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Medium temperature operation of fuel cells using thermally stable proton-conducting composite sheets composed of phosphosilicate gel and polyimide

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Abstract

Fuel cells using a composite sheet composed of phosphosilicate (P_2O_5-SiO_2, P/Si = 1 in mole ratio) gel powder and polyimide operated up to 150 °C under a relatively low water vapor pressure. Maximum power density of the fuel cell increased with increasing operation temperature up to 150 °C and increasing humidity. No degradation was observed even after the continuous operation for 10 h at 150 °C and 4% relative humidity (RH) under 50 mA cm^{-2}. Sieving of the mechanically milled phosphosilicate gel powders to be less than 5 μm in size was found to improve the homogeneity and thus the proton conductivity of the resultant composite sheets. The conductivity of the composite sheet containing 75 wt.% of the sieved gel powder was 4×10^{-3} S cm^{-1} at 150 °C and 18% RH. Good contact between the composite sheet as an electrolyte and Pt-loaded carbon paper sheets as electrodes in the membrane electrode assembly (MEA) was very important to attain high performance of the fuel cells, which was achieved by the painting of phosphosilicate sol on the surface of the carbon paper and the hot-pressing of the MEA in vacuo.
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1. Introduction

Recently polymer electrolyte fuel cells (PEFCs) have attracted much attention as power sources of portable devices and electric vehicles. The operation conditions of the PEFCs are generally restricted to be lower than 100 °C and under high humidity due to the properties of commonly used perfluorosulfonate membranes such as Nafion®. Solid state proton-conductive membranes with high conductivity in the medium temperature range (100–200 °C) even under low humidity are highly required as the electrolytes for PEFCs [1–4]. Since the operation of PEFCs in the medium temperature range improves the utilization of total electric power generated in the cells and depresses the poisoning of Pt catalysts with CO in the fuel gases [5–8]. In addition, working of PEFCs under low humidity permits to reduce the weight and volume of humidifiers.

We have reported that sol–gel-derived phosphosilicate (SiO_2-P_2O_5) gels containing large amounts of phosphorus can keep a high conductivity of 1×10^{-2} S cm^{-1} even at 150 °C and 0.4% relative humidity (RH) [9–11]. Two types of proton-conductive membranes based on phosphosilicate gel have been studied aiming at the application to the electrolyte for the medium temperature PEFCs. One is a composite sheet composed of phosphosilicate gel powder and organic polymer such as thermoplastic styrene–ethylene–butylenes–styrene elastmer [12] and heat resistant polyimide [13].

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The other is a hybrid sheet in which inorganic and organic components derived from organosilane and phosphoric acid are covalently bonded [14–16]. With respect to the former membranes, we reported that the thermally stable proton-conducting composite sheets prepared from phosphosilicate gel powder and polyimide precursor showed conductivity of $2 \times 10^{-4}\,S\,cm^{-1}$ at 150 °C and 0.4% RH. In addition, the fuel cells using the composite sheet as an electrolyte operated with a power density of about $30\,mW\,cm^{-2}$ at 30 °C with 60% RH [13]. However, the performance of the fuel cells at medium temperature range has not been evaluated.

In the present work, medium temperature range operation of the fuel cell using phosphosilicate gel–polyimide composite sheet has been investigated. Assembling processes of the membrane and electrodes were optimized to achieve the high performance of the fuel cell in the medium temperature range. The size distribution of the powder particles was controlled by sieving the mechanically milled phosposilicate gel to improve the homogeneity and thus proton conduction of the resultant composite sheets.

2. Experimental

2.1. Preparation of composite sheets

Proton-conductive composite sheets were prepared from phosphosilicate gel powders and commercially available polyimide precursor (Unitika, U-imide-varnish type C). Phosphosilicate gel powders were obtained from tetraethoxysilane and H_3PO_4 by the sol–gel method; the procedures were essentially the same as reported in the previous papers [9–11]. The mole ratio of P/Si was fixed to 1.0. The dry gel powders heat-treated at 150 °C were further ground into fine powders of a few micrometers in diameter using a planetary ball mill (Fritsch, Pulverisette 7). Furthermore, in this study, the phosphosilicate gel powders were sieved with a 145 mesh to control the particle size of the powder less than about 5 μm. The sieved gel powder was then mixed with the *N,N*-dimethylacetoamide solution of a polyimide precursor with stirring for 30 min and the mixture was stirred under ultrasonic wave irradiation for additional 30 min. The gel powder:polyimide weight ratio was varied from 20:80 to 80:20. Yellowish composite slurries thus obtained were cast on a glass plate and developed using a squeegee and a spacer to control their thickness. The developed composite sheets on glass plates were heat-treated at 150 °C for 3 h and then 180 °C for 3 h.

2.2. Characterization of composite sheets

Electric conductivities of the composite sheets were measured under two kinds of atmospheres; at 30 °C and 60% RH, at 150 °C and 0.4% RH. The conductivities were determined by impedance data. Solartron SI1260 was used to obtain the impedance data in a frequency range of 10 Hz to 8 MHz.

For the measurements of conductivity at 150 °C and 0.4% RH, composite sheets mounted on the holder were kept at 30 °C and 60% RH for 3 h in a temperature and humidity controlled chamber (ETAC, SD-01) and consecutively inserted into a glass tube which was kept at 150 °C in an electric furnace. For the evaluation of the conductivities under practical cell operation conditions such as at temperatures from 80 to 160 °C under fixed water vapor pressure, or at 150 °C under various water vapor pressures, Autolab PGSTAT30 was used to obtain the impedance data in a frequency range of 10 Hz to 1 MHz. Water vapor pressure was controlled by changing the babbler temperature, and conductivity measurements were carried out in humidified N_2 with flow rate of $100\,ml\,min^{-1}$.

2.3. Preparation and evaluation of MEAs and fuel cells

The single fuel cell tests were carried out for the membrane/electrode assemblies (MEAs) which consisted of the composite sheet as an electrolyte and commercially available Pt-loaded ($1\,mg\,cm^{-2}$) carbon paper sheets (ElectroChem, EC-20-10-10) as electrodes. The MEAs were obtained by hot pressing the composite sheet between the Pt-loaded carbon paper sheets at 130 °C under about 11 MPa in vacuo for 10 min. An energy dispersive X-ray (EDX) microanalyzer (JEOL, JED2001) was used for observing the cross section of MEA. Current–voltage profiles in the fuel cells were obtained by using an electrochemical measurement system (Hokuto, HZ-3000). When current–voltage profiles of the fuel cell were measured, humidified H_2 and air by passing through the bubbler were provided to the cells. Temperature of the cell was controlled by holding the cell in an oven. Flow rates of pure hydrogen for anode and of air for cathode were 20 and $100\,ml\,min^{-1}$, respectively. Humidity dependence of the fuel cell performance was also examined.

3. Results and discussion

3.1. Formation and conductivity of composite sheets

Sieving of the pulverized phosphosilicate gel powder was found to be effective to prepare homogeneous and flexible composite sheet containing larger amounts of gel powder. Flexible composite sheets were obtained up to 75 wt.% of gel content using the sieved gel powders of less than 5 μm in size, whereas the upper limit to obtain flexible composite sheet was 70 wt.% without sieving. The elimination of agglomerate gel particles with large size should be an important factor to improve the flexibility and homogeneity of the composites.

Fig. 1 shows proton conductivities (a) after keeping at 30 °C and 60% RH for 3 h and (b) after consecutive keeping at 150 °C and 0.4% RH for 6 h of composite sheets containing various amounts of phosphosilicate gel powder. Closed and open circles represent the proton conductivity of composite sheets composed of gel powders with and without sieving, respectively. Conductivity of both composite sheets increases
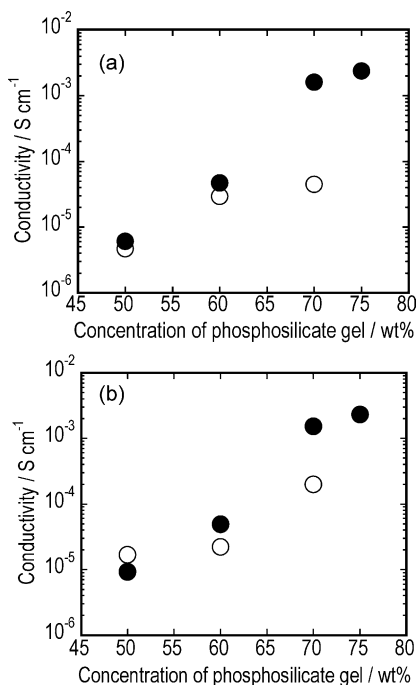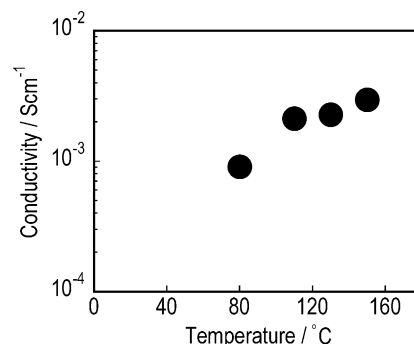
Fig. 2. Temperature dependence of conductivity of the composite sheet composed of 75 wt.% of phosphosilicate gel and polyimide under constant water vapor pressure of 150 mmHg.

was measured during cooling steps from 150 to 80 °C, the sheet showed almost same conductivities at each temperature as those in the preceding heating steps. Therefore, water vapor pressure of 150 mmHg is probably sufficient to keep constant proton conductivity in a wide temperature range up to 150 °C.

Fig. 3 shows the relative humidity dependence of conductivity for the composite sheet containing 75 wt.% phosphosilicate gel powders at 150 °C. Conductivity of the composite sheet increases with an increase in the relative humidity. It is noteworthy that very small humidification of 0.4% RH is sufficient to keep conductivity higher than 2×10^{-3} S cm^{-1} at 150 °C, and the fluctuation in conductivity with humidity change is relatively small.

3.2. Characteristics of MEAs and fuel cells using composite sheet

Fig. 4 shows (a) cross-sectional SEM image and corresponding EDX analyses of (b) P and (c) Si for the MEA which consists of the composite sheet and Pt-loaded carbon paper sheets. It was found from detailed SEM observation that the composite sheet had good contact with the carbon paper electrodes. Phosphorus and silicon elements are widely distributed in the MEA, indicating that phosphosilicate sol has permeated into carbon paper to act as a paste at the interface

Fig. 1. Composition dependence of conductivity for composite sheets composed of phosphosilicate gel and polyimide, which were kept (a) at 30 °C under 60% RH for 3 h, and (b) at 150 °C under 0.4% RH for 6 h. Closed and open circles represent the proton conductivity of composite sheets composed of gel powders with and without sieving, respectively.

with an increase in the amount of phosphosilicate gel both at 30 and 150 °C. The sheets obtained with sieved gel powder (closed circles) exhibit higher conductivities compared to those of the sheets without sieving (open circles) especially at higher contents of gel powder. This suggests that sieving of gel powder is effective to disperse the gel powders without aggregation and improve the packing density of the resultant composite sheet. These phenomena permit the formation of proton-conducting paths throughout the whole composite sheet. The sheet containing sieved gel powder of 75 wt.% shows high conductivities of 2.2×10^{-3} S cm^{-1} at 30 °C under 60% RH and maintains almost the same value even after the consecutive keeping at 150 °C and 0.4% RH for 6 h.

Fig. 2 shows the temperature dependence of conductivity for the composite sheet containing 75 wt.% phosphosilicate gel powders under a constant water vapor pressure of 150 mmHg. At 80, 110, 130 and 150 °C, the water vapor pressure corresponds to 42, 14, 7 and 4% RH, respectively. The temperature was raised stepwise and the measurements were carried out after keeping at each temperature for 2 h. Conductivity of the composite sheet increases with increasing temperature from 80 to 150 °C and the value is as high as 3.0×10^{-3} S cm^{-1} at 150 °C. At 160 °C and 150 mmHg of water vapor pressure (3% RH), conductivity of composite sheet gradually decreased with keeping. This is probably caused by the evaporation of strongly adsorbed water in phosphosilicate gel [10,13]. When conductivity of the composite sheet
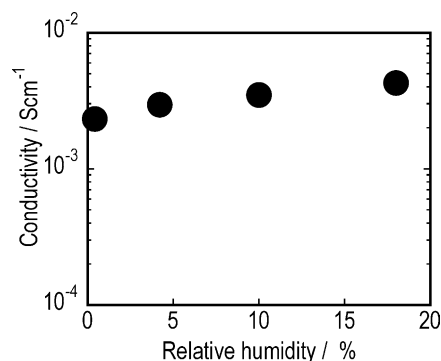

Fig. 3. Relative humidity dependence of conductivity of the composite sheet composed of 75 wt.% of phosphosilicate gel and polyimide at 150 °C.
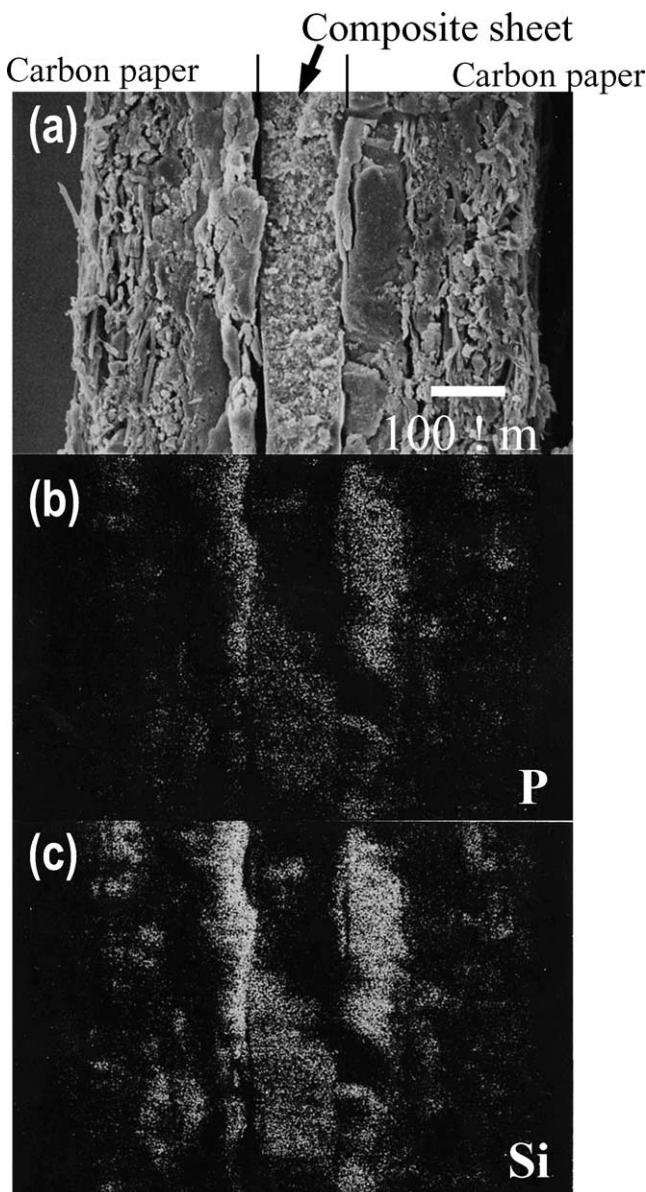
Fig. 4. SEM photograph (a), P (b) and Si (c) distribution map determined by EDX of the cross-section of an MEA with composite sheet containing 75 wt.% of phosphosilicate gel and Pt-loaded carbon electrodes immersed in phosphosilicate sol.
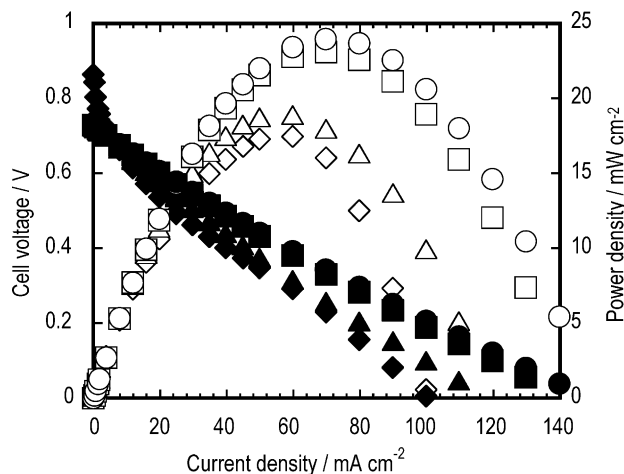

Fig. 5. Cell voltage (closed symbols) vs. current density with the resulting power density plots (open symbols) for a fuel cell using an MEA consisting of the composite sheet containing 75 wt.% of phosphosilicate gel. The cell operated at 80 °C ($\blacklozenge$, $\lozenge$), 100 °C ($\blacktriangle$, $\triangle$), 120 °C ($\blacksquare$, $\square$) and 130 °C ($\bullet$, $\circ$) under 150 mmHg water vapor pressure.

between the composite electrolyte and the carbon paper electrodes.

Fig. 5 shows cell voltage versus current density with the resulting power density plots for a fuel cell using a MEA which consists of the composite sheet containing 75 wt.% phosphosilicate gel as an electrolyte and Pt-loaded carbon paper sheets as electrodes. The cell operated under 150 mmHg water vapor pressure at various temperatures, which corresponded to 42, 20, 10 and 7% RH at 80, 100, 120 and 130 °C, respectively. Closed diamonds, triangles, squares and circles represent the current–voltage characteristics of the fuel cells at 80, 100, 120 and 130 °C, respectively. Open diamonds, triangles, squares and circles represent the calculated current–power

density plots of the fuel cells at 80, 100, 120 and 130 °C, respectively. The open circuit voltage of the cell at 80 °C is about 0.85 V, whereas the voltage of the cell decreases to be about 0.70 V at temperatures higher than 100 °C. Open circuit voltage remains almost constant, i.e. 0.7 V, when the temperature increases from 110 to 130 °C. At temperatures lower than 100 °C, the pores in the composite sheets are closed due to absorbed water, whereas at temperatures higher than 100 °C, the physically absorbed water evaporates to lead to H_2 cross-over. The slopes of current–voltage curves decrease with increasing operation temperature, which is probably due to an increase in proton conductivity of the composite sheet as shown in Fig. 2. Maximum power density increases with an increase in the operation temperature, which demonstrates that the fuel cells using the MEA consisting of the composite sheet as an electrolyte have high potentiality to operate in the medium temperature range.

Relative humidity dependence of the cell voltage versus current density with the resulting power density plots for this fuel cell at 150 °C is shown in Fig. 6. The cell construction is the same as in Fig. 5. Closed circles, triangles and squares represent the current–voltage characteristics of the fuel cells under 4, 10 and 18% RH, respectively. Open circles, triangles and squares represent the calculated current–power density plots of the fuel cells under 4, 10 and 18% RH, respectively. Open circuit voltage is about 0.70 V under each relative humidity. The slopes of current–voltage curves decrease with an increase in the relative humidity. This corresponds to a decrease in the total resistance of the cell which is mainly due to an increase in the proton conductivity of the composite sheet as an electrolyte as shown in Fig. 3.

Changes in cell voltage during a continuous operation under a current density of 50 mA cm^{-2} at 150 °C and 4% RH are shown in Fig. 7. The cell construction is the same as in Figs. 5 and 6. At the beginning of the operation the voltage
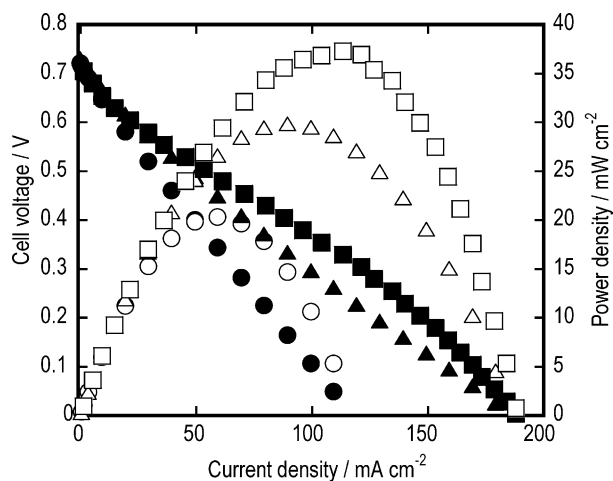
Fig. 6. Cell voltage (closed symbols) vs. current density with the resulting power density plots (open symbols) for a fuel cell with the same construction as in Fig. 5. The cell operated at 150 °C under 4% RH (●, ○), 10% RH (▲, △) and 18% RH (■, □).
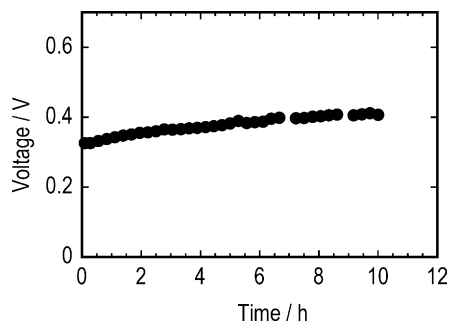

Fig. 7. Variations in cell voltage at 50 mA cm^{-2} with operation time at 150 °C under 4% RH. The cell construction is the same as in Figs. 5 and 6.

is 0.33 V and increases to be more than 0.4 V with operating time for 10 h. The increase in the cell voltage can be ascribed to a decrease in the total resistance of the cell, which is probably due to the decreases in charge transfer resistance of oxidation reaction and in the resistance of composite sheet. The performance of the cell is still low for the practical application. However, these results demonstrate that the fuel cell using the composite sheet as an electrolyte can continuously operate at medium temperatures even under low humidity.

4. Conclusions

Flexible composite sheets containing phosphosilicate gel up to 75 wt.% have been obtained using mechanically milled and then sieved gel powders of less than 5 μm in size. The conductivity of the composite sheets containing 75 wt.% of gel powder was 2×10^{-3} S cm^{-1} at 150 °C under 0.4% RH and increased to be 4×10^{-3} S cm^{-1} under 18% RH at the same temperature. These results indicate that the composite sheets obtained in the present study maintain high conductivity at medium temperatures even under very low humidity and the fluctuation in conductivity with humidity change is small. A fuel cell using an MEA which consisted of the composite sheet as an electrolyte operated up to 150 °C under water vapor pressure of 150 mmHg which corresponds to 4% RH. Power density of the fuel cell increased with an increase in the relative humidity at 150 °C. No degradation was observed for the fuel cell after continuous operation for 10 h at 150 °C under 4% RH with 50 mA cm^{-2}.

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