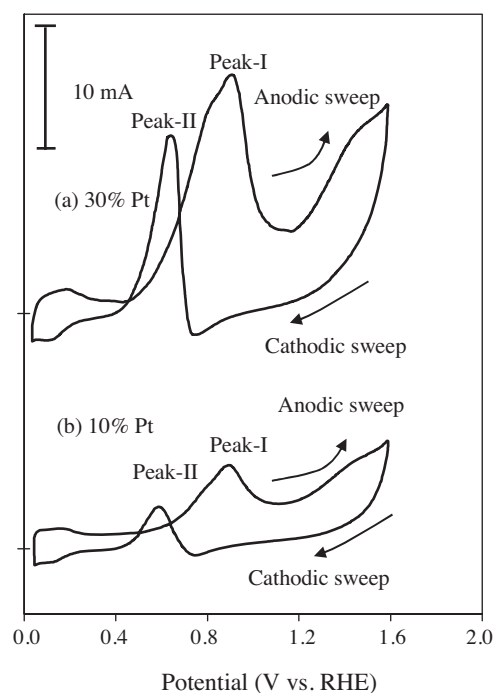
Figure 7. Comparison of cyclic voltammograms of 0.2 M CH_3OH in 0.5 M H_2SO_4 obtained at 50 mV s^{-1} scan rate on (a) 30% Pt catalyst and (b) 10% Pt catalyst.

data of maximum power density corresponding to the peak of the plots in Figure 9 are presented in Table 3. The MEA1 prepared from 30% Pt catalyst produced higher power density (185 mW cm^{-2}) as compared with MEA2 prepared from 10% Pt catalyst (113 mW cm^{-2}). The maximum power density obtained from MEA3, prepared from 10% Pt catalyst by maintaining the same Pt loading as in MEA1, was also less than MEA1. This observation was not proved by the cyclic voltammetric study of catalyst-coated working electrodes. This means that it is necessary to study the catalysts by testing of MEAs in the PEM fuel cell for in-depth investigation. The lower power density obtained from MEA3 as compared with MEA1 is attributed to the fact that in 10% Pt catalyst the Pt atoms are distributed far away from each other due to the presence of more carbon contents (90%) and hence many of the Pt atoms may not be available for electrochemical conversion. Moreover, 3 times more 10% Pt catalyst was applied per cm^2 of an electrode of MEA3 for getting the same Pt loading as in MEA1. This makes the catalyst layer thicker in MEA3, due to which most of the Pt particles did not remain in close contact with the membrane. Moreover, the thick layer of catalyst may hinder the conduction of protons, formed during oxidation of hydrogen gas, from the catalyst sites toward the membrane for onward passage through it to the cathode side. The importance of thin layer of catalysts in MEAs has been recognized by many authors and in this context different techniques are being employed for getting a thin coating of catalyst on electrodes of MEAs.[22,38] Thus it is better to use 30% Pt catalyst instead of using 3 times more 10% Pt catalyst for preparing MEAs of the PEM fuel cell.
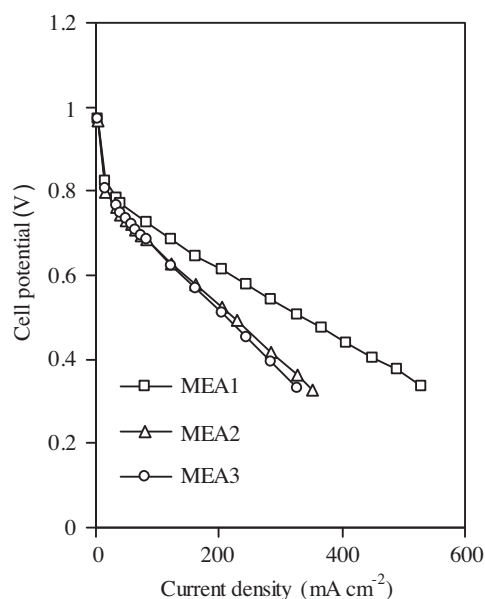
Figure 8. Comparison of plots of cell potential versus current density of PEM fuel cell with MEA1, MEA2, and MEA3 (MEA1 and MEA2 contained 1.67 mg cm^{-2} of 30% and 10% Pt catalyst respectively while MEA3 prepared from 10% Pt catalyst contained the same amount of Pt as in MEA1, i.e. 0.5 mg Pt cm^{-2}).
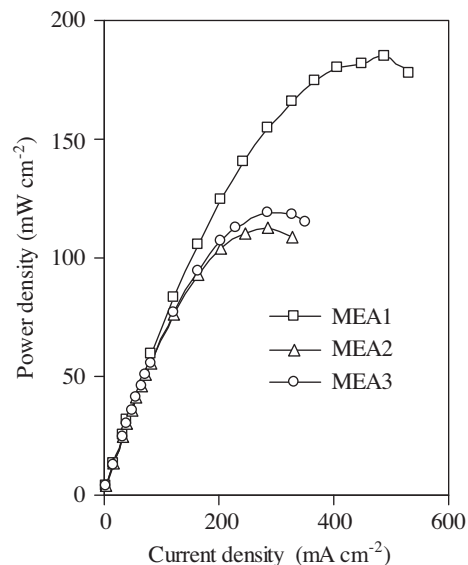
Figure 9. Comparison of plots of power density versus current density of PEM fuel cell with MEA1, MEA2, and MEA3.

Effect of additional gas diffusion layer on the performance of MEAs

An additional gas diffusion layer in the form of Teflon® treated Toray carbon paper was placed on both sides of MEAs during testing of the PEM fuel cell. It was noted that without additional carbon paper the cell potential dropped rapidly on drawing current as shown in Figure 10. This rapid drop in cell potential is mainly due to improper electrical contact of electrodes with the monopolar plates of the PEM fuel cell. This electrical contact may be improved by further tightening of nut and bolts but too much tightening of bolts may damage the MEAs. The additional carbon paper fills up any gap present between the electrode and flow field area of the monopolar plate, thereby improving the electrical contact. The additional carbon paper also provides a medium for diffusion of reactant gases to the catalyst present on the electrodes of MEAs. Without these carbon papers, a large portion of an electrode may not be available for electrochemical conversion of reactant gases due to compression of lands of flow field area of monopolar plates onto the electrodes of MEAs.

In the PEM fuel cell stack with a large number of cells the water removal problem exists on the cathode side, therefore, it may be useful to use additional carbon paper only on the hydrogen side for improving electrical contact of electrodes of MEAs with the flow field regions of monopolar/bipolar plates of the PEM fuel cell stack.

Advantages of cyclic voltammetry in evaluation of performance of catalysts

There are varieties of physical and electrochemical methods used for characterization of PEM fuel cell catalysts prior to preparation of MEAs.[9−14,19,38] The main purpose of alternate characterization techniques is to guess the

utility of a given catalyst in a PEM fuel cell. The physical methods such as X-ray diffractometry, transmission electron microscopy, and scanning electron microscopy have their own importance but one cannot prove from such physical data whether a given catalyst will catalyze a certain heterogeneous electron transfer process or not. Cyclic voltammetry is the only electrochemical technique that may be used for evaluation of the real surface area and kinetic parameters of heterogeneous electron transfer processes. The kinetic data of oxidation-reduction reactions obtained from cyclic voltammetry may be utilized to predict the utility of a given catalyst in catalyzing certain electrochemical processes.
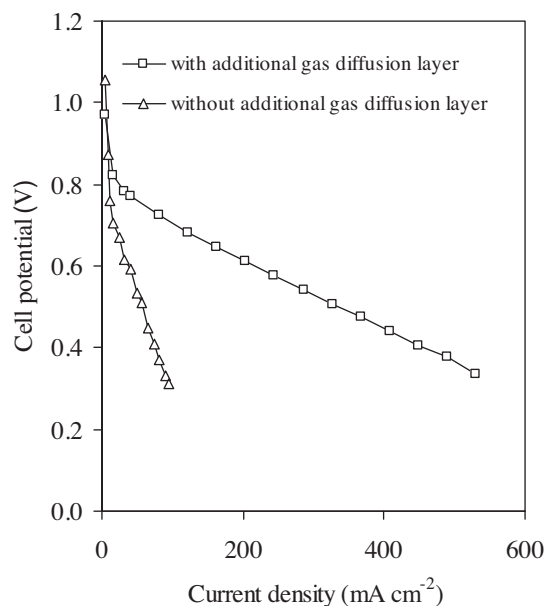

Figure 10. Comparison of plots of cell potential versus current density of PEM fuel cell using MEA1 with and without additional gas diffusion layer in the form of carbon paper.

Conclusions

Two different catalysts containing 10% and 30% Pt catalysts supported on Vulcan XC-72 carbon were studied to find their utility in a PEM fuel cell. The Pt particle sizes of both catalysts were in the same range. The real surface area and rate of electro-oxidation of methanol on 30% Pt catalyst was significantly higher as compared with the same amount of 10% Pt catalyst, which indirectly showed that the presence of 30% Pt catalyst in MEAs may be more suitable for obtaining higher power density from the PEM fuel cell. Testing of MEAs prepared from 10% and 30% Pt catalysts in a PEM fuel cell confirmed that 30% Pt catalyst having higher Pt loading is more suitable for obtaining high performance MEAs. In MEA with 10% Pt catalyst the Pt particles do not remain in close contact with the membrane and hence the performance of the 10% Pt catalyst is lower than that of the 30% Pt catalyst in the PEM fuel cell. Utilization of additional carbon paper is also emphasized wherever electrical contact between the electrode of MEAs and the flow field area of the monopolar/bipolar plate is poor. It is concluded that nanosize carbon supported Pt catalysts having higher Pt loading are more suitable catalysts for PEM fuel cells.

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