J Appl Electrochem (2009) 39:1003–1009
DOI 10.1007/s10800-008-9752-7

ORIGINAL PAPER

Experimental analysis of platinum utilization in a DMFC cathode

Balaji Krishnamurthy · S. Deepalochani

Received: 18 July 2008 / Accepted: 2 December 2008 / Published online: 24 December 2008

Abstract An experimental analysis of platinum utilization in a DMFC cathode is performed. The chief objective of this work is to elucidate the effect of Nafion and polytetrafluoroethylene (PTFE) on platinum utilization values on the cathode. Polarization curves indicate that the performance of a DMFC is sensitive to the Carbon/Nafion (C/N) and Nafion:PTFE (N/P) ratio in the catalyst layer. Our analysis shows that supported Pt/C catalysts have a much higher platinum utilization value than unsupported catalysts. Platinum utilization is a maximum at a C/N ratio of 2.5 and at a N/P ratio of six. Platinum utilization is more sensitive to the Nafion content in the catalyst layer than the Teflon content.

Keywords Nafion · Teflon · Cyclic voltammetry · DMFC · Platinum utilization

1 Introduction

Direct methanol fuel cells (DMFC) are the most promising alternatives to lithium ion batteries in the portable power electronics applications market. Several companies like MTI micro fuel cells, Motorola and Samsung are pursuing this technology with an aim of commercializing the technology. The oxygen reduction reaction in a DMFC is very critical in determining its performance. Thus, it is very important to analyze the platinum utilization on the cathode side since it serves a very important role in reducing oxygen on the cathode side. Very little data exists in literature on evaluating platinum utilization values on the cathode of a DMFC. The platinum utilization on the cathode of a DMFC is affected by a wide variety of factors including Nafion content, Teflon content, carbon content, ruthenium crossover, methanol crossover and subsequent methanol oxidation on the cathode side. The effect of ruthenium crossover on platinum activity has been studied by Mukerjee et al. [1]. Very few papers exist on the methanol crossover and its subsequent oxidation at the surface of the cathode catalyst and its impact on platinum utilization. Wei et al. [2] uses a random cluster model to analyze the platinum utilization in the cathode catalyst layer of a proton exchange membrane fuel cells. The authors theoretically study the variation of platinum utilization as a function of the carbon:ionomer:PTFE content. Farhat et al. [3] has developed a mathematical model which predicts an increase in power density with decrease in platinum particle size. To the best of our knowledge, there is no theoretical work which studies the platinum utilization on the cathode of a DMFC in literature. Pozio et al. [4] points out that the electrochemical active surface area of platinum catalyst decreases with platinum loading for a PEFC.

Figure 1 shows a nine layer membrane electrode assembly (MEA) used for testing platinum utilization. The MEA consists of anode backing layer, anode microporous layer, anode active layer, catalyst coated membrane surface (anode side), membrane, catalyst coated membrane surface (cathode side), cathode active layer, cathode microporous layer and cathode backing layer. Catalyst surface utilization in this context refers to the proportion of metal atoms involved in an electrochemical reaction in the catalyst layer. This proportion is usually determined via cyclic

B. Krishnamurthy (✉) · S. Deepalochani
Center for Fuel Cells, International Advanced Center for Powder Metallurgy and New Materials, Medavakkam, Chennai 600010, India
e-mail: balaji.krishb1@gmail.com

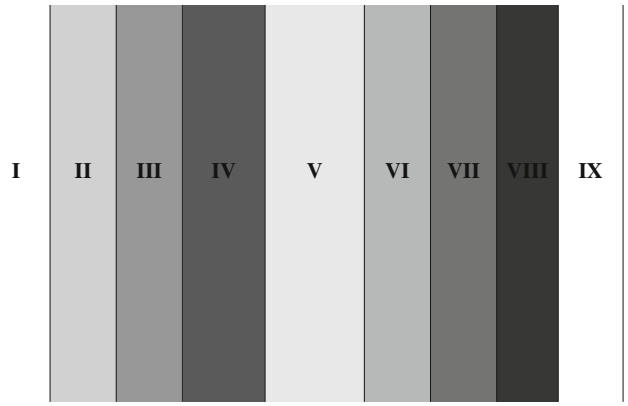

Fig. 1 Schematic of a nine layer MEA used in a Direct Methanol fuel cell. *Note*: I—Anode backing layer-carbon; II—Anode micro porous layer; III—Active layer; IV—Catalyst coating on membrane (anode side); V—Membrane; VI—Catalyst coating on membrane (cathode side); VII—Active layer; VIII—Cathode microporous layer; IX—Cathode backing layer-carbon

voltammetry (CV) measurements in an inert atmosphere. The hydrogen adsorption charge in the underpotential deposition region is directly proportional to the number of platinum surface atoms taking part in the hydrogen adsorption reaction. The difference between the catalyst utilization of metal blacks and metal on carbon catalysts has been widely observed [5–7]. McBreen et al. [8] has studied the catalyst utilization at the electrode membrane interface applying platinum screen as model electrodes. Tu et al. [9] has reported microelectrode studies at the same interface using Pt black and Pt/C catalysts. The authors observe that the Pt can be electrochemically active even without contact with the solid polymer electrolyte. Paulus et al. [10] has reported a large variation in catalyst utilization depending on the different nature of the active layer and the applied pretreatment. The authors postulate that the gas diffusion electrodes containing active layers of supported platinum shows wide variation in platinum utilization values depending on the different nature of the active layer and the applied pretreatment. The authors postulate that Nafion impregnation causes an increase in platinum utilization.

Pozio et al. [4] has pointed out the variability in the measurements of cathode catalyst measurements. Pickup et al. [11] has analysed the platinum utilization in a PEM fuel cell. The author predicts that the catalyst utilization is about 76% for a Nafion loading of 0.9 mg cm^{-2}. Velayudhatham et al. [12] estimates the platinum utilization to vary from 18% to 30% with varying Teflon content in a PEM fuel cell. Tamizhmani et al. [13] points out that to use a sensitive technique like cyclic voltommetry to obtain reproducible results, one has to use a constant Pt/C on the electrode. Ticianelli et al. [14] points out the large degree of uncertainty in the measurements owing to a double layer charge. Xiaoling et al. [15] report a platinum utilization of 45% on the PEM fuel cell cathode. Schmidt et al. [16] uses ring disk electrodes to characterize the high surface area of electro catalyst. The authors report a platinum utilization of 100%. Teng et al. [17] points out the discrepancies in measured electrochemical surface area for catalysts prepared by different methods. The effect of Teflon content on DMFC performance has been studied by Krishnamurthy et al. [18]. The authors postulate that the Teflon loading plays a more significant role in the cathode MPL than in the cathode BL. The PTFE content affects the platinum utilization on the cathode and an optimum PTFE content of 20% in the cathode MPL and in the cathode BL works ideally. Popov et al. [19] has studied the effect of carbon content in the microporous layer of a PEMFC on the performance of a PEM fuel cell. The authors postulate that the best fuel cell performance is seen with the lowest carbon loading (thin MPL) along the lines of Newman's [20] theoretical work. However, none of the above mentioned studies study the interaction between the Nafion and PTFE content in the catalyst layer and its subsequent impact on catalyst utilization values.

Figure 2 shows the interaction between the Nafion particles, PTFE particles and catalyst particles in a catalyst layer [18]. At lower contents of Nafion and PTFE, the ionic

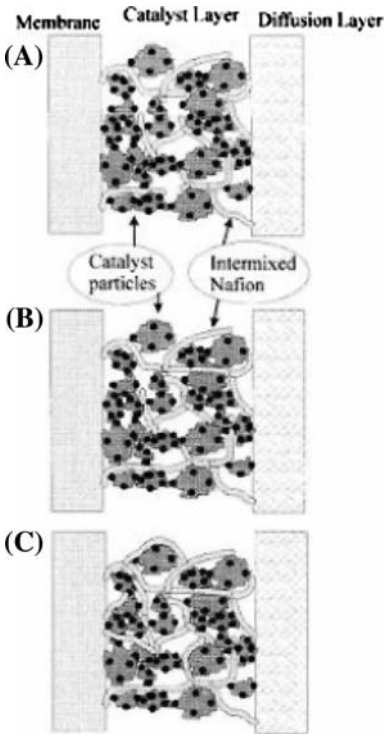

Fig. 2 Schematic of interaction of Nafion and PTFE particles with Platinum catalyst in a DMFC cathode (reproduced from Ref. [2]). **a** Low Nafion content and PTFE content reduces ionic conductivity, **b** Excessive Nafion blocks the catalyst particles, **c** Optimal Nafion and PTFE content is critical for ideal performance

conductivity of the catalyst layer is lower. At higher contents of Nafion, the ionomer particles block the catalyst sites reducing the catalyst utilization. However, increasing the PTFE content in the catalyst layer increases the hydrophobicity driving the Nafion into the active layer. However, the increasing Teflon content leads to pore blocking in the catalyst layer leading to not only a reduction in the catalyst utilization but also decreasing oxygen transport in the cathode owing to increased mass transfer resistance. Thus, the interplay between the Nafion content and the PTFE content in the cathode catalyst layer is extremely critical in determining the performance of a DMFC. In this study, we have tried to focus on studying the influence of Nafion and PTFE content in the cathode catalyst layer on the performance of a DMFC.

2 Experimental

2.1 Membrane electrode assembly fabrication

Nafion 117 membrane was boiled in hydrogen peroxide for 1 h and in water for half hour. The membrane was converted to sodium form by boiling successively in sodium hydroxide and water. The membrane was coated with 40% Pt-Ru/C (1 mg cm^{-2}), obtained from Arora Mathey on the anode and 40% Pt/C cathode (2 mg cm^{-2}) on the cathode. To make the catalyst slurry, the catalyst was mixed with isopropyl alcohol and deionized water and sonicated till the catalyst particles get dispersed. The required amount of Nafion was added with ethylene glycol to make the slurry. An optimized amount of Teflon is added to the catalyst slurry. The catalyst slurry prepared was brush painted over Nafion 117 membrane and vacuum baked for 2 h at 130 °C. The dried membrane was boiled in 1 M sulphuric acid for 1 h 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 was sandwiched between the two electrodes and pressed at 150 °C under a pressure of 1000 psi.

Interdigitated flow fields with channels machined into graphite blocks were used in the fuel cell assembly. About 30 cm^2 cells were used for fuel cell testing.

2.2 Fuel cell testing

Fuel cell testing station built at the Center for Fuel Cell Technology, Chennai was used to test the performance of 30 cm^2 cells. A 1 M methanol feed at a flow rate of 10 mL/min was used as the anode feed. The cells were allowed to equilibrate for several hours before testing. The fuel cell was given an hour to reach steady state performance. Cyclic voltammograms and catalyst utilization studies were studied using an Autolab, PGSTAT100. The potentiostat has a current range of 0–10 A (with a booster) and a frequency range of 1 MHz to 0.01 Hz. The CV measurements were made by passing hydrogen on the anode and argon on the cathode. Catalyst utilization was calculated from the area under the hydrogen adsorption/desorption curves. Cyclic voltammograms were obtained at 20 mV/s. The catalyst utilization values did not change at different values of sweep rates.

3 Results and discussion

Figure 3 shows the performance of a DMFC with two different values of Carbon/Nafion (C/N) ratio in the cathode catalyst layer. The performance variation of a DMFC when the C/N ratio in the cathode catalyst layer is varied from 1.25 to 2.5 is seen to be large especially in the mass transport limited region. Figure 4 shows the performance of a DMFC for two different values of Carbon:PTFE (C/P) ratio in the cathode catalyst layer. The C/P ratio is varied from 3.8 to 7.6 and the variation in the polarization curves is seen in Fig. 4. It is seen that the C/N ratio plays a far more important role in the performance of a DMFC than the Carbon/PTFE (C/P) ratio. While a variety of factors including methanol crossover, water crossover, MEA impedance and catalyst utilization plays a part in determining performance, our chief aim in this work is to study the role of C/N ratio and C/P ratio on platinum utilization on the cathode and its consequent effect on the DMFC performance.

3.1 Evaluation of platinum utilization

Table 1 shows a sample of the MEA's tested with all their compositions. MEA 1 shows that the weight ratio of Nafion

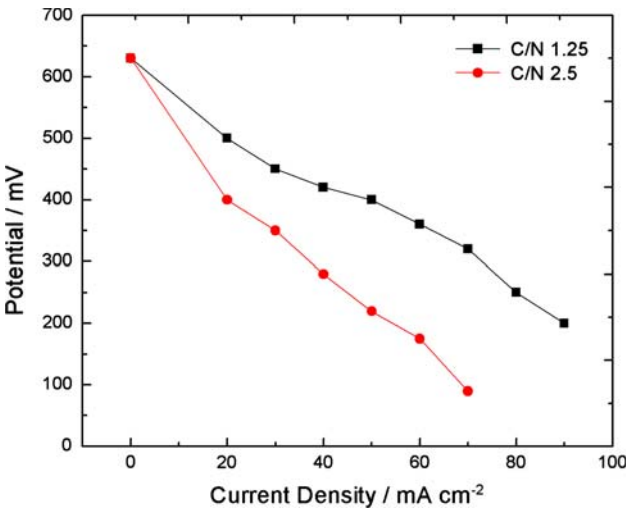

Fig. 3 Effect of Carbon/Nafion ratio on the performance of a DMFC

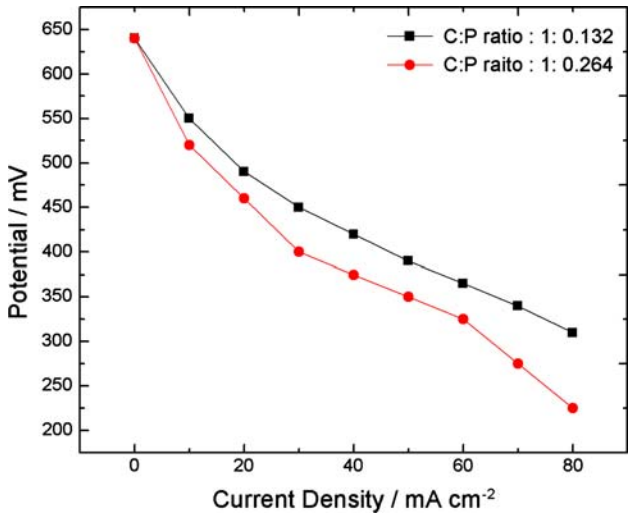

Fig. 4 Effect of Carbon/PTFE ratio on the performance of a DMFC

and Carbon is varied from 30 to 24 mg and 30 to 12 mg, in the catalyst layer, for the two different values of C/N ratio. MEA 2 shows the composition in the cathode catalyst layer for a Nafion:PTFE (N/P) ratio of six (Fig. 7). The carbon content in this case is fixed at 30 mg. MEA 3 shows the composition of the catalyst layer for a platinum loading of 2 mg cm^{-2} (Fig. 8) for a cathode catalyst of 20% Pt/C. The catalyst utilization is seen to be 55% in this case.

Table 2 shows the platinum utilization being studied for Fig. 8. The particle sizes of 2.7 nm for 40% Pt/C and 20% Pt/C are obtained from the manufacturers (Arora Mathey). Platinum black particles have a particle size of 2 nm. The electrochemical surface area (ESA) (m^2/g) is given by $S = 6000/\rho d$ [4]. The platinum utilization values listed out in Table 1 are obtained for a N/P ratio of six.

3.2 Influence of weight ratio of Carbon/Nafion on platinum utilization

Wie et al. [2] has studied the variation of platinum utilization as a function of ionomer content to carbon content for different percentages of Pt/C in the cathode of a PEMFC. Since we have been unable to find any work evaluating the platinum utilization in a DMFC theoretically, we have used Wie's model as a basis for comparison. Theory shows that the highest platinum utilization occurs for an ionomer to carbon ratio of 1 with different contents of Pt. The author postulates that the higher the Pt content in Pt/C, the wider the allowable weight ratio of carbon to ionomer for increased platinum utilization. Figure 5 shows the cyclic voltammogram for a C/N ratio of 1.25 used to measure platinum utilization values. The area under the hydrogen adsorption desorption curve is evaluated to estimate platinum utilization values. Figure 6 shows the performance of a DMFC with three different catalysts. It can be seen that 40% Pt/C gives the best performance for a DMFC. While there are several reasons for this performance variation including cell impedance, methanol crossover etc. our chief focus has been understanding the catalyst utilization with these different catalysts. Figure 7 shows the catalyst utilization of supported and unsupported platinum catalyst as a function of C/N ratio. A peak catalyst performance of 65% is seen for a C/N ratio of 1.25 for Pt/C (40%). The catalyst utilization is seen to reduce at higher values of C/N ratio. At lower platinum content (20% Pt/C), the peak platinum utilization is seen to reduce to 56%. The variation of platinum utilization in this case seems to follow the same trend of 40% Pt/C. However, the platinum utilization values in the case of platinum black

Table 1 MEA composition

SI no	MEA composition	Nafion loading (mg)	PTFE loading (mg)	Carbon loading (mg)	Catalyst utilization (%)
MEA1	40% Pt/C (2 mg cm^{-2}) Cathode catalyst 40% Pt-Ru/C (1 mg cm^{-2}) Anode catalyst	24	5	30	
MEA2	40% Pt/C (2 mg cm^{-2}) Cathode catalyst. 40% Pt-Ru/C (1 mg cm^{-2}) Anode catalyst	30	5	30	65
MEA3	20% Pt/C (2 mg cm^{-2}) Cathode catalyst. 40% Pt-Ru/C (1 mg cm^{-2}) Anode catalyst	24	4	30	55

Table 2 Catalyst utilization measurements for supported and unsupported catalysts

Nature of particle	Particle size (nm)	Electrochemical surface area ($m^2\ g^{-1}$)	Total surface area ($m^2\ g^{-1}$)	Catalyst utilization (%)
40% Pt/C	2.7	67	103	65
20% Pt/C	2.7	57	103	55
Pt black	2.0	49	140	35

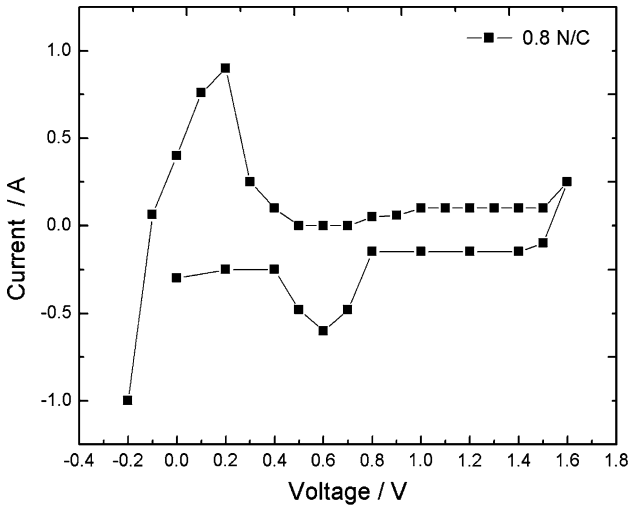

Fig. 5 Cyclic voltommogram to evaluate Platinum utilization on the cathode. The potential scan was performed at 20 mV/s

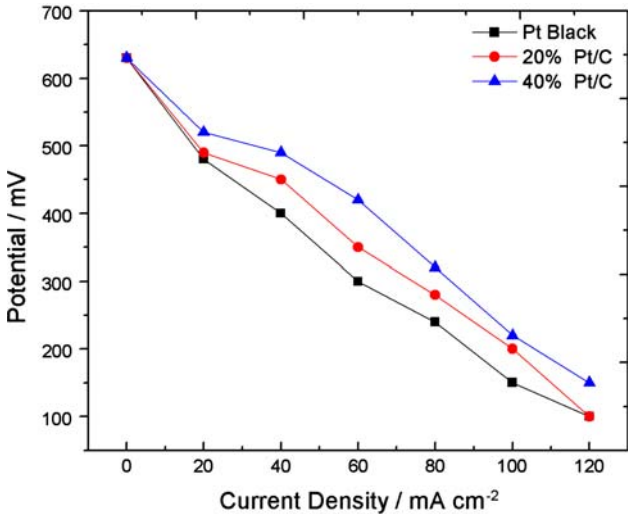

Fig. 6 Performance of a DMFC for three different cathode catalysts (40% Pt/C, 20% Pt/C and Pt Black)

does not seem to vary much with the C/N ratio. The reason behind this can be understood as follows. At higher values of C/N ratio, the low values of Nafion content lower the ionic conductivity among the catalyst particles. At optimum values of C/N ratio, the optimization between the porosity and ionic conductivity enhances the catalyst utilization value and hence the performance of the DMFC. At lower values of C/N ratio, 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. Wie et al. [2] postulates that the peak platinum utilization occurs at a C/N ratio of 1 for both 40% Pt/C and 20% Pt/C.

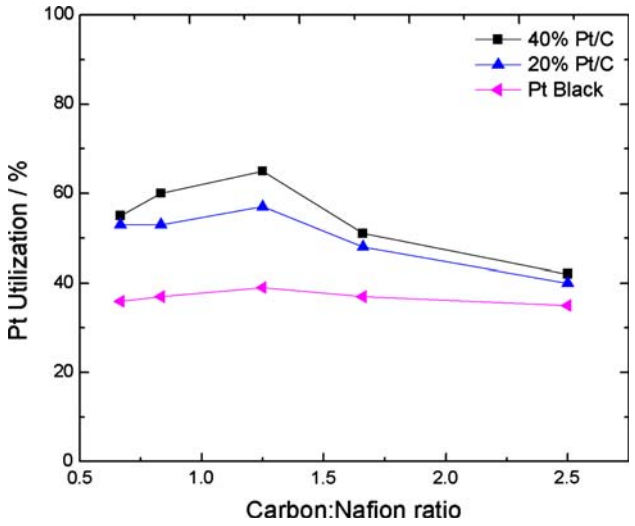

Fig. 7 Platinum utilization values as a function of Carbon/Nafion ratio

At values of C/N lower or higher than 1, the platinum utilization seems to reduce. Our experimental results seem to confirm the theoretical trend except the peak platinum utilization occurs around a C/N ratio of 1.25.

3.3 Influence of PTFE content on Platinum utilization

The effect of PTFE content on platinum utilization can be studied by either the C/P (Carbon/PTFE) ratio or the N/P (Nafion:PTFE content). Figure 8 shows a comparative plot showing the platinum utilization values for three different values of N/P ratio. The impact of the N/P ratio is critical in a catalyst layer since the two parameters work in

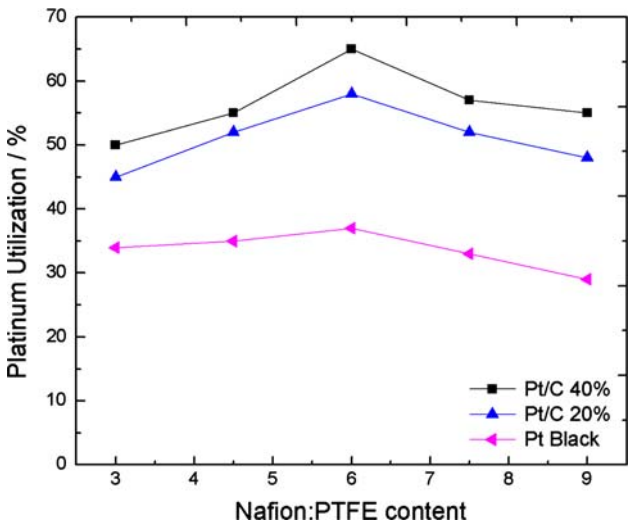

Fig. 8 Platinum utilization values as a function of Nafion:PTFE ratio

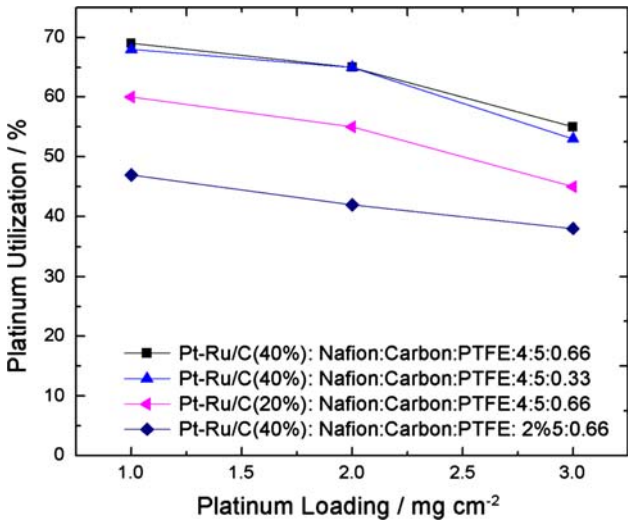

Fig. 9 Platinum utilization as a function of Nafion/Carbon/PTFE ratio

opposition. From Fig. 2, it can be seen that when the Nafion content is increased in the catalyst layer on the membrane and in the active layer, the Nafion blocks the catalyst sites and reduces platinum utilization. Increasing the PTFE content increases the hydrophobicity in the catalyst layer and tends to push the Nafion away into the electrode layer increasing catalyst utilization. However, increasing PTFE content tends to block the pores in the catalyst layer leading to a decrease in oxygen transport and reduced access to the catalyst sites. Thus, the N/P ratio in the catalyst layer is very critical to DMFC performance and plays a complex role in understanding the performance of the DMFC system. Figure 8 shows that the critical N/P ratio is about six. When the ratio is less than six, the lower amounts of Nafion or the higher amounts of PTFE content reduce the ionic conductivity of the catalyst particles. When the ratio is more than six, the excess Nafion blocks the platinum sites resulting in reduced utilization.

Figure 9 shows the impact of platinum loading on platinum utilization for three different loadings on the cathode. The platinum utilization is seen to decrease as a function of platinum loading since with increase in the number of platinum sites, the increase in the number of platinum sites being blocked also increases. The sensitivity of platinum utilization to the Nafion:Carbon:PTFE ratio in the catalyst layers is shown by Fig. 9. A change in the Nafion ratio in the Nafion:Carbon:PTFE content from 4 to 2 is seen to reduce the platinum utilization on the cathode from 66% to 43% showing how sensitive platinum utilization is to the content of the Nafion in the catalyst layer. On the other hand, reducing the PTFE ratio in the Nafion:Carbon:PTFE ratio from 0.66 to 0.33 does not seem to affect the platinum utilization much.

4 Conclusions

From the experimental analysis, the following conclusions can be drawn about the impact of ionomer content, Teflon content and platinum content on the performance of a direct methanol fuel cell.

1. A C/N ratio of 1.25 provides optimum cathode catalyst utilization. When the C/N ratio is decreased, the cathode catalyst utilization seems to decrease. 40% Pt/C shows a higher catalyst utilization value than 20% Pt/C. The C/N ratio seems to have a minimal impact on catalyst utilization when platinum black is used as catalyst.
2. The catalyst utilization is seen to be the highest when the N/P ratio is about six in the cathode catalyst layer. Platinum utilization is seen to be extremely sensitive to the Nafion content in the catalyst layer. Changing the Nafion content by a factor of 2 in the Nafion:Carbon:Teflon ratio in the catalyst layer is found to reduce the platinum utilization by over 20%.

Acknowledgements The author would like to thank the Director, ARCI, Hyderabad and DST, Government of India for financial assistance and ARCI for a fellowship to S. Deepalochani and support for this work. The author would also like to thank the Director, CFCT, Chennai, where the work was done. Further, the author would like to thank Dr. Ramya Krishnan for useful discussions and help with graphs.

References

1. Gancs L, Hult BN, Hakim N, Mukerjee S (2007) Electrochem Solid State Lett 10:B150
2. Wei ZD, Ran HB, Liu XA, Liu Y, Sun CX, Chan SH, Shen PK (2006) Electrochim Acta 51:3091
3. Farhar ZN (2004) J Power Sources 138:68
4. Pozio A, Francesco M, Cemmi A, Cardenelli F, Giorgi L (2002) J Power Sources 105:13
5. Raistrick ID, Van Zee JW, Kinoshita K, White RW, Burney HS (1986) Electrochem Soc Pennington 86:172
6. Raistrick ID US Patent No 4. 876:576
7. Ticianelli EA, Derouin CR, Redondo A, Srinivasan S (1988) J Electrochem Soc 135:2209
8. McBreen J (1985) J Electrochem Soc 132:1112
9. Tu WY, Liu WJ, Cha CS, Wu BL (1998) Electrochim Acta 43:3731
10. Paulus UA, Verizidus Z, Schnyder B, Kuhnke M, Scherer GG, Wokaun A (2003) J Electroanal Chem 541:77
11. Guangchun L, Pickup P (2003) J Electrochem Soc 150:C745
12. Velayutham G, Kaushik J, Rajalakshmi N, Dhathatreyan KS (2007) Fuel Cells 7:314
13. Tamizhmani G, Dodelet JP, Guay D (1996) J Electrochem Soc 143:18
14. Ticianelli EA, Beery JG, Srinivasan S (1991) J Appl Electrochem 21:597
15. Xiaoling C, Baolian Y, Ming H, Jingxin Z, Yaguang Q, Jingrong Y (1999) J Power Sources 79:75

16. Schmidt TJ, Gasteiger H, Stab GD, Urban PM, Kolb DM, Behm RJ (1998) J Electrochem Soc 145:7
17. Teng Z, Wang G, Wu B, Gao Y (2007) J Power Sources 164:105
18. Krishnamurthy B, Deepalochani S, Dhatha KS (2008) Fuel cells July 2008
19. Sehkyu P, Jong-Won L, Popov BN (2006) J Power Sources 163:357
20. Weber AZ, Darling RM, Newman J (2004) J Electrochem Soc 151:A1715