Reports

Polarization Characteristics of Ion-Exchange Membrane Fuel Cells*

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The performance of the fuel cell consisting of platinized nickel screen electrodes and an anion-exchange membrane equilibrated with an aqueous solution of potassium hydroxide, and that consisting of platinized platinum screen electrodes and a cation-exchange membrane equilibrated with an aqueous solution of sulfuric acid, were studied. The polarization characteristics of the anodes and the cathodes of these cells were evaluated. The effective area of the electrodes was 4.8 cm² each. The cell was operated using commercial hydrogen and oxygen at a constant temperature. The potentials of the electrodes were measured versus an auxiliary standard electrode.

The cells having membranes equilibrated with electrolyte solutions of higher concentrations showed better performances than those having membranes equilibrated with the electrolyte solutions of lower concentrations at ambient temperature (20°C). However, at elevated temperatures, an appreciable improvement in performance was observed for the latter cell, whereas the effect was small for the former cell. In all the cases, polarization at low current densities, i.e., activation polarization, was observed with the cathode. The main concentration polarization of an anion-exchange membrane fuel cell was observed with the anode, but that of a cation-exchange membrane fuel cell was observed with the cathode. Thus, it was concluded that the concentration polarizations were caused by the slow diffusion rates of the hydroxyl or hydrogen ions in the membrane.

1. Introduction

Perry, Jr.¹⁾ reported in 1960 on the polarization characteristics of ion-exchange membrane fuel cells. In his work, the

polarization of the electrodes of an anion-exchange membrane fuel cell was investigated. In the present study, the effect of elevating the temperature on the performance of anion- and cation-exchange mem-

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A: ion-exchange membrane
 B: electrode
 C: filter paper
 D: neoprene rubber
 E: electrolyte solution
 F: auxiliary standard electrode

Fig. 1 Cell structure.

brane fuel cells operated with hydrogen and oxygen, and the polarization characteristics of the electrodes in these cells, were investigated.

2. Experimental

The structure of the ion-exchange membrane fuel cell is shown in Fig. 1. This structure was similar to that of the cells which had been used in the previous work

2),3). The membranes used were Selemion ASG, an anion-exchange membrane, and Selemion CMG-10, a cation-exchange membrane (Asahi Glass Co. Ltd.). Table 1 shows the properties of these membranes. The anion-exchange membrane was equilibrated with an aqueous solution of potassium hydroxide and the cation-exchange membrane was equilibrated with an aqueous solution of sulfuric acid. The electrode was a platinized nickel screen or a platinized platinum screen and its effective area was 4.8 cm^2 . The platinization was done by electroplating with a current density of 20 mA per cm^2 of base-metal in a bath which contained 3 g of chloroplatinic acid and 20 mg of lead acetate in 100 ml water. The gases fed to the fuel cell were commercial hydrogen and oxygen. The cell was operated in a constant temperature air bath and the gases saturated with water vapor were fed at the same temperature. The potentials of the hydrogen and the oxygen electrodes were measured versus a mercuric oxide electrode or a mercurous sulfate electrode. The pressure of the gases was kept at 2 cm water above atmospheric, and the flow rates were 15 ml per a minute (in the case of cation-exchange membrane fuel cells) or 20 ml per a minute (in the case of anion-exchange membrane fuel cells).

3. Results

The effects of elevating the temperature, on the cell performances of the anion-exchange membrane fuel cells having membranes equilibrated with 0.1 and 1N aqueous solutions of potassium hydroxide are shown in Fig. 2 and Fig. 3. By elevating the temperature, a better performance was generally obtained. However, a limiting temperature was observed for each cell. The larger effect of temperature on the performance was shown in the case of the cell having a membrane equilibrated with an electrolyte solution of a lower concent-

Table 1 Properties of Ion-Exchange Membranes (25°C)

	Selemon ASG	Selemon CMG-10
exchange ion	anion	cation
thickness mm	0.21*	0.22**
humidity %***	20*	22**
conductivity $\Omega^{-1} \cdot \text{cm}^{-1} \cdot 10^{-3}$		
equilibrated with		
0.1 N KOH	2.91	-
0.5 N KOH	10.3	-
1 N KOH	14.1	-
0.1 N H ₂ SO ₄	-	2.7
1 N H ₂ SO ₄	-	9.8
4 N H ₂ SO ₄	-	22.4

* Cl form ** Na form *** wet membrane

platinized Ni | Selemon ASG | platinized Ni
H₂ screen | with 0.1N KOH | screen O₂
165 mesh | 165 mesh |

○: 20°C, ●: 30°C, △: 40°C, ▲: 50°C, ×: 60°C, +: 70°C

Fig. 2 Cell E.M.F. vs. current density curves of an anion-exchange membrane fuel cell (1).

platinized Ni | Selemon ASG | platinized Ni | O₂
H₂ screen | with 1N KOH | screen
165 mesh | 165 mesh |

○: 20°C, ●: 30°C, △: 40°C, ▲: 50°C

Fig. 3 Cell E.M.F. vs. current density curves of an anion-exchange membrane fuel cell (2).

ration. On the contrary, that effect was smaller in the case of the cell having a membrane containing an electrolyte solution of a higher concentration. But the latter showed a better performance than the former at ambient temperature (20°C).

The effects of elevating the temperature and the concentration of the electrolyte solution contained in the membrane on the cell performances of the cation-exchange membrane fuel cells were the same as those obtained in the case of the anion-exchange membrane fuel cells. Fig 4 and Fig. 5 show the effect of elevating the temperature on the performances of the cells having the cation-exchange membrane equilibrated with 0.1 and 4 N aqueous solutions of sulfuric acid.

The polarization characteristics of both electrodes of the anion-exchange

Fig. 4 Cell E.M.F. vs. current density curves of a cation-exchange membrane fuel cell (1).

Fig. 5 Cell E.M.F. vs. current density curves of a cation-exchange membrane fuel cell (2).

Fig. 6 Polarization curves of the electrodes of an anion-exchange membrane fuel cell.

membrane fuel cell are shown in Fig. 6. The electrode potentials were measured versus an mercuric oxide electrode. Polarization at low current densities, i.e. activation polarization, was observed with the

Fig. 7 Polarization curves of the electrodes of a cation-exchange membrane fuel cell.

oxygen electrode, but concentration polarization was mainly observed with the hydrogen electrode.

The polarization characteristics of both electrodes of the cation-exchange membrane fuel cell are shown in Fig. 7. In this case, both activation- and concentration-polarization phenomena were observed with the oxygen electrode and the hydrogen electrode was hardly polarized at all.

4. Discussion

Activation polarization of both anion- and cation-exchange membrane fuel cells was observed with the oxygen electrode. This fact shows that a better oxygen electrode has yet to be developed, if an improvement of the ion-exchange membrane fuel cells is to be achieved.

In the case of the cation-exchange

membrane fuel cell, concentration polarization was observed almost only with the oxygen electrode, but, in the case of the anion-exchange membrane fuel cell, that was mainly observed with the hydrogen electrode. The reasons for these facts were assumed to be as follows: The electrode reactions of the fuel cell having a cation-exchange membrane equilibrated with an aqueous solution of sulfuric acid are similar to the reactions of the fuel cells containing an acidic solution as the electrolyte. During the performance of the cation-exchange membrane fuel cell operating with hydrogen and oxygen, the reaction shown in equation (1) proceeds on the anode, and reaction (2) proceeds on the cathode:

The concentration polarization on the cathode could be caused by the shortage of oxygen, the slow diffusion rates of the hydrogen ions in the membrane, or the accumulation of the water produced on the electrode surface. Among them, it is presumed that the shortage of oxygen is not the main factor because the electrode is constructed of a simple metallic screen and the oxygen supply is by far excessive to that theoretically required. Further, as found in the previous works³⁾⁴⁾, water accumulation on the electrode was not serious in the normal cell operation, the problem of the accumulation of the product water on the electrode surface is not important. From the reasons cited above, it is concluded that the concentration polarization on the cathode is caused by the slow diffusion rates of the hydrogen ions in the membrane.

In the case of the fuel cell having an anion-exchange membrane equilibrated with an aqueous solution of potassium hydroxide, the anode reaction is given by equa-

tion (3), and the cathode reaction by equation (4)^{5),6)}

The perhydroxyl ion formed in equation (4) is decomposed in a catalytic reaction, expressed by equation (5).

It is concluded that the main concentration polarization on the anode is caused by the slow diffusion rates of the hydroxyl ions in the membrane, in analogy to the case of the hydrogen ions in the membrane of the cation-exchange membrane fuel cell.

The limiting currents of the ion-exchange membrane fuel cells are controlled by the concentration polarization. The larger limiting currents obtained by elevating the temperature are made possible by the diffusion rates of the ions in the membrane being larger than those at ambient temperature.

5. Conclusions

The performance of the fuel cell consisting of platinized nickel screen electrodes and an anion-exchange membrane equilibrated with an aqueous solution of potassium hydroxide, and that consisting of platinized platinum screen electrodes and a cation-exchange membrane equilibrated with an aqueous solution of sulfuric acid, were studied. The polarization characteristics of the anodes and the cathodes of these cells were evaluated.

The performances of the cells depended on the operating temperature. With the cells having membranes equilibrated with electrolyte solutions of lower concentrations, better performances were obtained at elevated temperature. On the contrary, the cells having membranes equilibrated with electrolyte solutions of higher concentrations possessed more desirable performances at ambient temperature, and

the effect of elevating the temperature on the performances of these cells were small.

As to the cell performance; polarization at low current densities, i.e. activation polarization, was observed with the oxygen electrode for both anion- and cation-exchange membrane fuel cells. The concentration polarization of an anion-exchange membrane fuel cell was mainly observed with the hydrogen electrode. On the other hand, in the case of the cation-exchange membrane fuel cell, this was observed with the oxygen electrode. These concentration polarizations controlled the limiting currents of the cells. It is concluded that the concentration polarization is caused by the slow diffusion rates of hydroxyl ions (in the case of the anion-exchange membrane fuel cell) or hydrogen ions (in the case of the cation-exchange membrane fuel cell) in the membrane.

The larger limiting current achieved by elevating the temperature is caused by the faster diffusion rates of the ions in the membrane.

It has been made obvious that a better oxygen electrode and membranes in which the respective ions could diffuse with faster rates have to be developed, if an improvement of the ion-exchange membrane fuel cells is to be obtained.

Literature:

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Hydrogen Reduction of Niobium Pentachloride*

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The reduction of gaseous niobium pentachloride with hydrogen was carried out under various conditions. The behavior of niobium tritaoctachloride obtained by the hydrogen reduction of the pentachloride at the temperature of 550°C was examined under an argon or hydrogen atmosphere. Also, some thermodynamic considerations concerning the reaction between niobium pentachloride and hydrogen were made. The reaction between gaseous niobium pentachloride and hydrogen began at a temperature of about 400°C. At the temperature range between about 400° and 550°C, it may be considered that the pentachloride was reduced with hydrogen to the tetrachloride which, in turn, disproportionated into the tritaoctachloride and pentachloride. At temperatures above about 600°C, the reactions may be considered as follows: The pentachloride was reduced with hydrogen to the tritaoctachloride which disproportionated into niobium, the pentachloride and the tetrachloride. Then, the pentachloride and tetrachloride produced were reduced with hydrogen to the tritaoctachloride which disproportionated in the same way.

1. Introduction

On hydrogen reduction of niobium pentachloride, only a small number of studies have been reported. Süe¹⁾, Schäfer et al.²⁾ and Brubaker et al.³⁾ found that niobium trichloride may be obtained by hydrogen reduction of the pentachloride at a temperature of about 500°C. McIntosh et al.⁴⁾

described that niobium was obtained by hydrogen reduction of the trichloride at temperatures between about 600° and 700°C. Recently, Schäfer et al.⁵⁾ showed that NbCl_{2.67}, having a smaller content of chlorine than the trichloride, was obtained by hydrogen reduction of the pentachloride at temperatures between 500° and 550°C, and that the so-called niobium trichloride

* The original written in Japanese can be seen in *Denki-Kagaku* 33, 159 (1965).