

## Hydrogen Transport through Palladium Foil Placed in Nafion Electrolyte of H<sub>2</sub>/O<sub>2</sub> Fuel Cellsorption.

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### Abstract

Placing a hydrogen conducting, methanol impermeable metallic barrier like palladium (Pd) is a well-known method for preventing methanol crossover through solid polymer electrolyte for direct methanol fuel cells (DMFC). Applying a bias potential between the anode and the barrier can further develop this concept so that the hydrogen transfer rate is enhanced. Since hydrogen diffuses in Pd as atomic form while it moves through nafion electrolyte as ion, it has to be reduced or oxidized whenever it passes the interface formed by Pd and the electrolyte. We performed experiments to measure the hydrogen transport through the Pd membrane placed in Nafion electrolyte of hydrogen/oxygen fuel cell (PEMFC). Applying a bias potential between the hydrogen electrode of the cell and the Pd membrane facilitated the hydrogen passage through the Pd membrane. The results show that the cell current measured with the Pd membrane placed reached almost 40 % the value measured with the cell without Pd membrane. It was found that the current flown through the bias path is only a few percent of the cell current.

## 1. Introduction

Direct methanol fuel cells (DMFC) employing proton exchange polymer electrolyte have recently gained considerable interest owing to their attractiveness as a candidate for vehicular applications. One of the major chemical problems in DMFC is fuel cross over and its impact on cathode operation and system energy efficiency [1,2]. The vast majority of the polymer electrolyte fuel cell work has been performed using Nafion as the electrolyte. As far as DMFC is concerned, the electrolyte has significant disadvantages. The methanol crossover rate across Nafion 117 is about  $100 \text{ mA/cm}^2$  and the resulting cathode performance decay as well as the loss of fuel are simply not acceptable.

There have been several attempts to circumvent the crossover. One approach so far is to use basic polymers doped with inorganic acids [3,4]. A tenfold decrease in the methanol crossover resulted from the use of those polymers, but a complete blocking is still far from realization. An alternative approach is based on a barrier concept [5] or on morphology change of the membrane [6]. In the design utilizing the barrier concept, a film of a methanol impermeable protonic conductor, such as a metal hydride, is inserted in proton exchange polymer electrolyte such as Nafion. A barrier such

as Pd foil placed in Nafion electrolyte can basically block transportation of any molecules or ions except hydrogen. As is well known, hydrogen atoms are dissolved in Pd lattice readily. The maximum atomic ratio of H to Pd reaches almost 0.8. As shown in Fig. 1 hydrogen ions approaching the interface between Pd and Nafion should be reduced first and then converted into H atoms. Hydrogen atoms are first adsorbed on the Pd surface and then, diffuse through the Pd lattice in atomic form. As the atoms reach the other surface of Pd barrier interfacing with Nafion, these atoms now have to oxidized again and are transported as ions until they reach the oxygen electrode (cathode). But the past work employing this approach relied solely on the reduction or oxidation of hydrogen on the barrier surface at near the thermodynamic potential established by the concentration of the involved species [5]. The modification of the potential of the barrier can make the reduction or oxidation at either surface of the barrier take place at much favorable overpotential. In our study we first applied the barrier concept to proton exchange membrane fuel cell (PEMFC). A bias potential was then applied to a Pd foil placed in the membrane. If, with such arrangement, it is proven that the barrier with bias potential does certainly work, the concept can be directly applied to DMFC. One aspect to be considered in such application is that the current flown

through the bias path should be a small fraction of the fuel cell current. In this report we present the outline of our approach and some data that support legitimacy of our approach.

## 2. Experimental

### Electrodes

Commercial carbon gas diffusion electrodes loaded with platinum ( $0.4 \text{ mg Pt cm}^{-2}$ , Globe Tech Co.) were used as both the cathode and the anode. To increase the three-dimensional contacting areas between the solid electrolyte and the catalytic platinum layer, the catalytic surface was impregnated with  $0.8 \text{ mgcm}^{-2}$  Nafion® (Aldrich Chemical Company). The electrodes were dried for 2 hours at  $80^\circ\text{C}$  to remove residuary solvents like isopropyl alcohol and water. The smooth Pt electrode with low surface area was also prepared by evaporating platinum of about  $300 \text{ \AA}$  thickness on a carbon paper.

Nafion® 117 was used in this study as the proton exchange membrane. The following procedure was used in the pretreatment of the membrane: (1) The membrane was boiled in 3 wt%  $\text{H}_2\text{O}_2$  solution for one hour; (2) then rinsed in boiling deionized water for 2 hours to remove any organic compounds; (3) boiled in 0.5M  $\text{H}_2\text{SO}_4$  for one hour to remove metal compound and to exchange  $\text{Na}^+$  with  $\text{H}^+$ ; (4) and finally rinsed in boiling deionized water for 2 hours.

### Membrane-Electrode Assembly (MEA)

The treated membrane was hot pressed to Pt ( $0.4 \text{ mgcm}^{-2}$ ) anode and cathode separately ( $120^\circ\text{C}$ , 70atm, 90sec). A 24  $\mu\text{m}$  thick Pd foil (99.9%, Aldrich) was thin coated with Nafion ionomer. Fig. 2 shows the Pd foil sandwiched between the two Nafion membranes and hot pressed at low pressure (10atm). Electrochemical deposition of Pd was made on some of the foil samples to increase their surface area. During the deposition the foil was used as the cathode in 2%  $\text{PdCl}_2$  solution (dissolved in 2N  $\text{HCl}$ ). The hydrogen or oxygen gas was fed into the anode or cathode of PEMFCs through a humidifier that had been insulated and heated. The temperatures of the electrochemical cell and humidifiers at the cathode and the anode were set at  $60^\circ\text{C}$ ,  $65^\circ\text{C}$  and  $70^\circ\text{C}$ , respectively [7]. The cell currents and terminal voltages were measured to plot the  $i$ - $V$  curves. In all experiments, the total flow rate of the gas mixture was  $300 \text{ ml min}^{-1}$  while the pressure of the mixture was set to be one bar. The terminal voltage control was realized by applying different load resistors between electrodes.

### Application of a bias potential

Fig. 3 shows the application of a bias potential on the Pd foil against the hydrogen electrode (anode). A potentiostat (EG&G Model 263A) in its galvanostatic

mode or a voltage divider with high resistance (over one mega ohm) was used to apply a bias potential to the Pd foil with respect to the anode. A DC battery and a resistor of megaohm range can provide a bias potential with drawing a very low current of 1 mA range through the bias circuit.

### 3. Results and Discussion

The complete cell arrangement is shown in Fig. 4. Also shown in the figure are the electrochemical potentials of hydrogen, oxygen electrodes and the Pd barrier. Although the surface of Pd foil is rather smooth, the microscopic details of its terrain should be rough. When this foil is pressed against Nafion film, the interface would not achieve a full contact between the constituting atoms or molecules of each phase. A better contact can be achieved if the foil surface is coated with the Nafion ionomer. Better contact reduces the resistance at the interface. The cell performance with or without the ionomer coating is shown in Fig. 5. It clearly shows that the ionomer treatment remarkably improved the cell performance.

With the foil treated with the ionomer another improvement in the cell performance was achieved when a bias potential is applied at the foil. The performance of the cell with or without the bias application is shown in Fig. 6.

Fig. 6 shows that application of the bias potential on the foil also contributes for improvement of the cell performance. At the hydrogen electrode (anode) the hydrogen molecules are oxidized sending electrons to external circuit and protonic ions to the opposing oxygen electrode through Nafion electrolyte. Without voltage modulation of the Pd foil, the electrochemical potential of the foil is determined by the concentrations of hydrogen atom or ion at the interface. The *i*-*V* curves shown in Fig. 6 confirm that the Pd foil with the voltage modulation exhibits a large improvement in performance.

But there should be an optimum value in the bias potential applied on Pd barrier. For example, at 0.3 V the cell current increased from 5 to 30 mAcm<sup>-2</sup>. But if the bias potential is increased beyond a critical value that is around -0.2 V against the anode, the cell performance starts to decrease. It should be reminded that a favorable potential at one interface where the hydrogen reduction reaction occurs has the adverse effect at the other interface where the oxidation reaction occurs. Thus an optimal bias potential or current should exist. The dependence of the cell performance on the bias current is shown in Fig. 7. As the bias current density was increased over 3 mAcm<sup>-2</sup> the cell performance was deteriorated significantly. These bias currents correspond to bias potential in the range of 0.05 ~ -0.15 V referred to the anode. It

confirms the existence of the optimum bias value.

Going back to the point of reducing the resistance of the interface between the foil surface and the polymer electrolyte, an increase of the interfacial area certainly should be a contributing factor. Electrochemical deposition of palladium on the foils surface increased the surface area substantially. From the cyclo-voltammogram of the foil shown in Fig. 8 we can see that the surface area of the foil after deposition is about ten times higher than that of untreated foil. The effect of the surface area of the Pd foil on i-V curve is shown in Fig. 9.

Throughout the entire voltage range of the cell, the current flowing through the bias path was adjusted to be about  $3 \text{ mAcm}^{-2}$ , which is only a few percent of the cell current that ranges from 100 to  $300 \text{ mAcm}^{-2}$ . It is true that the performance of the cell with the barrier is still far below that of the cell without the foil (the baseline). At 0.4 V the cell with the modification delivers only 40% of the current of the baseline. However, the 25 m Pd foil is too thick as a barrier, particularly the operating temperature is much below  $90^\circ\text{C}$ . If a thin, preferably in the range of hundred nano meter and continuous Pd film can be fabricated, the cell performance can be greatly improved with the potential modification on the inserted Pd barrier. Furthermore, such a thin Pd film does not have to be sandwiched between two Nafion sheets.

As long as a direct contact between the Pt catalyst of the anode and Pd barrier can be avoided, Pd film can be placed right next to and hot pressed against the anode to reduce the thickness of MEA. Thus the barrier concept demonstrated with PEMFC can be extended to DMFC.

#### 4. Conclusions

To prove a barrier concept that could be applicable to DMFC a Pd foil was placed to nafion electrolyte of PEMFC and the cell performance was tested. Even though the performance was much lower than that of the cell without the barrier, it steadily improved by making a series of treatments on the barrier surface. The treatment that contributed for improving the performance includes coating of the surface of the Pd foil with Nafion ionomer, depositing Pd on the foil surface so that its surface area is increased and finally application of a bias potential on the foil. The terminal voltage at  $50 \text{ mAcm}^{-2}$  jumped from below 0.2 V to 0.7 V after the series of the treatments. The power consumption for such modification was less than 1 % of the operational power of the cell. However, the power density of PEMFC even after such treatments is still in the range of  $0.035 \text{ Wcm}^{-2}$  and it has to be improved to meet requirements expected for practical use.

## Acknowledgements

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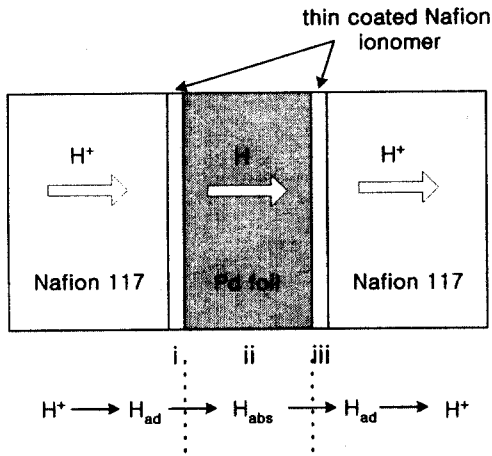


Fig. 1 Hydrogen transport through Nafion/Pd/Nafion

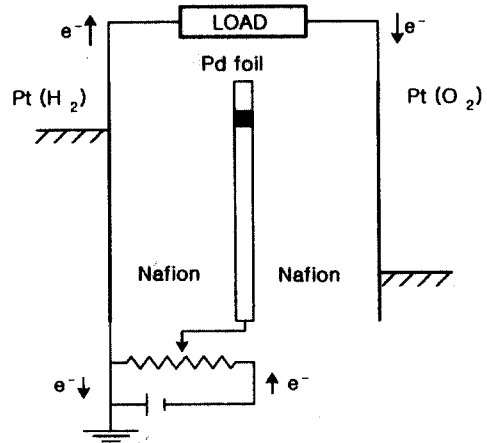


Fig. 3 Adjustment of the potential at the Pd foil with respect to anode and cathode

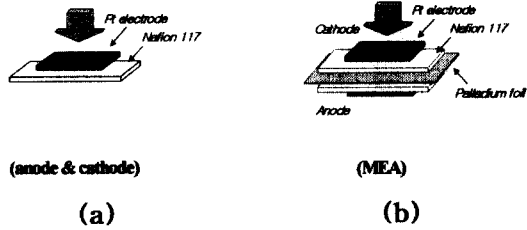


Fig. 2 Membrane-Electrode Assembly (MEA); (a) Anode and cathode and (b) MEA

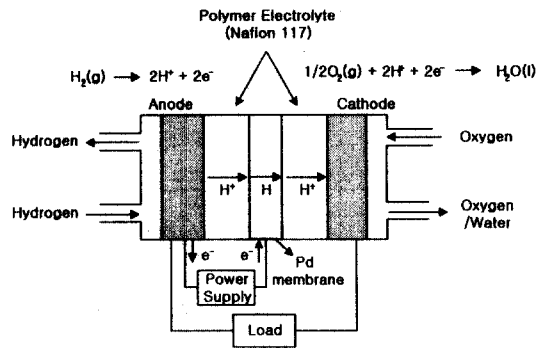


Fig. 4 Experimental setup

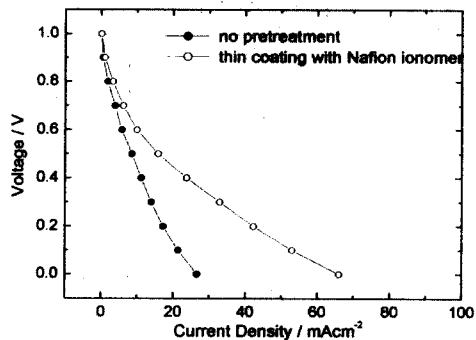


Fig. 5 Effect of Nafion ionomer pretreatment of Pd foil surface on the cell performance

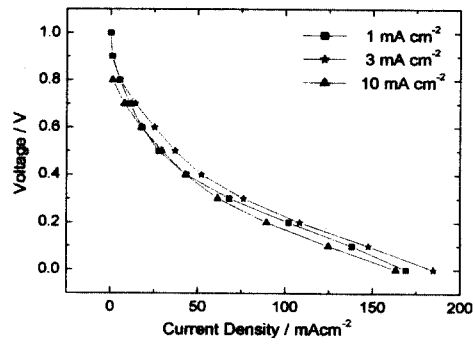


Fig. 7 Determination of optimum bias potential

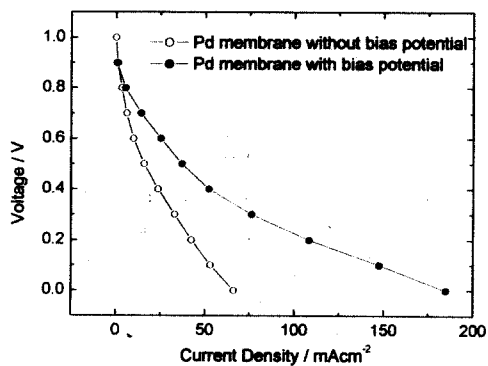


Fig. 6 Effect of bias potential application at the Pd foil on the cell performance

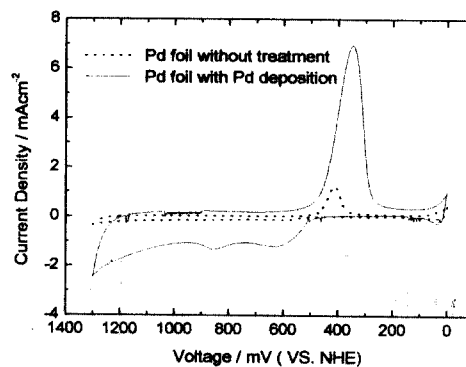


Fig. 8 Cyclic voltammogram of Pd foil



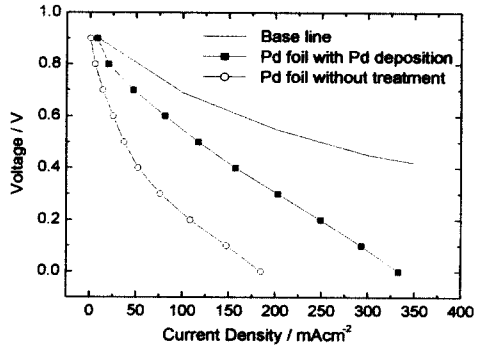


Fig. 9 Effect of surface area increase of the Pd foil on the cell performance