

고체고분자 전해질 계면에 접한 수소 산소 혼합 가스의 전압전류 특성

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Voltage-Current Profiles of Hydrogen-Oxygen Mixture Gas
at Polymer Electrolyte Interface

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요 약

전해질로서 Nafion[®]과 같은 고체고분자막과 수소/산소 가스가 계면을 형성할 경우의 전압전류특성을 측정하였다. 사용된 가스는 수소와 산소의 조성비를 달리하여 혼합한후 공급하였다. 사용된 전극은 상업용 탄소 기체 확산 전극을 이용하였으며 전극의 분산된 촉매와 전해질과의 접촉을 용이하게 하기위해 5% Nafion[®]을 발라주었다. 직류전원 공급장치를 이용하여 산화 전극과 환원 전극에 걸어주는 전압을 조정하였다. 전압전류의 분석결과로부터 에너지효율은 수소/산소혼합물의 수소농도에 예민하게 의존함을 알 수 있었다.

Abstract

Voltage-current profiles are measured when hydrogen-oxygen gas is in contact with solid polymer membrane (Nafion[®]) as the electrolyte. The feed gas is prepared by mixing

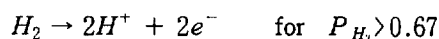
hydrogen and oxygen gas in various ratios. The carbon gas diffusion electrodes contacting the electrolyte are treated by platinum catalyst. The platinum surface is impregnated with a 5% Nafion[®] solution to ensure its good surface contact with the electrolyte. The constant voltage between anode and cathode was applied by a DC power supply. The results on the profiles show that the energy efficiency critically depends on the hydrogen concentration in H₂/O₂ mixture gas.

1. Introduction

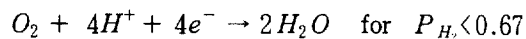
In recent years there have been so much interests in the fuel cell developments using solid polymer membrane. Because of the advantages of solid electrolyte over liquid electrolyte mainly in terms of simplicity in fabrication, solid polymer membrane fuel cells have been regarded as a promising candidate for transportation applications. A practical method for supplying hydrogen fuel for the fuel cells is to reform the primary hydrocarbon into a hydrogen rich gas. But this method still needs some kind of purification process to remove impurities such as CO. The purification processes include pressure swing adsorption (PSA), high temperature diffusion through a metal membrane, solvent adsorption of CO and CO₂, low temperature water-gas-shift reaction, preferential oxidation (PROX) and internal preferential oxidation^[1]. For the case of using fossil fuels as the raw material for producing hydrogen gas, the impurities such as CO have to be removed before use in fuel cells^[2].

On the other hand new methods for hydrogen generation have been reported as shown in metal/water reaction using electrical discharges

or plain high surface contacts. H-Power Corporation suggested a method in which iron sponge reacts with water to produce hydrogen at over 700°C. The feasibility on incorporating this method to fuel cells has been studied^[3]. Hydrogen can be generated by electrical discharge through metal/water system^[4] or through fuel electrode placed in water^[5-7]. It is also known that radiolysis of water by nuclear energy generates the mixture of hydrogen and oxygen. When the H₂-O₂ mixture is to be used for the fuel cell, the electrode utilizing the mixture can perform in either way as hydrogen or oxygen electrode depending on the mixing ratio^[8]. For example when platinized electrode utilizes the mixture gas in contact with liquid electrolyte, the electrode acts as either the hydrogen electrode



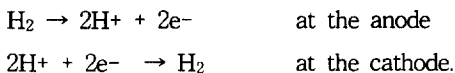
or the oxygen electrode



When a bright platinum is used as the electrode instead of platinized platinum, a hydrogen-oxygen mixed potential is established

for the whole range of hydrogen mole fraction. This phenomenon is ascribed to the slow progress of $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ reaction at the low surface electrode compared to the diffusion rate.

It has not been reported that the phenomenon described above also applies to the fuel cell system with solid polymer electrolyte. If the electrode utilizing the mixture gas is in contact with the polymer membrane electrolyte and acts as either hydrogen or oxygen electrode, the gas component at the other electrode should be oxygen or hydrogen, respectively, in order to make the cell energy-producing system, namely fuel cell. Instead, we arranged the cell configuration so that it acts as a material producing (hydrogen separating) system,



If a pure hydrogen gas is used at the anode, the voltage required to derive the above reaction should mainly come from the ohmic drop across the polymer membrane, assuming that the overvoltage of the hydrogen electrode is low. When the mixture gas of varying ratio is used at the anode, there are possibilities of mixed potential establishment or increase of hydrogen overvoltage due to interference of its oxidation (anodic) reaction by oxygen, namely altering the nature of the electrode surface. Such possibilities, if the cell is rearranged into the fuel cell, would lower the energy density or decrease the fuel cell voltage. The applied voltage between the electrodes then should manifest the combination of the iR drop across the membrane and the

over-voltage at anode.

$$\eta = ViR + \eta_{\text{anode.}}$$

This study is aimed at determining at what energy efficiency hydrogen can be separated from oxygen as its mole fraction varies. We have not attempted to discern the energy loss mechanism. We simply tried to measure the current due to proton conduction and the applied voltage, comparing them with the i - V characteristics of the H_2 - O_2 fuel cell. One final word—the hydrogen-oxygen gas easily explodes in water-free environment if electric spark or catalytic surface is available. For a hydrogen-oxygen-water vapor system, water vapor significantly reduce the probability of the explosive hydrogen-oxygen reaction^[9]. In this study, the mixed gas of hydrogen and oxygen is saturated with water vapor.

2. Experimental

Nafion 115(equivalent weight=1100, 0.127 mm thickness ; Du Pont) was used in this study as the polymer membrane. The membrane was prepared by following procedures. In order to remove organic compounds the membrane was boiled in 2.84 wt.% H_2O_2 solution for 1 hour. Then, it was rinsed in boiling deionized water for 2 hours. In order to remove metal compound on the membrane, it was boiled in 0.5M H_2SO_4 for 1 hour. Finally, it was rinsed in boiling deionized water for 2 hours. Commercial carbon gas diffusion electrodes(0.4 mg Pt/cm², Globe Tech Co.) are used as both

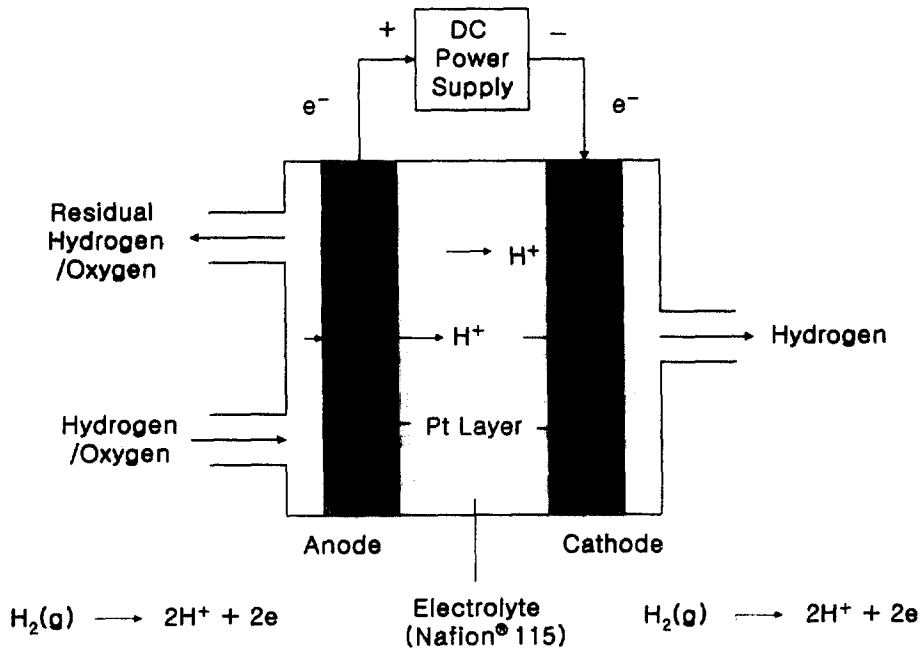


Fig. 1 The principle of a hydrogen separation device

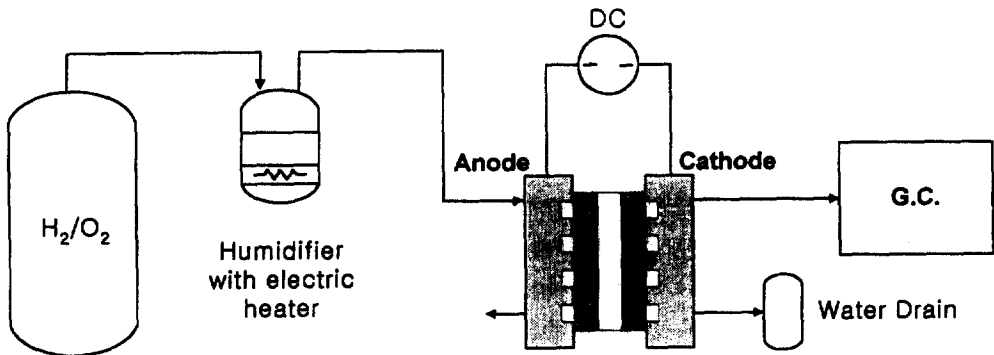


Fig. 2 Schematic of the experimental apparatus for the hydrogen separation using solid polymer membrane

the cathode and the anode. In order to increase the three dimensional contacting areas between solid electrolyte and platinum layer, the platinum surface is impregnated with a 5%

Nafion solution(Aldrich Chemical Company). The electrodes were dried in the dry oven for 2 hours to remove residential solvent like isopropyl alcohol and water. The pretreated

membrane and electrodes were bonded together by heating the components under 130 °C and 1000 atm for 3 min.

The principle of the electrochemical separation of hydrogen gas using polymer is shown in Fig. 1 A schematic diagram of the experimental apparatus for the hydrogen separation is shown in Fig. 2 Viton gasket, carbon block, copper current collector are secured to both the sides of the membrane and electrode assembly using bolts and nuts. The mixed gas containing hydrogen and oxygen was analyzed by a gas chromatograph (Hewlett-Packard 5890) and was fed into the anode through humidifier which was insulated and heated. Also, the line from humidifier to anode was heated and insulated by heating band. The temperature of the separation device and humidifier were set at 50°C and 60°C, respectively. The pressure of the supplying gas into the anode was measured using a pressure sensor (VALCOM®). The potential between the anode and cathode was adjusted by a DC power supply to ensure a certain current to flow between them.

3. Results and Discussions

Fig. 3 shows the current for hydrogen transport through the proton exchange membrane (Nafion®) as the function of the applied voltage and the hydrogen content in its mixture with oxygen. The purity of the hydrogen gas separated was tested using gas chromatography. Its concentration was near 100%. Fig. 3 shows that when the hydrogen

percentage falls to the value lower than the stoichiometric value 67%, the applied voltage between the anode and the cathode should be at least 1V, indicating that the energy efficiency is very low. This low efficiency is ascribed to the fact that the anode contacting the mixture gas now acts as the oxygen electrode. In other words, with the pure hydrogen gas contacting the cell should act now as the fuel cell as P_{H_2} falls below 0.67. The external power supply not only provides the voltage due to the ohmic loss across the polymer electrolyte but also compensates the electro motive force (emf) established between the electrodes owing to the sudden reversal of the system to the energy producing one (fuel cell). On

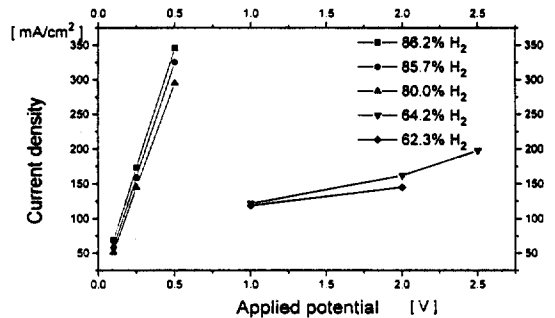


Fig. 3 Current density vs. applied electrical potential difference

the other hand, as the hydrogen concentration increases to a value over 67%, there is no need to compensate the emf establishment. When the hydrogen concentration is over 80%, the voltage to induce about 50mA/cm² of the current density was around 0.1V.

The electrical power necessary to purify the hydrogen gas from the mixture of various

Table 1 The applied voltage which draws 100 mA/cm² current density for the hydrogen separation from its oxygen mixture.

	PEMFC	86.2% H ₂ conc.	85.7% H ₂ conc.	80.0% H ₂ conc.	64.2% H ₂ conc.
Potential (V)	0.78	0.145	0.164	0.182	~0.604**
Power (mW/cm ²)	78	14.5	16.4	18.2	60.4
Power ratio*** (%)		18.6	21.0	23.3	77.4

* Fuel cell voltage

** It was estimated by linear regression

*** The ratio of the power consumption for the separation to the power generation of the PEMFC

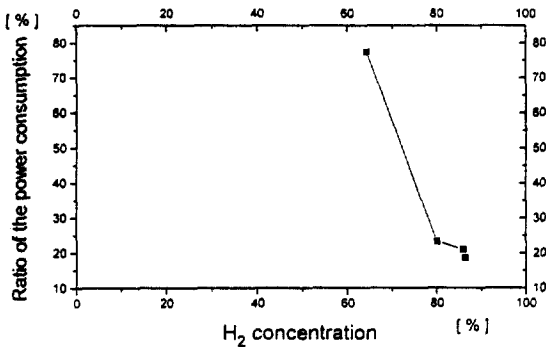


Fig. 4 The ratio of the power consumption for hydrogen separation to the power generation from PEMFC vs. hydrogen concentration

concentration is obtained by finding from Fig. 3 the applied voltage which draws a certain current density. The voltages which draws 100mA/cm² current density are shown in Table 1 for the mixtures of varying hydrogen concentration. We did not perform the test for 100% pure hydrogen. The i-V plot for the pure gas should manifest

mainly the iR loss through membrane. To obtain the genuine power consumption value, the iR loss of this pure hydrogen should be subtracted from the power values shown in Table 1. The cell voltage of PEMFC(Proton Exchange Membrane Fuel Cell) vs. current density in ref.10 was used as the reference line, and the ratio of the power consumption for hydrogen separation to the power generation from PEMFC is also shown in Table 1. These power ratio clearly indicates that as the hydrogen concentration reaches near 86%, the power ratio falls below 19%. As the hydrogen concentration falls to 64%, lower than the stoichiometric value(67%), the ratio increases drastically as expected. In this case, the applied voltage should compensate any development of fuel cell voltage in addition to taking account of iR loss through the membrane and the anodic overvoltage. It is not clear yet what causes the decrease in energy efficiency with higher oxygen content. It could be due to the combination of oxygen interference in hydrogen oxidation kinetics by altering the chemical nature of the electrode surface and the occurring of local oxidation-reduction at mixed potential. More through investigation should be done to discern this aspect.

4. Conclusions

When a cell is constructed in such a way that it separates hydrogen from its mixture with oxygen using an external power source, the energy efficiency critically depends on the hydrogen mole fraction. When the hydrogen mole fraction is lowered from 0.86 to 0.8, it is found

that the energy efficiency drops by more than 10% on average. The decrease in the energy efficiency could be ascribed to the interference of the hydrogen anodic kinetics by coexisting oxygen.

Acknowledgment

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