Jurnal Teknologi

Full paper

Study of the Variation of Catalyst Loading in Cathode for SPEEK/CSMM Membrane in Direct Methanol Fuel Cell (DMFC)

S. E. Rosli[a], M. N. A. Mohd-Norddin[a*], J. Jaafar[a], R. Sudirman[b]

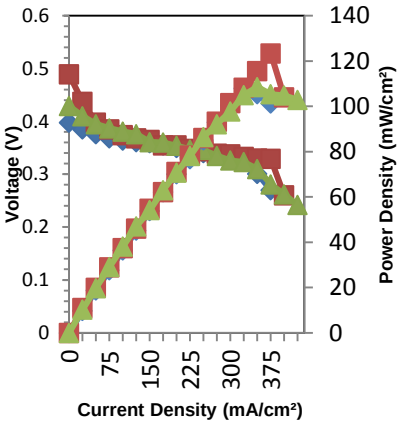
[a]*Advanced Membrane Technology Research Center (AMTEC) Material and Manufacturing Research Alliance (MMRA), Faculty of Petroleum and Renewable Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
[b]*Biomedical, Instrumentation & Electronic Research Group Infocomm Research Alliance, Faculty of Electrical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*

*Corresponding author: anam@petroleum.utm.my

Article history

Received :15 September 2013
Received in revised form :
17 November 2013
Accepted :15 January 2014

Graphical abstract



Abstract

Variation of anode catalyst loading for modified sulfonated poly (ether ether ketone) (SPEEK) with charged surface modifying macromolecules (cSMM) membrane was studied, in order to get the higher performance in DMFC. The best optimal anode catalyst loading was 4 mgcm^{-2} for 30% Pt/Ru based on our previous result for this application. The modified SPEEK/CSMM membrane was characterized to ensure its better performance in term of water uptake and methanol permeability. In cathode side, the effect of 5% and 10% Pd/C in 2,4 and 6 mgcm^{-2} of catalyst loading has been investigated with a fuel cell assembly. The preparation method of catalyst ink and membrane electrode assembly (MEA) was based on Dr. Blade method and hot pressing by using catalyzed diffusion media (CDM) method. The air flowrates were varied from 25-1000ml min^{-1}, while 1M methanol concentrations, 1 ml min^{-1} of methanol flowrate and 60°C operating temperature were kept constant. These parameters were tested on the performance of single cell DMFC with 4 cm^2 electrodes.The optimization catalyst loading will enhance the DMFC performance. It was found, the best optimal cathode catalyst loading was 4 mgcm^{-2} for 10% Pd/C with 4 mgcm^{-2} for 30% Pt/Ru in anode side for this application.

Keywords: Direct methanol fuel cell (DMFC); sulfonated poly (ether ether ketone) (SPEEK); charged surface modifying macromolecules (cSMM); catalyst loading

1.0 INTRODUCTION

The structure of electrode in direct methanol fuel cell (DMFC) normally is comprised of a catalyst layer and a diffusion layer, then being carbon paperor carbon cloth. It is challenge to develop an electrode with high stability and good electrical conductivity in the fuel cell environment [1]. The important part to improve the performance of DMFCs is the electrode structure as well as the interface between the membrane and the electrode [2]. Technology of fuel cell depends on two key materials which are membrane and electro-catalyst.

Nowadays, sulfonated poly (ether ether ketone) (SPEEK) get more attention to replace Nafion in DMFC [3-5]. The membrane surfaces of SPEEK is hydrophilic that have a tendency to favor water uptake and proton conductivity [6]. Improvement of membrane in hydrophilicity will conduct proton conductivity to be better. Modification of SPEEK with other polymer for example with cSMM have further improved performance in DMFC [7]. The main disadvantage of the DMFC system is the low power density that is caused by the poor kinetics of the catalyst reactions. In addition, cost and performance of DMFC depends greatly on catalyst used in the electrode [8].

Performance losses at cathode associated with methanol crossover arise due to most Pt-based cathode systems are catalytically active to methanol oxidation. The solution of this problem is to develop alternative oxygen reduction catalyst that are inactive to methanol oxidation through modified cathode structure and component [9]. Palladium particles were recognized as the ideal non-platinum catalysts for oxygen reduction reaction (ORR). ORR is employed cathode reaction in fuel cells. Palladium has 4 electron pathway for the ORR same as platinum and its activity for ORR is only surpassed by platinum [10].

Catalyst loading in electrodes is important parameter to control because it is related to cell performance. High catalyst loading is required in DMFs to achieve high power density but it also contributes to increased cost.[11] So, it is important to optimize the catalyst loading. SPEEK/cSMM membrane is very potential for replacing Nafion but had not been studied on the optimum catalyst loading. In this work, a DMFC using SPEEK/cSMM membrane with different cathode catalyst loading of palladium is develop to get the higher power density. Meanwhile, on anode side, 4 mgcm^{-2} of 30% Pt/Ru were used as reported as the best catalyst loading for anode in our previous work [12].

2.0 EXPERIMENTAL

2.1 Preparation of SPEEK/cSMM Modified Membrane

10 g of SPEEK was dissolved in 90 g DMAC to make a 10 wt% of original SPEEK solution. 0.416 g of CSMMs and 10 g of SPEEK was mixed to make 4 wt% of CSMM in total solid [13]. Before mixtures were cast onto a glass plate, both mixtures were stirred for 24 hours. Then, the membrane was dried at 100°C for 24 hours in a vacuum oven. The membrane was converted into H^+ - form by immersing it onto a 1M sulfuric acid solution for 24 hours at the room temperature. Lastly, the membrane was blotted dry with absorbent paper before it was air dried.

2.2 Preparation of Cathode Catalyst Ink

Carbon paper (TGP-H-120, Toray) was used on the anode and cathode side. The carbon paper designed to maintain electrical contact while not impeding mass transport of electrode reactants and products from the flow-fields and electrode surfaces are referred to as the gas diffusion layers (GDL). Nafion solution was prepared to afford the more close contact between the platinum clusters and polymer electrolyte membrane Catalyst inks were prepared by mixing each of 5% and 10% of Pd with Nafion solution (10 wt.-%, Fuel Cell Store) in ethylene glycol. Ethylene glycol was the best dispersion agent in catalyst ink for the better performance of the membrane electrode assembly. The prepared catalyst inks with loading 2, 4, 6 $mgcm^{-2}$ were uniformly casted on the carbon paper in a 4 cm^2 area for a cathode side. The loading was determined by weighing the dried MEA.

2.3 Preparation of MEA

The SPEEK/cSMM membrane was sandwiched between the anode and cathode. MEAs are prepared by hot pressing the membranes at 100°C for 90 seconds on the prepared electrodes.

2.4 Single-cell Test

DMFC performance test were carried out in a 4 cm^2 single cell MEA using a Propower (Fuel cell analyzer PRO200F) fuel cell test station. For each catalyst loading of anode, the DMFC test was carried out at 1M methanol and 60°C of operating temperature. The flow rate of methanol (anode side) is changed initially at 25 until 1000 ml min^{-1} respectively. The polarization curves of current, voltage and power are recorded using the built in computer program in propower which is interfaced with built in minicomputer and monitor screen.

3.0 RESULTS AND DISCUSSION

3.1 Cathode Catalyst Loading in 5% Pd

Figure 1 shows that the DMFC performance using 5% Pd in current density and power density with increasing cathode catalyst loading from 2 to 4 $mgcm^{-2}$. A further increase in catalyst loading from 4 to 6 $mgcm^{-2}$ gives the power density decreased by 43.98%. The maximum power densities obtain from each of catalyst loading is 38, 117.6 and 65.275 $mWcm^{-2}$ respectively. In order to increase the cell performance as well as the better kinetics of the oxygen reduction reaction (ORR), higher catalyst loading is needed. Based on our results, an optimal catalyst loading in the cathode is 4 $mgcm^{-2}$.

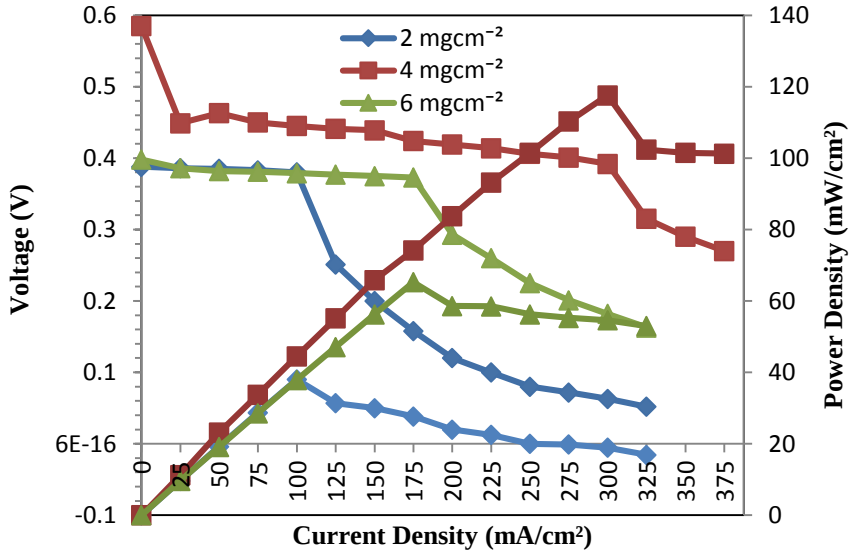


Figure 1 The power density and voltage of DMFC as a function of current density at different catalyst loading for 5% Pd

3.2 Cathode Catalyst Loading in 10% Pd

The result of DMFC performance using 10% Pd in Figure 2 show the performance initially improved when catalyst loading was increased from 2 to 4 $mgcm^{-2}$, followed by a decreased when catalyst loading is 6 $mgcm^{-2}$. Increasing catalyst loading led to a decrease in kinetics polarization loss and increases the cell performance. The kinetic polarization loss become small and a further increase in catalyst loading when the catalyst loading exceeded 4 $mgcm^{-2}$ made the catalyst layer much thicker and decrease in the DMFC performance. Therefore, the optimal cathode catalyst loading can be concluded to be 4 $mgcm^{-2}$. The maximum power densities obtain from each of the catalyst loading is 107.9, 123.375 and 108.5 $mWcm^{-2}$ respectively.

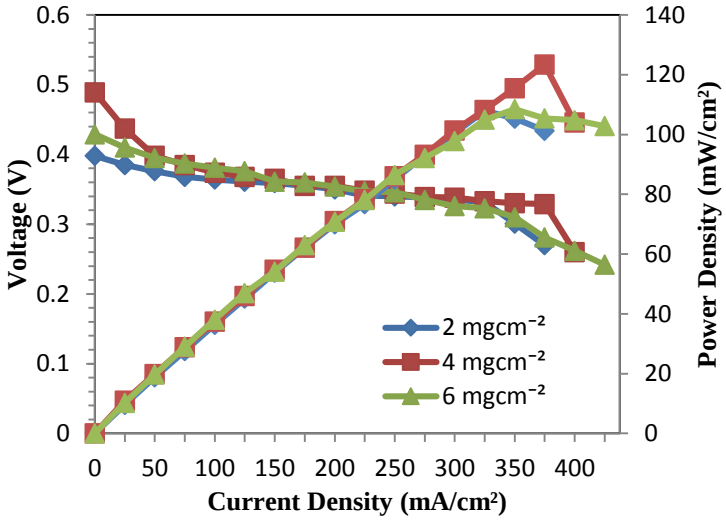


Figure 2 The power density and voltage of DMFC as a function of current density at different catalyst loading for 10% Pd

3.3 Performance Summary of DMFC

The summary of the influence increasing the catalyst loading at cathode for 5% and 10% Pd showed in Figure 3. Since DMFC performance is largely restricted by charge transfer kinetics, when operating in the kinetically controlled region, high catalyst loading should increase the cell performance. Comparing 10% Pd with 5% Pd, it gives the higher power density for each of catalyst loading. The increase of catalyst loading also increase the cell performance that can attributed the better kinetics of oxygen reduction reaction. However, the performance turns out to be insensitive to higher catalyst loading when the latter is sufficiently high for ORR. From the result we find that the fuel cell performance does not improve with catalyst loadings above 4 $mgcm^{-2}$ because the power density is decrease when passing from 4 to 6 $mgcm^{-2}$. Therefore, 4 $mgcm^{-2}$ would be a suitable catalyst loading for this application.

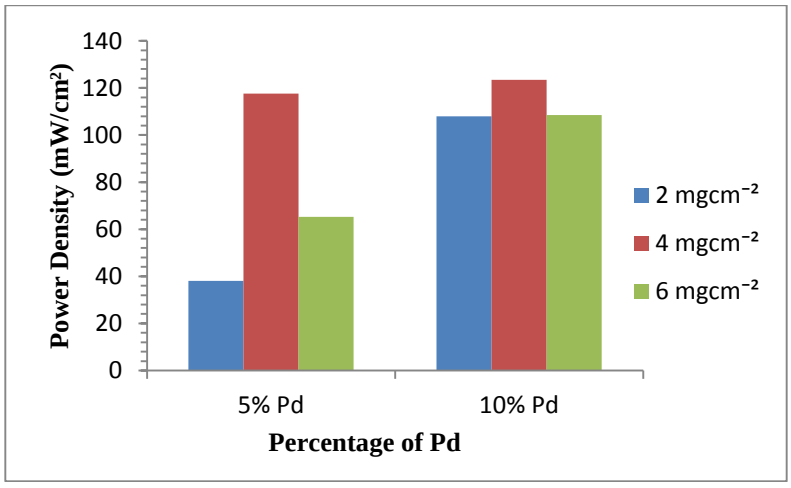


Figure 3 Summary of cell performance

4.0 CONCLUSION

Palladium particles were recognized as the ideal non-platinum catalyst for (ORR). Moreover, palladium is 70% less expensive than platinum. From the result, it show that using palladium in replacement of platinum at cathode still give the good performance in DMFC. In fuel cells, to get maximum power density, the higher cell voltage are required and high current density is predictable at lower overpotential (ORR).Catalyst loading in DMFC electrodes is important parameter to control because it is related to cell performance, electrode thickness and cost. Three catalyst loadings of 2, 4 and 6 $mgcm^{-2}$ were tested in 5% and 10% of Pd and 4 $mgcm^{-2}$ of Pd appears to be optimum. It was found, the best optimal cathode catalyst loading was 4 $mgcm^{-2}$ for this application. As a result, 4 $mgcm^{2}$ of 10% Pd is the best cathode catalyst loading based on SPEEK/cSMM membrane.

Acknowledgement

The author (S.E.Rosli) is thankful to the Ministry of Higher Education (MOHE) for the FRGS grants under the vote number of R.J130000.7842.4F132 for financial support and Research Management Centre (RMC), UTM for research management activities.

References

[1] Zainoodin, A. M., Kamarudin, S. K. & Daud, W. R. W. 2008. Electrode in Direct Methanol Fuel Cells. *International Journal of Hydrogen Energy*. 35: 4606–4621.

[2] Gogel, V. *et al.* 2004. Performance and Methanol Permeation of Direct Methanol Fuel Cells: Dependence on Operating Conditions and on Electrode Structure. *Journal of Power Sources*. 127: 172–180.

[3] Jones, D. J. & Rozière, J. 2001. Recent advances in the Functionalisation of Polybenzimidazole and Polyetherketone for Fuel Cell Applications. *Journal of Membrane Science*. 185: 41–58.
[4] Jung, H.-Y. & Park, J.-K. 2009. Long-term Performance of DMFC Based on the Blend Membrane of Sulfonated Poly(ether ether ketone) and Poly(vinylidene fluoride). *International Journal of Hydrogen Energy*. 34: 3915–3921.
[5] Yang, T. 2008. Preliminary Study of SPEEK/PVA Blend Membranes for DMFC Applications. *International Journal of Hydrogen Energy*. 33: 6772–6779.
[6] Norddin, M. N. a. M., Ismail, a. F., Rana, D., Matsuura, T. & Tabe, S. 2009. The Effect of Blending Sulfonated Poly(ether ether ketone) with Various Charged Surface Modifying Macromolecules on Proton Exchange Membrane Performance. *Journal of Membrane Science* 328: 148–155.
[7] Norddin, M. N. A. M. *et al*. 2008. Characterization and performance of Proton Exchange Membranes for Direct Methanol Fuel Cell: Blending of Sulfonated Poly(ether ether ketone) with Charged Surface Modifying Macromolecule. *Journal of Membrane Science*. 323: 404–413.
[8] Baldauf, M. & Preidel, W. 1999. Status of the Development of a Direct Methanol Fuel Cell. *Journal of Power Sources*. 84: 161–166.
[9] Reeve, R., Christensen, P., Dickinson, a., Hamnett, a & Scott, K. 2000. Methanol-tolerant Oxygen Reduction Catalysts Based on Transition Metal Sulfides and Their Application to the Study of Methanol Permeation. *Electrochimica Acta*. 45: 4237–4250.
[10] Álvarez, G. F., Mamlouk, M. & Scott, K. 2011. An Investigation of Palladium Oxygen Reduction Catalysts for the Direct Methanol Fuel Cell. *International Journal of Electrochemistry*. 1–12 .
[11] Hashim, N., Kamarudin, S. K. & Daud, W. R. W. 2009. Design, Fabrication and Testing of a PMMA-based Passive Single-cell and a Multi-cell Stack Micro-DMFC. *International Journal of Hydrogen Energy*. 34: 8263–8269.
[12] Rosli, S. E., Mohd-Norddin, M. N. A, Jaafar, J., Sudirman, R. 2013. Study on Catalyst Loading Using SPEEK/CSMM Membrane in DMFC. *Power Engineering and Optimizing Conference*. 13: 234–237.
[13] Rana, D. 2008. Charged Surface Modifying Macromolecules in Polymer Electrolyte Membrane. 49: 91–102.