Performance of Platinum Black and Supported Platinum Catalysts in a Direct Methanol Fuel Cell

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Catalyst utilization studies are very important in PEM and Direct Methanol Fuel cell systems. This article studies the effect of nafion content on the catalyst utilization of Platinum Black and Platinum/Carbon electrodes when used as cathodes in a Direct Methanol fuel cell. It is seen that the effect of nafion content is more pronounced in the case of supported catalysts than in the case of unsupported catalysts. Polorization curves indicate that supported catalysts perform much better compared to unsupported catalysts.

1. INTRODUCTION

Catalyst utilization measurements in PEM (Proton Exchange membrane) and Direct Methanol fuel cells (DMFC) systems are significant in terms of understanding the performance of fuel cells. Catalyst utilization measures the proportion of Platinum atoms involved in an electrochemical reaction. This proportion usually involves measurement using cyclic voltommetry in an inert atmosphere. Under these conditions, the H-adsorption charge in the underpotential deposition region (V<400 mV) is directly proportional to the number of Platinum surface atoms taking part in the hydrogen adsorption desorption reaction. This is a general way to describe Platinum utilization. However, hydrogen adsorption and desorption curves give only an approximate measurement of catalyst utilization and do not indicate catalyst activity accurately. There is a difference between catalyst utilization on metal blacks and metal on carbon. However, while this has been studied in literature [1-3], it has not been very well understood. Paulus [4-5] has reported a large variation in catalyst utilization values

depending on the nature of the active layer used and the applied pretreatment. The authors postulate that gas diffusion electrodes containing active layers of carbon supported Pt before and after nafion impregnation show a catalyst utilization of 4% and 35% respectively. In the case of gas diffusion layer with an active layer of Pt-black, a surface utilization of more than 50% was observed. Catalyst utilization measurements suffer from a wide variability in measurements owing to a variety of factors. These factors have been discussed below.

2. ANALYSIS OF LITERATURE AND DISCREPANCIES

Peter Pickup [6] studies the Platinum utilization as a function of varying ionomer content in a PEM fuel cell. The authors evaluate that the Platinum Utilization for a nafion loading of 0.9 mg/cm^2 is 76% using a total surface area of Platinum of 87m^2/g. Zhong Xie [7] evaluates the Electrochemical Surface area of Platinum catalyst (using 20%Pt/C -E-TEK) on the Gas Diffusion layer. The authors evaluate the specific surface area of Platinum catalyst to vary from 64.5 to 85.9 m^2/g for various nafion loadings. Using an overall surface area of Platinum of 87m^2/g used by Pickup [6] et al, leads to a Platinum utilization value ranging from 74% to 98%. Velayudhatham [8] *et al*. estimates the catalyst utilization of Platinum to vary from 18.7% to 30.8 % for three different values of PTFE loadings. The authors use a total surface area of Platinum of 238 m^2/g for their calculations. Table 1 shows the variability in catalyst utilization values reported by different authors.

Table 1. Variability in catalyst utilization values as reported by various authors

Author	GDE structure/membrane/support	Electrochemical Surface Area(ESA) (m^2/g)	Catalyst Utilization (%)
Peter Pickup	Pt/C/Nafion/Vulcan XC-72	66	76%
Zhong Xie	20%Pt/C/Nafion/Vulcan XC-72	85.9	98.73%
Velayudhatam	20%Pt/C/Nafion/PTFE	62.5	23%
Tamizhmani	Pt/C +nafion/glassy carbon	87	100%
Ciureanu	Pt/C/teflonized carbon paper	14	16.09%
Perez[18]	Pt/C/Vulcan XC 72	58	66.67%
Balaji	Pt/C/nafion/teflonized carbon paper	57	65.64%
Pozio	Pt/C/Vulcan XC-72	106	98.14
Antolini	Pt/C+nafion/carbon paper	68-115	78-132.1%
Xiaoling Chen	Pt/C+nafion/carbon paper	140	45.4%
Fournier[19]	Pt/C+nafion/glassy carbon	57	65.51%

Tamizhmani [9] *et al*. has spread a very low volume of a catalyst ink(Pt/C + nafion) on carbon electrode before measuring catalyst utilization. Tamizhmani [9] points out that to use a sensitive technique such as Cyclic Voltammetry to obtain reproducible results, one has to use a constant weight

of Pt/C on the electrode. In our experience, even with a constant Pt/C ratio, obtaining consistently reproducible results is difficult using Cyclic Voltammetry. Ciureanu and Wang [10] report an Electrochemical Surface area which is unreasonably low(14%). Ticianelli [11] points out the large degree of uncertainity in the measurements owing to a large double layer charge. Antolini [12] and Balaji [13] *et al*. have pointed out the discrepancies which can occur in the catalyst utilization values when varying values of ionomer content is used in the catalyst layer. Pozio [14] *et al*. has studied the variation of the Electrochemical Surface Area as a function of Platinum loading. The authors postulate that at constant conditions the higher the Platinum loading, the lower is the Electrochemical Surface area(Platinum utilization decreases with increasing Platinum loading). While the operating conditions play a vital role in studying the electrochemical surface area, the catalyst utilization values are also determined by the average particle size of Platinum catalyst used and the overall surface area of Platinum used. Table 2 shows the catalyst utilization values as a function of catalyst particle diameter.

Table 2. Catalyst utilization as a function of particle diameter

Author	Catalyst	Diameter of Platinum particles(nm)	Surface area of Platinum catalyst(m^2/g)	ESA(m^2/g)	Catalyst Utilization(%)
Peter Pickup	20% Pt/C (E-TEK)	2-4 nm	87	66.12	76%
Xialong Chen	20%Pt/C(E-TEK)	2 nm	140	63.56	45.4%
Schmidt	20%Pt/C(E-TEK)	3.7nm	----------------	--------------	----------------
G.Velayudatham	20%Pt/C(E-TEK)	------------	238	62.5	23.3%
B.Krishnamurthy	20%Pt/C	2.7 nm	103	56.25	55.12

The operating conditions are different in some of these cases. Peter Pickup [6] has used an operating fuel cell testing station at 80^0 C and a Solartron 1286 Electrochemical interface to make the catalyst utilization measurements. The authors use 20%Pt/C (E-TEK Inc) as their cathode catalyst. The total surface area of Platinum is seen to be 87m^2/g which results in a Platinum Utilization value of 76 percent. Xiaoling Cheng [15] has studied the Platinum utilization in a PEM fuel cell in their work. Their experimental setup is the same as used by Peter Pickup [6]. The authors use an average particle size of Platinum catalyst in 20% E-TEK electrode as 2nm and use the density of Platinum as 21.4g/cm^3 to estimate the surface area of Platinum to be 140m^2/g. Based on this the authors estimate the ESA to be 63.6m^2/g and the Platinum utilization to be 45.4%. Schmidt [16] *et al.* uses rotating ring disk electrodes to characterize the surface area of high surface area electrocatalysts. The authors use 20% Pt/Vulcan XC 72 fuel cell catalyst on glassy carbon electrodes to measure the Electrochemical Surface area of Platinum catalysts. The authors postulate a Platinum diameter of 3.7nm and evaluate the catalyst utilization to be 100%. Pozio [6] *et al.* has already pointed the discrepancies which can occur when using Cyclic Voltammetry to measure catalyst utilization. The authors point out that the Gas diffusion Electrode preparative method is critical in influencing the value of catalyst utilization

measurements. The authors postulate that the catalyst ink must be prepared preferentially without binding agents like nafion, PTFE(poly tetra-fluoro ethylene) etc; An exact control of Platinum loading and nafion volume is required to get a better control over catalyst utilization; the simplest and reproducible experiment seems to be the 3 electrode setup. However, most researchers prefer measuring Platinum Utilization in a fuel cell setup. Teng [17] *et al.* points out the difference in the measured Electrochemical Surface area for catalysts prepared by different methods. In addition to the experimental variation which affects the measured Electrochemical Surface Area, different authors tend to use different values of the surface area of Platinum which leads to varying values of catalyst utilization as shown in Table 2. This leads to measured values of Platinum Utilization for PEM fuel cells to range from 23.3% to 76%. The wide variability in Platinum utilization values is a cause for concern and should be addressed. However, the focus of this present work is different.

3. EXPERIMENTAL PART

3.1. Membrane Electrode Assembly Fabrication

Nafion 117 membrane is boiled in hydrogen peroxide solution for one hour and in water for half hour. The membrane is converted to sodium form by boiling successively in sodium hydroxide and water. The membrane is coated with (Pt-Ru)/C on the anode and Pt/C on the cathode. The catalyst slurry prepared is brush painted over nafion 117 membrane and vacuum baked for 2 hours at 130^0 C. The dried membrane is boiled in 1 M sulphuric acid for one hour and water for half hour. The diffusion medium comprising of carbon paper, carbon powder and binder prepared by proprietary process in our labs was used. The catalyst coated membrane in hydrogen form is sandwiched between the two electrodes and pressed at 150^0C under pressure. Interdigitated flow fields with channels machined into graphite blocks were used in the fuel cell assembly. $30cm^2$ cells were used for testing. The cathode catalyst is varied as 40%Pt/C, 20%Pt/C and Platinum Black respectively.

3.2. Fuel Cell testing

A fuel cell testing station built at the Center for Fuel Cell Technology, was used to test the dc performance of 30 cm^2 cells. The cells were given 2 hours to equilibrate for performance. Cyclic voltammetry and catalyst utilization studies were evaluated using an Autolab Model No. 30 PGSTAT 30 potentiostat/galvanostat. The applied potential range was in between 0 and 1.0V. A scanning rate of 20mV/s was used. It is to be noted that catalyst utilization measurements were made by measuring the area under the hydrogen adsorption desorption peak using the Autolab. The measurements were made after 4 hours of running the cell with methanol as the anode feed and air as the cathode feed.

4. RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltommogram used to measure the catalyst utilization in a Direct Methanol fuel cell. The cyclic voltommogram on the cathode is measured by passing hydrogen on the anode side and inert gas on the cathode. A cathodic sweep cylic voltommogram is shown in Figure 1(for a nafion loading of 33% on the cathode). The catalyst utilization is measured as follows: The charge connected to the hydrogen adsorption in the cyclic voltommogram is integrated in the hydrogen underpotential deposition region. The geometric Pt surface area corresponding to the resulting charge was based on the finding that a smooth polycrystalline Pt surface shows a H_{upd} charge of 210 μCcm^{-2}. By comparing the geometric surface area thus obtained to the overall Pt surface of the catalyst (manufacturers specification or calculation) the catalyst surface utilization is obtained. The electrochemical surface area is given by the following formula[9]

$$S = \frac{6000}{\rho d} \tag{1}$$

where ρ is the density of Platinum (21.4g/cc), S is the surface area m^2/g and d is the average particle size (nm). From the manufacturer's specification the particle size of Platinum black catalyst is taken to be 2 nm and the particle size of 20%Pt/C and 40% Pt/C catalyst is seen to be 2.7 nm.
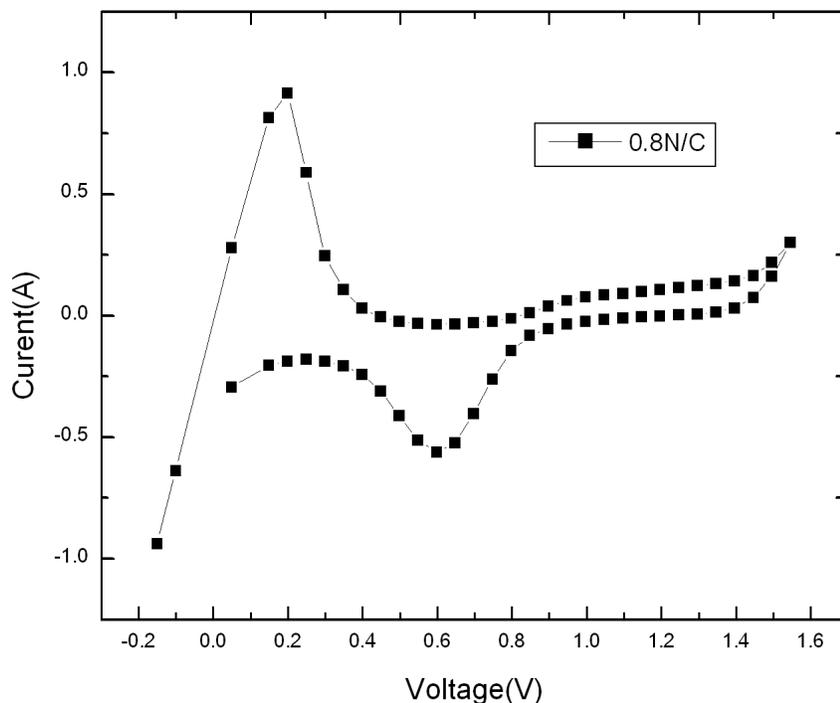
Figure 1. Cyclic Voltommogram used for catalyst utilization measurements for a cathode catalyst layer with 33% nafion. The sweep rate was fixed at 20mV/s.

Figure 2 shows the performance of a DMFC for varying nafion content in the cathode catalyst layer(40%Pt/C) holding the nafion content constant at 25% in the anode catalyst layer. The figure shows the variation of performance for four different ionomer contents in the cathode catalyst layer. Holding the ionomer content at an optimized value of 25% [19] in the anode catalyst, the ionomer content in the cathode catalyst layer is varied from 14% to 38%. The performance curves shows that the highest performance is seen for an ionomer content of 33%. When the ionomer content is increased to 38%, the performance is seen to decrease. The performance is seen to be lower when the ionomer content is reduced to 14% and 25%. Table 3 shows the catalyst utilization measurements at the cathode of DMFC for four different values of nafion content. It is seen that the highest catalyst utilization value of 65% is seen when the ionomer content is kept at 33% corresponding to the ideal performance of a DMFC.
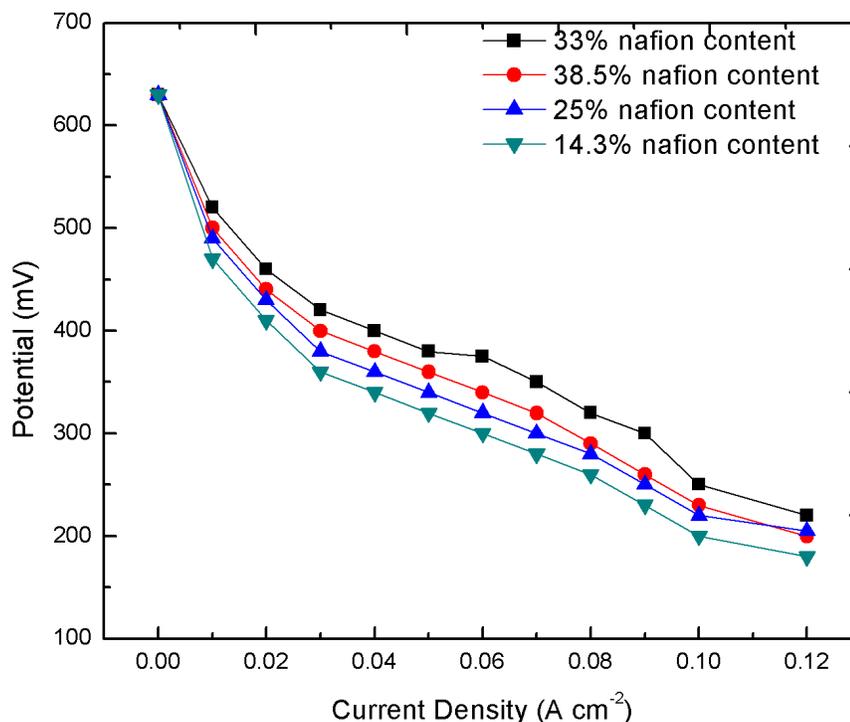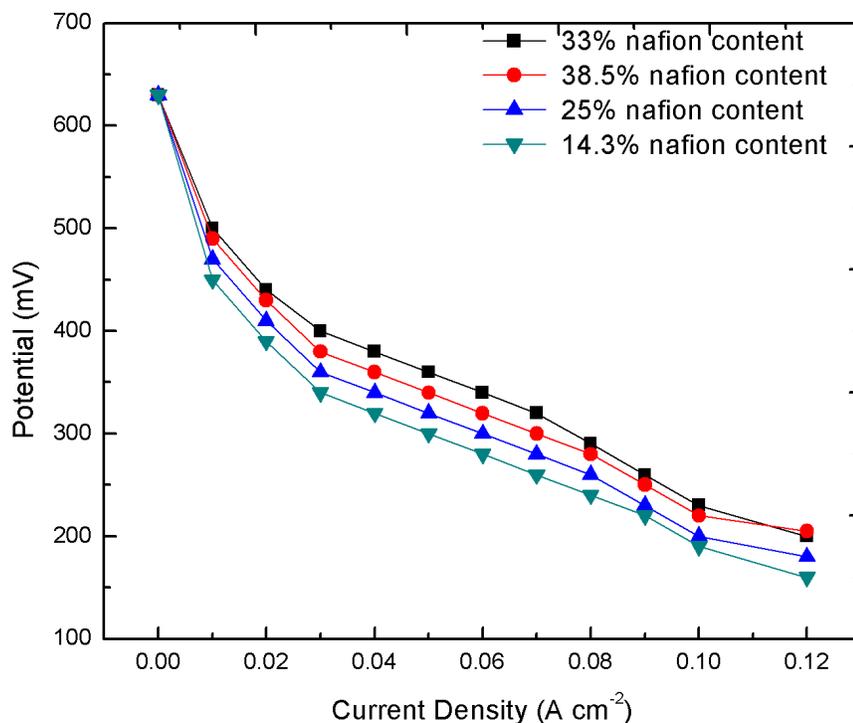

Figure 2. Performance curves for DMFC operation with 40%Pt/C catalyst with varying nafion content.

Table 3. Catalyst utilization in a DMFC cathode for a 40% Pt/C cathode catalyst

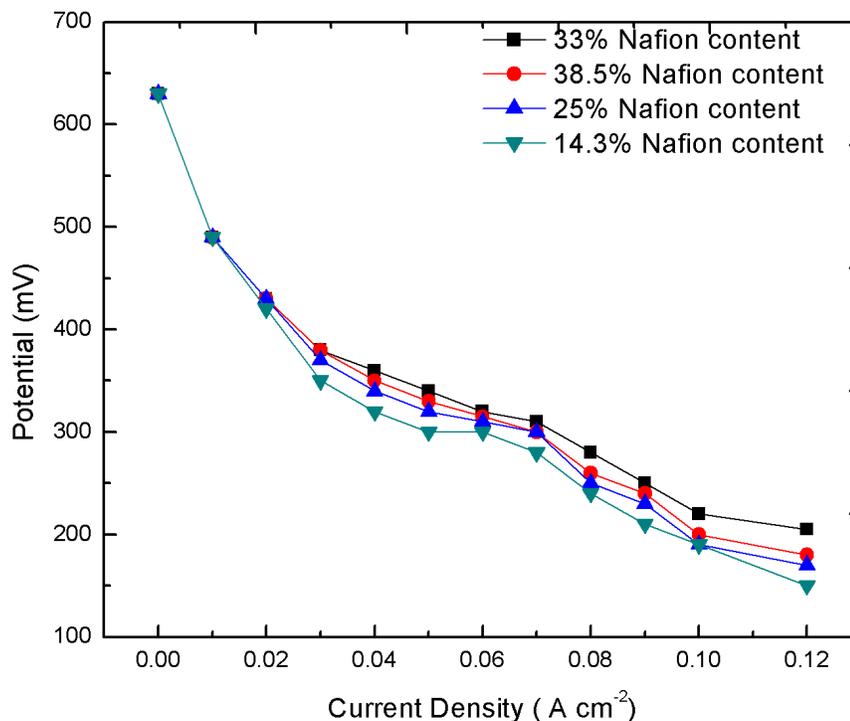| % Ionomer content in the catalyst layer	Electrochemical Surface Area(m^2/g)	Catalyst Utilization(%)
14	49.028	47.6
25	55.438	52.3
33	67.03	65.12
38.5	56.77	55.12

Figure 3 shows the performance of a DMFC when 20%Pt/C is used as a cathode catalyst for four different values of ionomer content. The polorization curves show a lower performance than the comparative curves when 40%Pt/C is used as a cathode catalyst. Table 4 shows the catalyst utilization values when 20%Pt/C is used as a cathode catalyst. The highest value of catalyst utilization is seen to occur at a nafion content of 33%. This shows that Platinum utilization on the cathode catalyst plays a significant role in influencing the performance of a DMFC.

Figure 3. Performance curves for DMFC operation with 20%Pt/C catalyst with varying nafion content.

Figure 4 shows the polorization curves when Platinum Black is used as a cathode catalyst. It is seen that varying nafion content in the cathode catalyst layer does not affect the performance of a DMFC much when Platinum Black is used as a catalyst. Table 5. shows the catalyst utilization values measured when the nafion content is varied from 14% to 38% when Platinum Black is used as a catalyst. The Platinum utilization values shows that there is limited variation in the catalyst utilization values when the nafion content is varied from 14% to 38%. This can be explained by the following reasoning. At lower values of nafion content, the ionic conductivity among the catalyst particles decreases. At optimum values of nafion content, the optimization between the porosity and ionic conductivity enhances the catalyst utilization value and hence the performance of the DMFC. At higher values of nafion content, the excess nafion tends to block the catalyst sites leading to lower catalyst utilization. Since supported catalysts tend to have a higher surface area than unsupported ones,

the reduction in catalyst utilization is more pronounced in the case of supported catalysts. Thus the variation of nafion content is found to have significant effect of catalyst utilization of metal black and metal/carbon catalysts.

Figure 4. Performance curves for DFMC operation with Platinum Black catalyst with varying nafion content.

Table 4. Catalyst utilization in a DMFC cathode for a 20% Pt/C cathode catalyst

% Ionomer content in the catalyst layer	Electrochemical Surface area(m^2/g)	Catalyst utilization(%)
14	43.26	42
25	48.41	47
33	56.25	55
38.5	49.749	48.3

Table 5. Catalyst utilization in a DMFC for a Platinum Black cathode catalyst

% Ionomer content in catalyst layer	Electrochemical Surface area($m^{2/}$/g)	Catalyst utilization(%)
14	49	35
25	50.4	36
33	53.9	38.5
38.5	50.4	36

5. CONCLUSIONS

The performance of a DMFC is studied with Platinum Black and supported Platinum catalysts as cathode catalysts. The effect of nafion content on catalyst utilization on these catalysts is studied. 40% Pt/C is seen to give the best performance for a DMFC when used as a cathode catalyst. At 33% nafion content in the cathode catalyst layer, 40% Pt/C catalyst is found to have the highest catalyst utilization of 65%. The catalyst utilization of Platinum Black catalyst is not found to change much with varying nafion content. The performance of a DMFC is not found to change much with varying nafion content when Platinum Black is used as a cathode catalyst.

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