

H₂/O₂ 연료전지의 나피온 전해질에 삽입된 팔라듐 막을 통한

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Hydrogen Transport through Palladium Foil Placed in Nafion Electrolyte of H₂/O₂ Fuel Cell

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The major technical problem preventing direct methanol fuel cell (DMFC) from being a legitimate candidate as a power source is crossover of methanol molecules through polymer electrolyte like nafion. Naturally the research has been focused on inventing efficient ways to circumvent the crossover problem. It is directed along two avenues; first in developing polymers that does minimize the transport of methanol molecules through it and the second in placing a barrier in the electrolyte to block the passage of methanol molecules. As the barrier material a palladium (Pd) membrane can be used since it allows the passage of hydrogen atoms only. 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. 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 30 % 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. The efficiency of hydrogen transport through the foil depends on its surface area.

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 mA cm⁻² and the resulting cathode performance decay as well as the loss of fuel are simple 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]. In this design, a film of a methanol impermeable protonic conductor, such as a metal hydride, is inserted in proton exchange polymer electrolyte, such as nafion. 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. In our study we applied a bias potential to the Pd membrane so that the reduction or oxidation takes place at much favorable overpotential. 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

The electrode-polymer electrolyte assembly was fabricated as follows. First, the Nafion117 membrane underwent ion exchange treatment in sulfuric acid to exchange Na^+ with H^+ . The treated membrane was hot pressed to Pt (0.4mgcm^{-2}) anode and cathode separately (120°C , 70atm , 90sec). A $24\ \mu\text{m}$ thick Pd foil (99.9%, Aldrich) was thin coated with nafion ionomer. Pd foil was sandwiched between the two Nafion membranes and hot pressed at low pressure (10atm). Hydrogen and oxygen gases were supplied into the Pt cathode and anode after being humidified. The cell temperature was maintained at 60°C . The cell performance curves were measured under the terminal voltage control realized by applying different load resistors. A DC power source was used to apply a bias potential to the Pd foil with respect to the hydrogen electrode.

3. Results and Discussion

Figure 1 shows a schematic of the experimental arrangement. Also shown in the figure are the electrochemical potentials (or the Fermi energy level) of hydrogen, oxygen electrodes and the Pd film. At the hydrogen electrode the hydrogen molecules are oxidized at the platinum electrode surface sending electrons to external circuit and protonic ions to the opposing oxygen electrode through nafion electrolyte. Without voltage modulation the Fermi level of Pd film (E_{F}) is determined by the concentrations of hydrogen atom or ion at the interface. Using a power source the electrode potential is raised to $E_{\text{F}2}$ at which hydrogen reduction is facilitated since $E_{\text{F}2}$ is an overpotential for hydrogen reduction. Figure 2 shows the cell current, i , vs. the terminal voltage, V , for the H_2/O_2 fuel cell with the Pd film inserted in the nafion electrolyte. The i - V curves show that the Pd film with the voltage modulation exhibits a large improvement in performance. As the overvoltage $E_{\text{F}2}$ is increased (which was materialized by imposing higher current) the i - V curves exhibit a steady improvements. A treatment of the Pd/nafion interface by coating the Pd foil with Nafion ionomer further improved the performance as shown in figure 3. This is believed to be due to the reduction of resistance at the interface. The effect of the surface area of the Pd foil on i - V curve is shown in figure 4. The foil of higher surface area was made by depositing electrochemically on both sides of a smooth foil. The cyclo-voltammogram of the foil with deposition shows that its surface area is about seven times higher than that of untreated foil. As seen in figure 4, the voltage drop of the treated Pd is much smaller than that of the smooth Pd once a wide range of current density.

References

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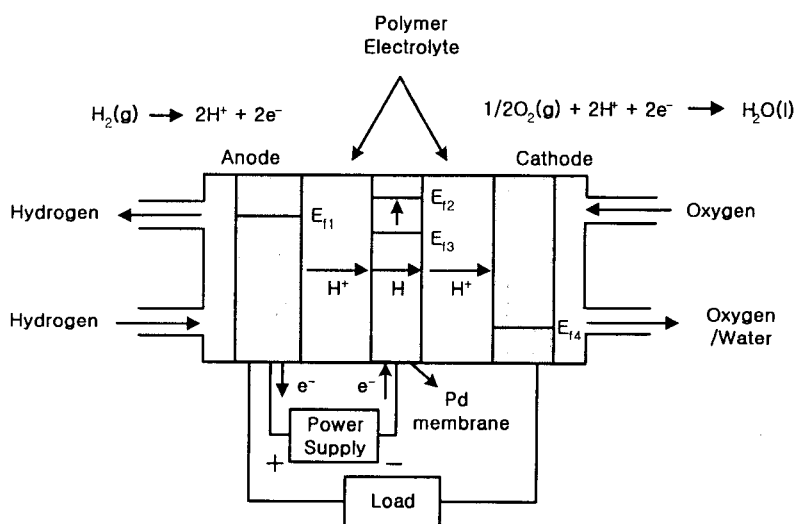


Fig 1. The schematic of experimental setup

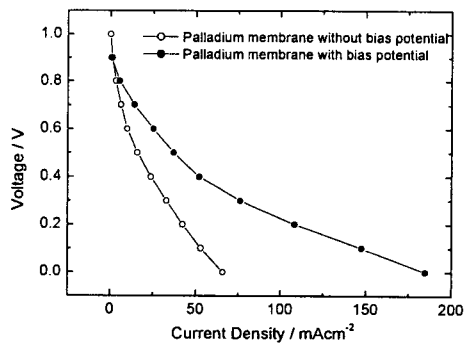


Fig 2. I-V curves of H₂/O₂ fuel cell in which a palladium foil is inserted to regulate the hydrogen passage

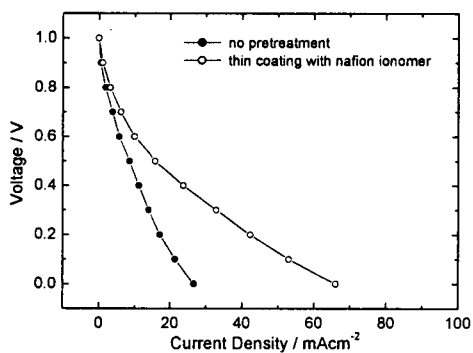


Fig 3. I-V curves of H₂/O₂ fuel cell in which the Pd foil is coated with Nafion ionomer

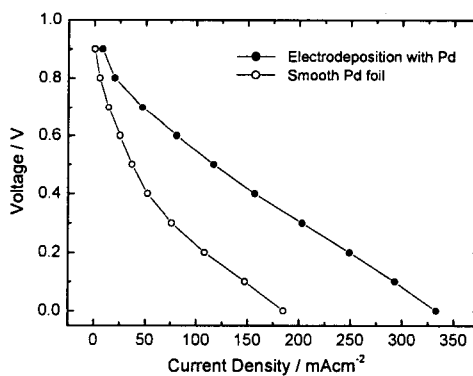


Fig 4. I-V curves of H₂/O₂ fuel cell in which a palladium foil electrodeposited with Pt