Short communication

Maximization of high-temperature proton exchange membrane fuel cell performance with the optimum distribution of phosphoric acid

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ABSTRACT

A proton exchange membrane fuel cell (PEMFC) using a controlled amount of phosphoric acid (PA) in a membrane-electrode assembly (MEA) is operated at 150 °C without humidification of the cells. The effects on MEA performance of Pt loading and the amount of PA in the cathode are investigated. The catalyst utilization is maximized by optimizing the PA content in the cathodes and results in lowering of the Pt loading in the MEA. In-situ cyclic voltammetry is used to confirm that the highest value of the active electrochemical area is achieved with the optimum amount of PA in the cathode. The transient response of cell voltage during current density–voltage experiments (*I–V* curve) is also found to be affected by the amount of PA in the electrodes.

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1. Introduction

Perfluorosulfonic acid (PFSA) polymer membranes (e.g., Nafion) are widely used as the electrolyte for proton exchange membrane fuel cells (PEMFCs). Although PFSA-type polymer membranes have many advanced features, there are still serious technical problems to be solved, including low cathode performance, high catalyst cost, and low tolerance to fuel impurities, especially carbon monoxide. Most of these shortcomings are due to the low operational temperature, typically of 80 °C, of the PEMFC. To overcome these shortcomings, other types of membrane that enable operation of the PEMFC at temperatures above 100 °C have been adopted [1–15].

Since Wainright et al. [1] reported the feasibility of the use of polybenzimidazole (PBI), it has been the most widely studied membrane for high-temperature PEMFCs [2–12]. Recently, various proton-conducting membranes based on different PBI structures have been introduced for high-temperature PEMFCs [13–15]. Polymers synthesized from benzimidazole-based monomers have high proton conductivity due to their high phosphoric acid (PA) doping capability. For the operation of PBI-based fuel cells, the PBI membrane is usually doped with about 500 mol % of PA [2,6,8]. There have also been some approaches in which PA is additionally utilized for electrode applications as well as for membranes for the purpose of doping the PBI as an ionomer inside the catalyst layers [2,5–10]. For this purpose, the amount of PBI as ionomer is usually optimized for the best cell performance with the amount of PA being applied to the PBI kept constant. The quantity of 500 mol% of PA might, however, prove excessive even taking into account that a portion of the PA contributes to the proton conductivity of the polymer electrolyte membrane, and that the excess PA disperses to the electrodes and is doped into them but cannot be adjusted precisely.

On assembling the PA-doped membrane and electrodes, the PA from the membrane diffuses into electrodes and acts as an ionomer in the electrodes. This spontaneous distribution of PA might prevent its effective distribution for maximizing the performance of the membrane-electrode assembly (MEA). In this study, the optimum PA content in electrodes, which do not contain proton-conducting polymers such as PBI, is investigated by impregnating the electrodes with PA in addition to using a PA-doped membrane. Because the excess PA content of the membrane makes it difficult to control PA distribution in the MEA, poly(2,5-benzimidazole) (ABPBI) with about 200 mol% of PA, which is known to show a proton conductivity comparable with that of PBI, is used [13–15]. The effects on MEA performance of cathode Pt loading and the PA contents of the cathode and anode are investigated in detail.

2. Experimental

In preparation of the polymer electrolyte membrane, 160 mol% of PA was doped into ABPBI, in which the weight of 1 mol of the repeating unit was 116 g mol⁻¹. ABPBI was produced by condensing 3,4-diaminobenzoic acid (DABA), which is a monomer, in a solution

of polyphosphoric acid. DABA was dissolved in polyphosphoric acid at 150 °C in a nitrogen atmosphere; the resulting solution was heated to 200 °C, then rapidly condensed into water at room temperature. A solution of the ABPBI using methanesulfonic acid as a solvent was cast as a membrane by means of the doctor blade method. The methanesulfonic acid in the membrane was evaporated at 200 °C, and then the membrane was immersed in distilled water to separate it from its support. The PA content in the membrane was controlled by immersing a dry membrane in PA (60 wt.%) at a temperature of 60 °C for 40 min. The level or amount of acid doped into the polymer electrolyte membrane was the initial amount of the acid contained in the polymer electrolyte membrane before commencing operation of the manufactured fuel cell. The doping level or acid content of an electrode is the initial quantity of the acid contained in the electrode before commencing operation of the manufactured fuel cell. The quantity of acid used for doping the polymer electrolyte membrane is expressed in "mol %", which is the mole percentage of doped acid per 1 mole of the repeating unit of the polymer.

The cathode catalyst layer was composed of a PtCo alloy supported on carbon (Tanaka Kikinzoku Kogyo, TEC36E52) and polyvinylidene fluoride (PVDF, Aldrich). The anode catalyst layer was composed of PtRu alloy supported on carbon (Tanaka Kikinzoku Kogyo, TEC61E54) and PVDF, and its Pt loading was about 1.4 mg cm^{-2}. The slurry for forming the catalyst layer was prepared by mixing the PVDF solution in n-methyl-2-pyrrolidone (NMP) and a solvent of NMP in an appropriate amount of carbon-supported catalyst. To obtain an undoped electrode, a homemade bar coater was used to apply the slurry to the carbon paper that was earlier covered with a microporous carbon layer (SGL, 35BC). The Pt loading of the electrode was controlled by adjusting the solvent composition and the coating conditions. A spray gun was used to prepare an electrode with the desired level of PA impregnation. A solution of 85 wt.% PA was sprayed on to the surface of the catalyst layer of the undoped electrode. The doped electrode was subsequently dried at a temperature of 120 °C for 2 h. The amount of PA doped on the membrane and the anode Pt loading remained virtually unchanged for the whole series of experiments. The variable parameters were the Pt loading on the cathode (1.1, 2.0 and 3.0 mg cm^{-2} Pt), and the amount of PA impregnated in the cathode (28, 66, 84, 153, 214 and 243 μmol cm^{-2} PA) and in the anode (15, 48, 100 μmol cm^{-2} PA). The doping amount, viz.,"μmol cm^{-2}", of acid in the electrode is expressed as the concentration in moles of acid contained in a unit geometric area of the catalyst layer.

Dry hydrogen (flow rate: 100 cc min^{-1}) for the anode and dry air (flow rate: 250 cc min^{-1}) for the cathode were used for the operation of the cell at 150 °C. The effective dimensions of electrode in the MEA were 2.8 × 2.8 cm. The MEA performance was monitored by controlling the voltage at 0.3 A cm^{-2}. The a.c. impedance of the cell was monitored at a frequency of 1 kHz (model 3566, Tsuruga). At the end of cell operation, to assess the active electrochemical area of electrodes in-situ, cyclic voltammetry (CV) was carried out by passing nitrogen on the cathode side at a temperature of 150 °C [16]. The voltammograms were obtained between voltages of 0.05 and 1.0 V vs. a standard hydrogen electrode (SHE) at a scan rate of 5 mV s^{-1}.

3. Results and discussion

3.1. MEA performance

MEAs composed of PA-doped membrane and PA-impregnated electrodes require a break-in period to reach maximum performance. Unlike Nafion-based PEMFCs, for which performance is
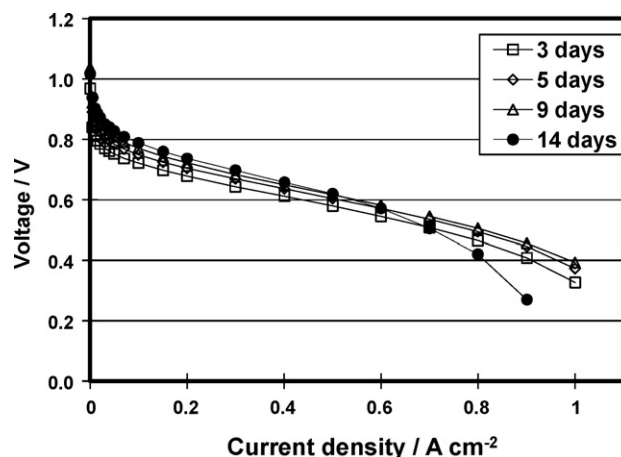

Fig. 1. *I–V* curve of MEA with 3.0 mg cm^{-2} Pt loading cathode and 153 μmol cm^{-2} PA impregnated in cathode during break-in period.

maximized within a couple of days, the break-in period of PBI-based PEMFCs is much longer [7,9]. Seland et al. [7] let their MEA cure for two weeks and attribute the longer break-in period to a slow PA absorption rate of PBI inside the catalyst layers. Fig. 1 shows the *I–V* curves measured on different days of the break-in period of cells that use a MEA with a 3.0 mg cm^{-2} Pt loading on the cathode and 153 and 48 μmol cm^{-2} of PA impregnation on the cathode and anode, respectively. During the break-in period, which was about two weeks for the cells operated in this study, the PA in the electrodes and membrane is thought to be redistributed in the MEA before the cell reaches a state where it can be operated at a constant voltage. While the operating voltage at low current densities gradually increases during the break-in period, the operating voltage at high current densities reaches a maximum in the middle of the break-in period, and mass-transfer limiting behaviour starts to appear at the end of the break-in period. Because the electrodes do not contain proton-conducting polymers, which can immobilize PA, it is believed that a portion of PA inside the electrodes starts to block the pores of the catalyst layer during the break-in period. For this type of electrode, which is operated without a proton-conducting polymer, the cell performance at high current densities is sacrificed but at low current densities has one of the highest levels attained among PBI-based PEMFC, to the best of our knowledge [2,4–12,14,15]. There have been few reports where an operating voltage of 0.7 V at 0.3 A cm^{-2} is reached at a temperature of 150 °C with non-humidified hydrogen and air.

When pure hydrogen is used as the fuel, the overpotential for the hydrogen oxidation reaction is negligibly small, even at high current densities [17]. The effects of Pt loading and PA in the cathode have been especially investigated because the sluggish oxygen reduction reaction causes large overpotential. Table 1 summarizes a set of experiments that have been conducted by varying the Pt loading and the PA content in the cathode. The PA content in anodes is constant at 48 μmol cm^{-2}. Numbers are assigned to each MEA in a way that the first numeral before a dash indicates the level of Pt loading and the second numeral after the dash is the PA content. For example, MEA 2-1 represents an MEA with 2 mg cm^{-2} cathode Pt loading and the lowest PA content in a series of experiments with the corresponding loading of Pt.

The effect of PA impregnation in the cathode on the performance of the MEA is displayed in Fig. 2 for a loading of 2 mg cm^{-2} Pt. Generally, MEA performance is enhanced to a certain degree by increase in the PA content in the cathode. MEAs with low PA content in the cathodes such as MEA 1-1 and 2-1, do not have sufficient ionomer to effect proton transfer from membrane to the catalyst. By con-

Table 1
MEA performance with various cathode Pt loadings and amounts of PA impregnated in cathode.

MEA	Pt loading (mg cm^{-2})	Amount of PA impregnation (μmol cm^{-2})	Voltage at 0.3 A cm^{-2} (V)
1–1	1.1	28	Cannot be activated
1–2	1.1	66	0.567
1–3	1.1	84	0.624
2–1	2.0	28	0.308
2–2	2.0	66	0.620
2–3	2.0	84	0.660
2–4	2.0	153	0.699
2–5	2.0	214	0.669
2–6	2.0	243	Cannot be activated
3–2	3.0	66	0.633
3–3	3.0	84	0.655
3–4	3.0	153	0.697

Fig. 3. Effects on MEA performance of cathode Pt loading and amount of PA impregnated in cathodes.

trast, excess PA content in the cathodes such as MEA 2–5 and 2–6 causes the gas network inside the cathodes to flood. The cell that used MEA 2–5 shows a decline in performance compared with that for MEA 2–4 which is found to have an optimum PA content in the cathode of 153 μmol cm^{-2}. The cell that uses MEA 2–6, in which the PA content in the cathode is higher than MEA 2–5, could not be activated, that is, application of even a small current causes an abrupt fall in cell voltage.

The effect of Pt loading and PA content in cathode on MEA performance is more clearly shown in Fig. 3. Although it is natural for the performance of MEAs to be improved with a higher loading of catalyst in the electrode, Fig. 3 shows that there is a saturation level of performance regardless of cathode Pt loading. By increasing the cathode Pt loading from 2 to 3 mg cm^{-2}, the cell voltage does not improve and stays unchanged at 0.7 V. The highest cell voltage can be achieved with a cathode Pt loading of 2 mg cm^{-2} if the optimum content of PA is present in the cathode; further increase in the loading does not improve the cell voltage.

The effect of PA impregnation in the anode on MEA performance is presented in Fig. 4 for a 2 mg cm^{-2} Pt loaded cathode (with a constant amount of PA in the cathode of 153 μmol cm^{-2}). The dependence of cell performance on PA content in the anode is not as pronounced as for the cathode, but the general tendency that excess- or insufficient PA content in the electrodes causes cell performance to decline does apply to the anode.
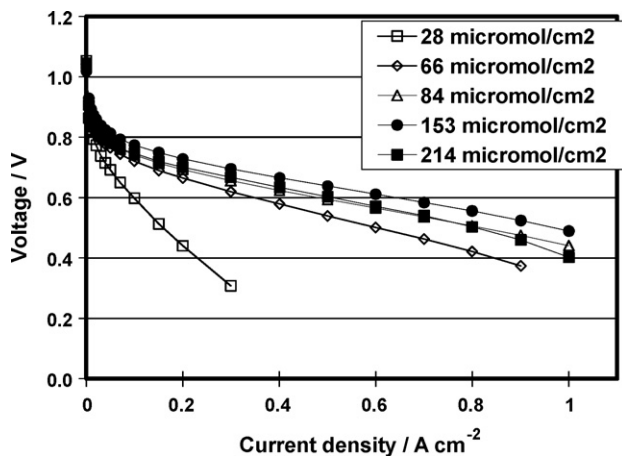
3.2. Transient MEA response

The I–V curves were collected in a way that current density was galvanostatically raised step-by-step from 0 A cm^{-2} (OCV state), and the cell voltage at each current density was recorded 2–3 min after application of the current. The MEA system investigated in the current study adopted the mobile liquid state of PA as ionomer in the electrodes as opposed to the immobile solid state of Nafion as ionomer utilized for low-temperature PEMFCs. The transient voltage response behaviour differs for MEAs with different amounts of PA in the electrodes. Changes in cell voltage and resistance from the OCV state after applying a current density of 0.3 A cm^{-2} are shown in Fig. 5.

For MEAs from 2–1 to 2–4, the cell voltage gradually rises and reaches steady-state values, and similarly the resistance values gradually decline, and reach steady-state values. As the PA content in the cathodes increases, the cell voltage of the MEA increases while the cell resistance values decrease. The impedance measured at 1 kHz reflects the ohmic overpotential of the MEAs, which consists of membrane resistance and contact resistance [18]. By adding more PA to the cathodes, the contact area between catalyst and ionomer increases and, possibly, the membrane proton conduc-
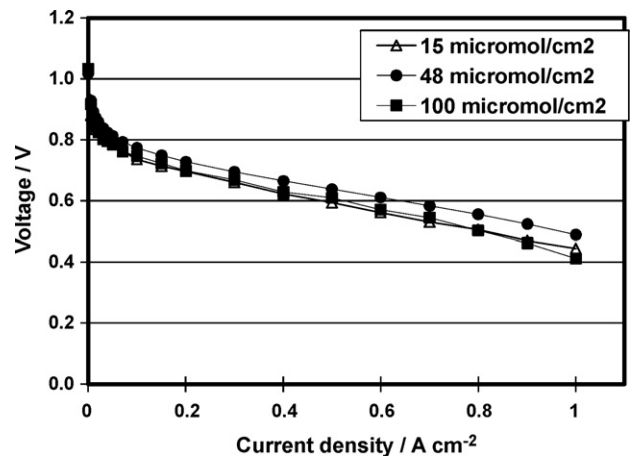

Fig. 2. I–V curve of MEA with 2.0 mg cm^{-2} Pt loading cathode and various amount of PA impregnated in cathode.

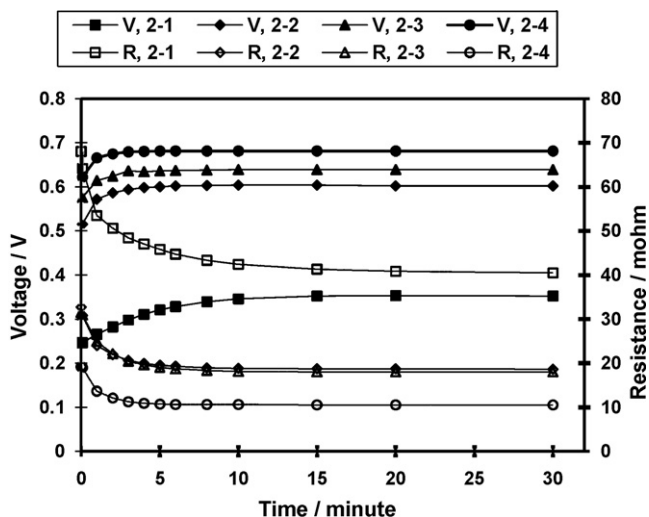**Fig. 4.** I–V curve of MEA with 2.0 mg cm^{-2} Pt loaded cathode and various amounts of PA impregnated in anode.

Fig. 5. Chronopotentiometry with switching current density from OCV state to 0.3 A cm^{-2} and its accompanying MEA resistance.

Table 2
Electrochemical active area of MEA and its performance.

MEA	Charge for hydrogen desorption (mC cm^{-2})	Electrochemical active area (cm^2)	Voltage at 0.3 A cm^{-2} (V)
2–1	8.3	39	0.308
2–2	19.1	91	0.620
2–3	30.3	144	0.660
2–4	38.5	183	0.699
2–5	39.0	185	0.669
2–6	38.7	184	Cannot be activated

tivity by absorbing PA from the electrode improves as well. The reduced ohmic overpotential results in higher MEA voltages.

Both voltage and resistance reach steady-state values within 5 min of applying the current for MEAs 2–2, 2–3, and 2–4. By contrast, MEA 2–1 that has an insufficient amount of PA in cathode for maximizing the utilization of catalyst requires a longer time to reach a steady-state value. This tendency that the higher the PA content in the cathode the shorter is the time taken to attain steady-state value holds for the other MEAs. The voltage of cells that contained insufficient amounts of PA in the cathodes respond more slowly to the current application because the reactions in the electrodes have to overcome a higher barrier created by the low proton accessibility to the catalyst and the limited area available for reaction in the electrodes.

3.3. Electrochemical active area

As mentioned in the previous section, the MEA performance is closely related to the total available PA content in the electrodes and the pattern of dispersal of PA inside the MEA. Although control over the dispersal of PA in each component of the MEA is exercised by the initial content of PA, it is not clear whether such dispersal remains unchanged during operation of the cells. To gain an insight into the final PA content in the electrodes, the active electro-
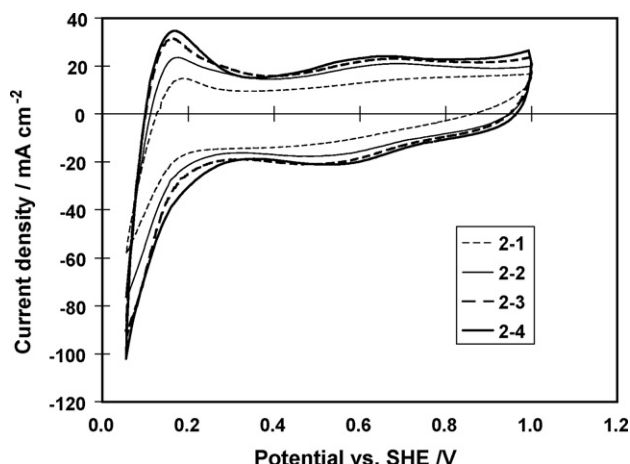
chemical area of electrodes, which eventually contributes to MEA performance, was evaluated by in-situ CV. The CVs of MEAs 2–1, 2–2, 2–3, and 2–4 are plotted in Fig. 6. The CVs of MEAs 2–5 and 2–6 are almost identical to those of 2–4 but are not included for the sake of clarity. The area enclosed by the CV curve is proportional to the charge passing in the electrochemical reaction. The anodic hydrogen desorption peak located around 0.15 V is usually utilized to evaluate the active electrochemical area. To calculate the active electrochemical area the background current generated by double-layer charging has to be subtracted from the value of the hydrogen desorption current. The background is deemed the minimum current density value at the potential where the hydrogen desorption peak disappears. The details of the active electrochemical areas of all the MEAs are summarized in Table 2. The availability of the active electrochemical area is directly related to the performance of the MEA, and any increase in active electrochemical area can be attributed to an increase in the area of contact between the catalyst and the ionomer. This hypothesis is further confirmed by the observation that MEAs with higher PA content in cathode have a higher double-layer charging current, which as mentioned earlier, is deemed the value of background current. Because double-layer charging arises from the surface interaction between the electrolyte (PA) and the electrode (catalyst and supporting carbon), the level of double-layer charging current is an index of the area of contact between the catalyst and the PA.

The positive correlation between the active electrochemical area and performance of the MEAs is not valid for MEAs 2–5 and 2–6. It is likely that the excess PA content in the electrodes cannot increase the active electrochemical area further but instead blocks the oxygen supply into the catalyst layer and causes the cell voltage to decline. For the analysis of flooded cells, techniques other than in-situ CV should be considered.

4. Conclusions

PEMFCs composed of PA-doped membrane and PA-impregnated electrodes have been operated at 150 °C without humidification of the cells. The effects on MEA performance of Pt loading and PA content in cathodes have been investigated. The utilization of catalyst can be maximized by exercising control over the impregnated PA content of the cathodes. That there is an increase in the active electrochemical area when there is an increase in PA content in the cathodes is confirmed by in-situ CV. Addition of PA in excess of the optimum content in cathodes does not increase the electrochemical area but causes a lowering of the cell performance. The voltage response after change in applied current density is also greatly affected by the PA content in electrodes.

Fig. 6. In-situ cyclic voltammograms of MEAs (2–1, 2–2, 2–3, and 2–4).

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