

직접메탄올 연료전지에서 금속막을 이용한 메탄올 크로스오버 방지

심재희, 구일교, 허원기, 이용무
아주대학교 분자과학기술학과

Prevention of Methanol Crossover in Direct Methanol Fuel Cells (DMFC)
by a Barrier Concept

J. H. Shim, I. G. Koo, W. K. Her, and W. M. Lee
Department of Molecular Science and Technology, Ajou University

1. Introduction

Direct methanol fuel cells (DMFC) employing proton exchange polymer electrolyte have recently gained considerable interest because of their attractiveness as the power source for electronic devices or vehicular applications^{1, 2}. However, it suffers from the fuel crossover and its impact on cathode operation and the consequent penalty in system energy efficiency³⁻⁷. Efforts to circumvent the methanol crossover in DMFC have been made basically along three different strategies.

(1) A large group of researchers have focused on developing different types of membranes that would not allow the methanol crossover as much as Nafion does. (2) A new cathode material is being developed. (3) A barrier concept^{8, 9}, a film of a methanol impermeable but protonic conductor, such as a metal hydride, is inserted in a proton exchange polymer electrolyte, such as Nafion. As the barrier material, a palladium (Pd) foil can be used since it allows the transfer of hydrogen atoms only. This concept was employed in the past by Smotkin's group⁸ and the performance of DMFC was remarkably improved when the surface of the foil was treated with platinization. Since hydrogen diffuses in Pd as an atomic form while it moves through the solid polymer electrolyte as an ion, it has to be reduced or oxidized whenever it passes the interface formed by Pd and the electrolyte. Thus, if a favorable potential were applied on the interface such oxidation or reduction reaction would be facilitated. However, the past work employing the barrier concept relied solely on the reduction or oxidation of hydrogen on the barrier surface at the electrode potential established by the concentration of the involved species and also by the current density. In our study we applied a bias potential to the Pd foil so that the reduction or oxidation takes place at a much favorable potential. A study based on the concept similar to this was made in the

past to determine the diffusion constant of hydrogen atoms in Pd¹⁰⁻¹³. In this report we present the outline of our approach and some data that support the legitimacy of our approach.

2. Experimental

Electrodes fabrication. Commercial carbon diffusion electrodes loaded with Pt-Ru (2 mg cm⁻²) were used as the anode or cathode, respectively.

Fabrication of membrane-electrode assembly with the barrier (MEAB). Nafion[®] 117 was used in this study as the proton exchange membrane was prepared by the following procedures. The membrane was boiled in 3wt% H₂O₂ solution for 1 hour and then rinsed in boiling deionized water for 2 hours to remove any organic compounds. It was then boiled in 0.5M H₂SO₄ for 1 hour to remove metal compound and to exchange Na⁺ for H⁺ in the membrane and finally rinsed in boiling deionized water for 2 hours. The treated membrane was hot pressed to the anode and cathode separately (120°C, 70atm, 90sec) to form membrane-electrode-assembly (MEA). A 25 μm thick Pd foil (99.9%, Aldrich) coated with thin Nafion ionomer was sandwiched between the two MEA and hot pressed at low pressure (10 bar) to form the complete MEAB.

Charging Pd foil with hydrogen. The finished MEAB was now connected to a DC power source that provided electrolytic current between the cell anode and the foil cathode. While hydrogen gas instead of methanol was supplied to the anode an electrolytic current, about 30 mAcm⁻², was allowed to flow for 30 minutes between the foil (acting as the cathode) and the cell anode.

Cell operation. The experimental setup is shown in Fig. 1. The cell currents and terminal voltages were measured to plot the i-V curves. The terminal voltage control was realized by applying different load resistors between electrodes. The concentration of methanol was 1 M. The operational temperature of the cell was maintained at 65 °C.

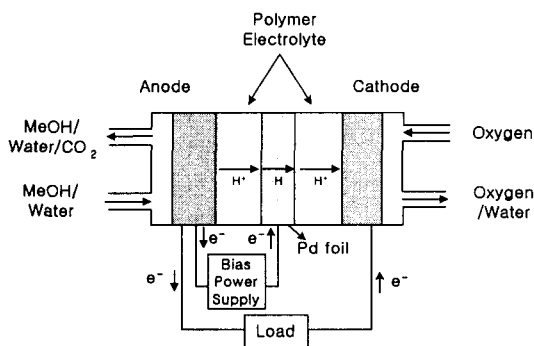


Fig.1. Experimental setup.

Application of a bias potential. A small power source was used as the provider of the bias current in the range of a few milli-amperes. The bias potential registered at the foil was almost constant in reference to that of the anode when a constant bias current was applied.

3. Results and Discussion

Performance of DMFC with Pd foil inserted The i - V curves of the DMFC with the foil inserted are shown in Fig.2. In the DMFC the effect of the bias potential application was much more striking than in the case of the PEMFC. The open cell voltage (OCV) of the DMFC with the insertion of Pd foil increased slightly from ca. 0.6 V to 0.7 V. There is a chance that blocking of the methanol crossover by the foil prevents the modification of the cathode potential that could lower the cell voltage.

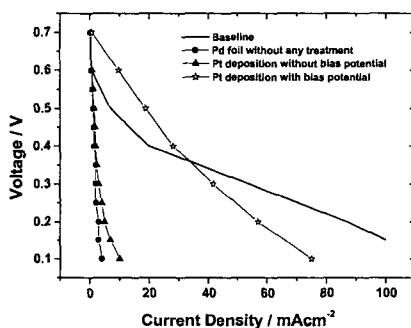


Fig.2. Performance of DMFC with Pd foil inserted.

Fig. 2 shows unique trends associated with the DMFC. Pt deposition improved the cell performance much more effective catalytic activity than the Pd foil without any treatment in helping the hydrogen reduction at the foil/Nafion interface in the DMFC.

The most remarkable result revealed in Fig. 2 was that when the current was maintained below ca. 40 mA cm⁻² the cells with the foil barrier outperformed the cell without the barrier. Only as the current density exceeded 40 mA cm⁻² the cell voltage then dropped more rapidly than that of the cell of no barrier. The results imply that at lower current densities the proton flux through the polymer electrolyte (Nafion) including the barrier was even higher than that through the electrolyte only.

The effect of temperature and methanol concentration Fig. 3 show the i - V curves of DMFC measured at various settings of the methanol concentration, respectively. It also show that in the cell with the barrier the change of concentration does bear almost no effect on the performance, as the current density is less than 40 mAcm⁻². The improvement of the proton flux is so large with placing the biased barrier that further improvement by changing the concentration becomes much less significant. Thus with

the current density limited under 40 mAcm^{-2} , changing the concentration from 0.1M to 2M did not make much difference in the cell performance. However, the concentration effect we can see that the effect is only clearly manifested under 0.5 M.

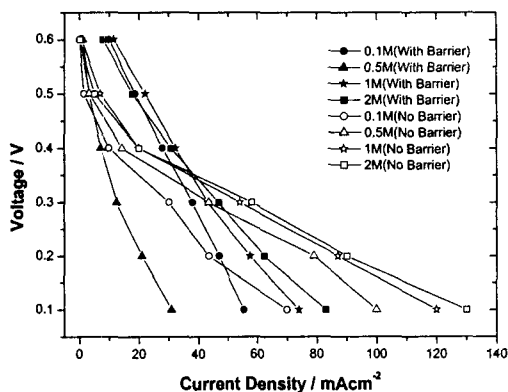


Fig.3. Various methanol concentration

4. Conclusions

Applying a bias potential on a Pd foil sandwiched between two sheets of Nafion in DMFC improved the performance of the cell in enhancing the hydrogen transfer rate through the foil while completely blocking the crossover of methanol. Most surprisingly, the cell with the biased foil barrier delivered higher power output than the cell of no barrier as long as the working voltage of the cell was maintained higher than 0.4 V. At such low current density the proton passage through the barrier is no longer the rate-determining step and thus the bias potential applied to the barrier can increase the proton flux significantly at the barrier/Nafion interfaces. But with the increase of the cell current, the charge transfer resistance at the foil/Nafion interfaces becomes the limiting factor for the overall conductance, thus the cell output falling below that of the cell of no barrier. At the low current region the change in the methanol concentration did not bear any effect on the cell performance.

Acknowledgements

The research was supplied by the Alternate energy Program through the Republic of Korea Ministry of Commerce, Industry and Energy.

5. References

1. A. Hamnett and G.L. Troughton, *Chem. Ind.*, **6**, 480 (1992)
2. X. Ren, P. Zelenay, S. Thomas, J. Davey and S. Gottesfeld, *J. Power Sources*, **86**, 111 (2000)
3. M. K. Ravikuma and A. K. Shukla, *J. Electrochem. Soc.*, **143**, 2601 (1996)

4. A. Heinzl, and V. M. Barragan, *J. Power Sources*, **84**, 70 (1999)
5. J. Cruickshank, and K. Scott, *J. Power Sources*, **70**, 40 (1998)
6. X. Ren, T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, *J. Electrochem. Soc.*, **147**, 466 (2000)
7. A. Kuver and K. Potje-Kamloth, *Electrochimica Acta*, **43**, 2527 (1997)
8. Cong Pu, W. Huang, K.L. Ley, and E.S. Smotkin, *J. Electrochem. Soc.*, **142**, L119 (1995)
9. W. C. Choi, J. D. Kim and S. I. Woo, *J. Power sources*, **96**, 411 (2001)
10. E. Gileadi, E. kirowa-Eisner and J. Penciner, *Interfacial Electrochemistry*, P.472 (1975)
11. S. Schuldiner and J. P. Hoare, *J. Electrochem. Soc.*, **103**, 178 (1956)
12. E. Gileadi and M. A. Fullenwider, *J. Electrochem. Soc.*, **113**, 926 (1966)
13. V. Breger and E. Gileadi, *Electrochim. Acta* **16**, 177 (1971)