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Effect of water vapor on proton conduction of cesium dihydrogen phosphate and application to intermediate temperature fuel cells

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Abstract

The proton conduction and superionic phase transition of cesium dihydrogen phosphate, CsH_2PO_4 (CDP), were investigated under various humid conditions to evaluate the applicability of a CsH_2PO_4 solid electrolyte to an intermediate temperature fuel cell operating between 230 °C and 300 °C. The phase stability, superionic phase transition, and reversibility of dehydration of CsH_2PO_4 were evaluated under different ambient water vapor concentrations, from 0 to 90 mol%, through the measurements of conductivity. The dependence of conductivity on the water vapor concentration and the demonstrated reversibility of dehydration clearly showed the range in which CsH_2PO_4 is applicable to the intermediate temperature fuel cell. Additionally, we evaluated the protonic transport number of CsH_2PO_4, which was almost unity, and demonstrated fuel cell operation at 250 °C using a single cell fabricated with the CsH_2PO_4 electrolyte.

1. Introduction

Cesium dihydrogen phosphate, CsH_2PO_4 (CDP), is a hydrogen-bonded ionic conductor that exhibits a superionic phase transition at T_c = ca. 230 °C leading to an abrupt increase in conductivity by four orders of magnitude, from 10^{-6} to 10^{-2} S cm^{-1} [1–3]. It has been reported that the superionic phase transition takes place at ca. 230 °C, being accompanied by a structural transformation from a monoclinic phase to a cubic phase [2, 3]. The superionic phase has been classified as a dynamically disordered hydrogen bond network that can enhance protonic conduction [3]. However, the nature of the CDP superionic phase has been much discussed in the past decade, since the dehydration of CDP (reaction 1) proceeds to form polymerization products above 200 °C in dry atmosphere and thus the conductivity decreases as time elapses [4–6].

$$n\mathrm{CsH_2PO_4} \rightarrow \mathrm{Cs}_n\mathrm{H_2P}_n\mathrm{O}_{3n+1} + (n-1)\mathrm{H_2O} \quad (n \geq 2). \tag{1}$$

Recently, we have demonstrated that the superionic phase transition takes place reproducibly and that the superionic phase can be stable in a humid atmosphere (H_2O partial pressure: 0.3 atm, temperature: 250 °C), suggesting that dehydration can be suppressed in such an atmosphere [7]. With the powder X-ray diffraction (XRD) measurement of CDP in the H_2O-saturated atmosphere, it has been reported that a structural transformation occurs at ca. 231 °C from the monoclinic phase ($P2_1$/m) to the cubic phase (Pm-3m) without any decomposition [8]. Thus, the previous studies show that CDP high-conducting phase is stable in appropriate humidity. This suggests that CDP has potential as a solid electrolyte for fuel cells operating in an intermediate temperature region of around 250 °C. Quite recently, it was reported that a single cell with a CDP solid electrolyte was fabricated and successfully operated at 235 °C in a humid atmosphere (H_2O partial pressure: 0.3 atm), and a thermal analysis showed that the dehydration reaction of CDP was suppressed under appropriate humid conditions [9]. An intermediate temperature solid electrolyte fuel cell, using fuels such as synthesis gas and methanol, would offer many advantages – such as improved catalytic activity, effective use of waste heat, and prevention of permeability through the electrolyte – in comparison with current commercial polymer-electrolyte fuel cells (PEFCs). Therefore, it is very important to investigate CDP conductivity characteristics in humid conditions. In measuring CDP conductivity, previous work used only a limited range of ambient conditions such as humidity. In the present research, we investigated in detail CDP conduction behavior, such as superionic phase transition and phase stability, under various humid conditions in order to study the influence of H_2O vapor partial pressure on CDP conductivity and on its applicability to the intermediate temperature fuel cell. Additionally, we fabricated a single cell with a CDP electrolyte to evaluate CDP protonic transport number and to demonstrate the single cell operation at 250 °C.

2. Experimental

2.1. *Conductivity measurements*

The conductivity of polycrystalline CDP was measured by ac impedance spectroscopy. The sample pellet for the conductivity measurement was prepared as follows (more detailed information of the sample preparation can be found in a previous study [7]). Polycrystalline CDP (Soekawa Chemical) was mechanically ground in an agate mortar for 30 min. According to XRD measurements of the powdered CDP, the detected peaks all originated from CDP, and no other peaks were observed. Then, the powdered samples were pressed at 3 ton cm^{-2} to form pellets (diameter: 10 mm, thickness 1.5–3.1 mm). The resultant pellets were calcined at 260 °C for 1 h in a small glass cell (relative density after calcination $>90\%$). Then, silver electrodes were attached to both sides of each pellet by silver paint after silver vapor deposition on the pellet surface. Conductivity was measured by ac impedance spectroscopy with a Hewlett-Packard 4192A impedance analyzer in the frequency range 10 Hz to 10 MHz. The pellet samples were set in a glass tube, and then gaseous mixtures such as dry Ar, Ar/H_2O, H_2/H_2O, and O_2/H_2O were supplied through the glass tube at atmospheric pressure. During the conductivity measurements, the temperature was maintained constant or changed stepwise from 150 to 300 °C. The conductivity, σ, of each sample was determined from the frequency dependence of the real and imaginary parts of the impedance plotted in a complex plane (Cole–Cole plot). The procedure for calculating conductivity derived from the obtained impedance spectra was also explained previously [7].

2.2. *Fabrication and operation of a single cell*

A particulate electrode was prepared using a carbon-supported platinum catalyst (Pt/C, 45.7 wt.% Pt, Tanaka Kikinzoku Kogyo). The Pt/C catalyst was spread on a carbon paper (Toray, thickness: 190 μm) pretreated with Teflon to achieve hydrophobicity. Pt was loaded on the electrode at 1.6 mg cm^{-2}, and the geometric electrode area was 0.13 cm^2. The Pt/C electrodes were attached to both sides of the CDP electrolyte (diameter: 10 mm, thickness ca. 1.2 mm) to fabricate a membrane electrode assembly (MEA). The MEA was set in a Pyrex glass tube. Both sides of the electrodes were kept in contact with Au meshes for current collection, and the tubes were sealed with flat rubber rings made of Kalrez perfluoroelastomer (DuPont Dow Elastomers). The protonic transport number was determined by measuring the electromotive force. Different hydrogen partial pressures were maintained at the two sides of the MEA with flowing H_2/Ar gas mixtures. The total pressure of the gas mixtures was kept at 1 atm, and the temperature was maintained constant at 150 °C. The operation of the H_2–O_2 fuel cell was demonstrated at 250 °C with a flowing H_2/H_2O gas mixture at the anode and with the flowing O_2/H_2O gas mixture at the cathode. Dc polarization curves were recorded in galvanostatic mode with a Potentiostat/Galvanostat 2000 (Toho Technical Research).

3. Results and discussion

3.1. *Conductivity measurements of CDP under various humid ambient conditions*

The conductivity of CDP was investigated under various of humidity conditions. The humidity dependence of conductivity, shown in Figure 1, was measured in

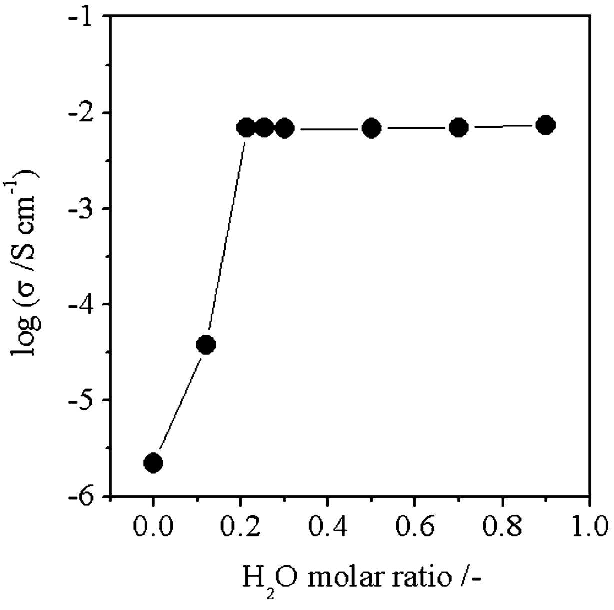

Fig. 1. Humidity dependence of CDP conductivity. Temperature: 250 °C; ambient condition: x mol% H_2O/Ar-balance (x = 0–90) in atmospheric pressure.

different water vapor concentrations between 0 mol% and 90 mol% at 250 °C. The CDP sample was kept for about 60 min at each water vapor concentration before the ac impedance was measured. The results showed that the conductivity, σ, significantly decreased when the water vapor concentration was below 20 mol%. This suggested that the dehydration (reaction 1) of CDP yielded polymerization products at water vapor concentrations below 20 mol%. In contrast, conductivity remained constant at around 1×10^{-2} S cm^{-1} in 20–90 mol% H_2O/Ar (high-conducting phase). This suggested that CDP dehydration could be suppressed at water vapor concentrations at or above 20 mol%, to maintain conductivity (ca. 1×10^{-2} S cm^{-1}). In addition, the phase stability of CDP in atmospheres of hydrogen or oxygen with water vapor was examined in relation to conductivity. We confirmed that conductivity remained constant around 1×10^{-2} S cm^{-1} for 24 h at 250 °C in 30 mol% H_2O/70 mol% H_2 and 30 mol% H_2O/70 mol% O_2. Next, the reversibility of the dehydration (reaction 1) at 250 °C was investigated by measuring conductivity as shown in Figure 2. When dry Ar was introduced into the system after the sample was kept in 30 mol%H_2O/Ar-balance for 1 h (marked (a) in Figure 2), the conductivity began to decrease, and dropped significantly for 1 h, from 1×10^{-2} to 8×10^{-6} S cm^{-1}. When a 30 mol% H_2O/Ar-balance gaseous mixture was again supplied to the system (marked (b) in Figure 2), the conductivity gradually increased, finally reaching the initial value (1×10^{-2} S cm^{-1}). This result suggests that the reaction between CDP and its polymerization product (dehydration) proceeds reversibly at 250 °C.

The conductivity of CDP in a heating process was also measured stepwise from 150 to 300 °C (Figure 3). The CDP sample was stabilized for 30 min at each temperature before ac impedance was measured. Figure 3a and 3b show the temperature dependence of the conductivity in 30 mol% H_2O/Ar-balance and in 90 mol% H_2O/Ar-balance, respectively, in the heating process. In the case of the 30 mol% H_2O/Ar flow condition, the conductivity increased monotonically with increasing temperature from 150 to 230 °C (low-conducting phase), then suddenly jumped up by three orders of magnitude as the temperature exceeded 230 °C. It is considered that this superionic phase transition is accompanied by a structural transformation from a monoclinic phase to a cubic phase [2, 3]. When the temperature was increased from 230 to 280 °C, the conductivity increased monotonically (high-conducting phase). The value of conductivity then began to fluctuate a little above 280 °C, and the conductivity suddenly dropped above 300 °C. After the measurement, it was observed that the sample pellet had melted. It has been reported that the melting point of CDP, which is measured in a Ni capsule, is ca. 345 °C [10]. The present melting temperature is thus lower than that in the previous literature [10]. The sample after melting was examined by XRD, showing that reaction (1) had occurred. Therefore, the CDP melting occurs at around 280 °C in company with dehydration under this humidified condition. In the case of the 90 mol% H_2O/Ar flow condition, the temperature dependence of conductivity in the heating process was similar to that in 30% H_2O/Ar, except in the low-conducting phase below 230 °C. The phase transition temperature in 90% H_2O/Ar coincided with that in 30% H_2O/Ar about 230 °C. When the temperature was increased from 230 to 300 °C, the conductivity increased monotonically. The value of conductivity in the high-conducting phase in 90% H_2O/Ar at each temperature was the same as that in 30% H_2O/Ar. It was also observed that in excess of 300 °C (300~310 °C), the conductivity suddenly dropped and the sample pellet melted. The XRD measurement suggested that the sample after melting had undergone reaction (1). The melting involving dehydration occurs at around 300~310 °C in 90% H_2O/Ar. On the other hand, the conductivity in the low-conducting phase decreased with increasing temperature from 150 to 230 °C. This tendency may be attributable to adsorbed water on the CDP surface.

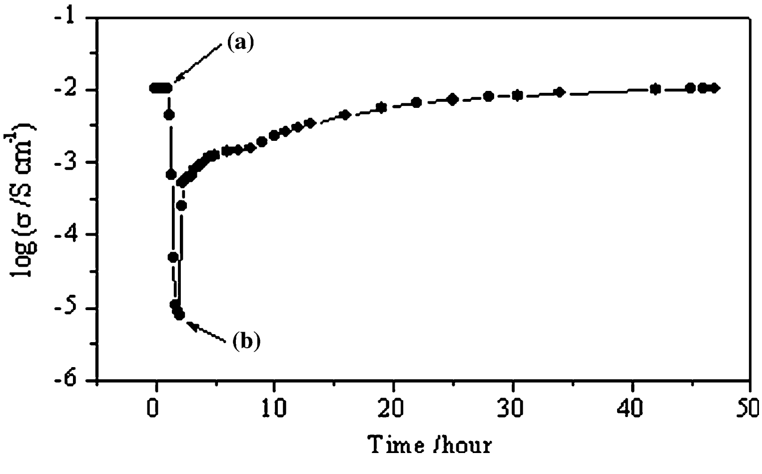

Fig. 2. Reversibility of CDP conductivity. Temperature: 250 °C; total pressure: atmospheric pressure; (a) stop of the supply of 30 mol%H_2O/Ar-balance and start of the supply of dry Ar; (b) restart of the supply of 30 mol%H_2O/Ar-balance.

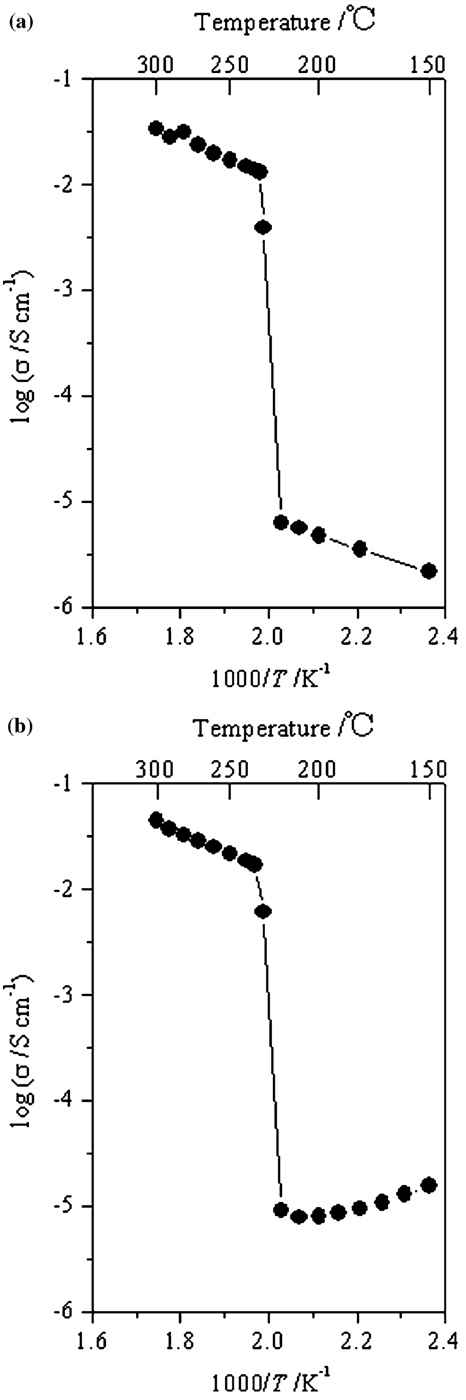

Fig. 3. Temperature dependence of CDP conductivity in a heating process. (a) 30 mol%H_2O/Ar-balance; (b) 90 mol%H_2O/Ar-balance; total pressure: atmospheric pressure.

Water molecules adsorbed on the CDP crystal surface would be expected to assist in protonic conduction on the surface. In the low-conducting phase, surface protonic conduction significantly enhances conductivity. In fact, the conductivity in 90% H_2O/Ar at 150 °C is more than seven times larger than that in 30% H_2O/Ar at the same temperature. As the temperature increases from 150 to 230 °C, relative humidity is decreased and the concentration of adsorbed water molecules is also decreased. Therefore, conductivity in the low-conducting phase, which depends on the relative humidity, is expected to decrease with increasing temperature. Above 230 °C, as already mentioned, the change in humidity does not strongly affect the phase transition temperature and the conductivity in the high-conducting phase. In this phase, the conductivity of bulky CDP becomes high in comparison with the surface conductivity. Thus, water molecules adsorbed on the CDP surface do not contribute to the enhancement of conductivity in the high conduction phase.

Based on the above results, a tentative phase diagram of CDP as a function of water partial pressure and temperature was drawn in Figure 4. The phase transition temperature from the low-conducting phase to the high-conducting phase (superprotonic phase) was obtained from results in Figure 3. The region in which the dehydration proceeded was estimated from results in Figure 1 (point 4 in Figure 4) and thermal analyses in the previous studies [7, 9] (points 3 and 6 in Figure 4). Also, XRD measurements suggest that the melting of CDP occurred, being accompanied by dehydration under the present humid conditions (points 5 and 7 in Figure 4). Figure 4 clearly shows the region of superprotonic phase, suggesting that CDP can be used as a solid electrolyte material for a fuel cell operated at intermediate temperature, such as around 250 °C.

3.2. *Evaluation of protonic transport number of CDP and fuel cell operation with CDP electrolyte*

We evaluated the protonic transport number of CDP, which to our knowledge had not been reported before, by measuring the electromotive force. The configuration of the electrochemical cell was as follows.

$$H_2(g, p_2\text{atm}), \text{Pt/C}|\text{CDP solidelectrolyte}|\text{Pt/C}, H_2(g, p_1\text{atm}), \qquad (2)$$

where pressure p_1 was kept constant at 1 atm of pure hydrogen and pressure p_2 was changed between 1 and 4×10^{-4} atm of pure hydrogen. Pt/C particulate electrodes were used for both sides of the cell. If CDP is a proton conductor, i.e., a protonic transport number, t_H, is equal to unity, then electromotive force, E, can be expressed as follows:

$$E = -t_H \frac{RT}{2F} \ln \frac{p_2(H_2)}{p_1(H_2)} \qquad (3)$$

where R, T, and F are the gas constant, temperature, and Faraday constant, respectively. The electromotive force was measured at two temperatures (room temperature and 150 °C), taking into account the onset temperature of reaction (1) under dry conditions (~200 °C) in order to avoid the dehydration process [7]. The electromotive force at room temperature was unstable against elapsed time, and its relaxation time was too slow to be measured. Meanwhile, stable and reproducible results were obtained when the

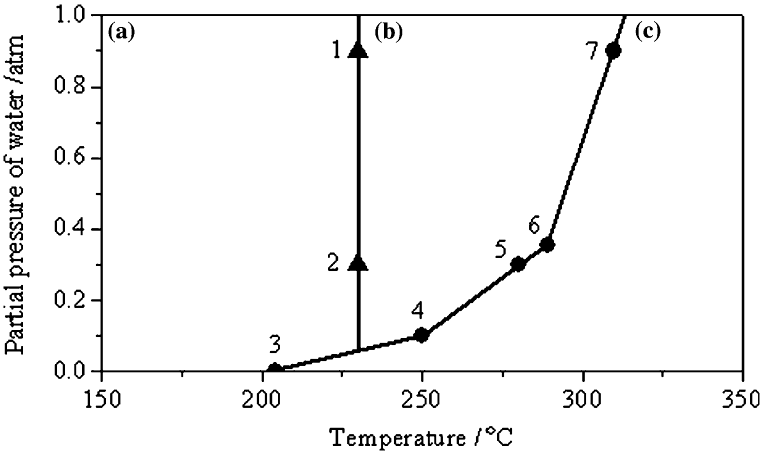

Fig. 4. Proposed phase diagram of CDP. Area (a): low-conducting phase (monoclinic phase); area (b): superprotonic phase (cubic phase); area (c): the dehydration of CDP proceeds to form polymerization products (reaction 1). Points 1, 2, 4, 5, and 7 were obtained from this work (see the text). Points 3 and 6 were obtained from thermal analyses in the previous studies [7] and [9], respectively.

electromotive force was measured at 150 °C. Figure 5 shows the electromotive force plotted against ln $p_2(H_2)/p_1(H_2)$ at 150 °C. The experimental values of the electromotive force were almost the same as the ideal values calculated by Equation 3, suggesting that the proton was a practical mobile charge carrier in CDP. In fact, the t_H value was determined as 0.99 ± 0.01 by fitting the experimental data with Equation 3, which is almost unity.

Finally, fuel cell operation was demonstrated at 250 °C. The dc polarization curves were measured in a galvanostatic mode by stepping up the current density from 0 to 60 mA cm^{-2} (forward process) and then stepping it down from 60 to 0 mA cm^{-2} (backward process). The cell was kept for 10 min at each current density to stabilize the cell voltage before it was measured. As shown in Figure 6, the dc polarization curve in the forward process coincides with that in the backward process, suggesting the CDP electrolyte and the interface between the electrolyte and the electrode are stable in the present humidified fuel cell operation. The open circuit voltage (945 mV) is, however, lower than the theoretical value (1144 mV: Nernst potential). The difference is probably due to gas leakage, since the electromotive force measurement suggests that the protonic transport number of CDP is almost unity. Although the present demonstration of fuel cell operation shows the stability of the CDP electrolyte, the cell performance is not so high. This is due to ohmic

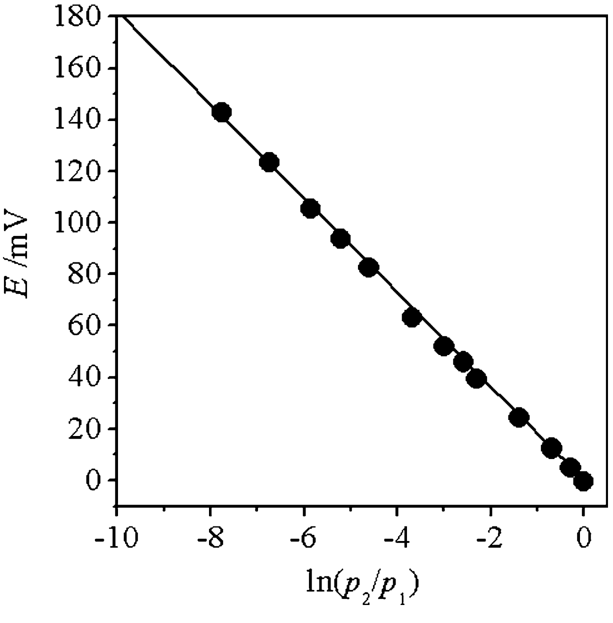

Fig. 5. Electromotive force plotted vs. ln $p_2(H_2)/p_1(H_2)$. Temperature: 150 °C; filled circle: experimental data; solid line: estimated value (t_H = 1).

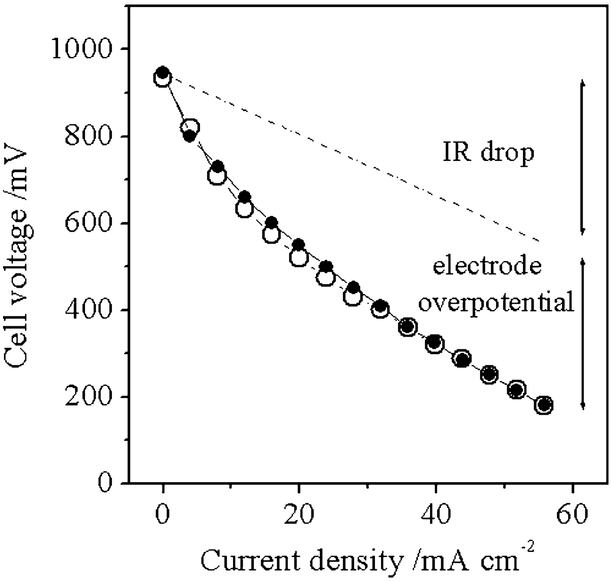

Fig. 6. Cell voltage vs. current density in the fuel cell operation. Temperature: 250 °C; total pressure: atmospheric pressure; anode: 30 mol% H_2O/70 mol% H_2 at the flow rate of 286 ml min^{-1} (sccm); cathode: 30 mol% H_2O/70 mol% O_2 at the flow rate of 286 ml min^{-1} (sccm); filled circle: experimental data in the forward process; open circle: experimental data in the backward process; broken line: IR drop by CDP electrolyte, which was estimated from the conductivity data in Figure 3a.

loss by the electrolyte and to electrode overpotentials, as shown in Figure 6. In the present study, the CDP electrolyte is relatively thick (ca. 1.2 mm), and the proton-conducting networks in the electrodes are not optimized. The structure of the three-phase boundary in the electrode should be developed and a thin film electrolyte should be fabricated. We will undertake both of these in future work.

4. Conclusions

The superionic phase transition was observed at ca. 230 °C from a low-conducting phase to a high-conducting phase in ambient humid atmospheres of 30 mol% H_2O/Ar-balance and 90 mol% H_2O/Ar-balance. Conductivity in the low-conducting phase was influenced by the water vapor concentration, while that in the high-conducting phase was independent of changes in the water vapor concentration. At 250 °C, the high-conducting phase was maintained in ambient atmospheres exceeding 20 mol% H_2O, while the dehydration of CsH_2PO_4 proceeded in ambient atmospheres below 20 mol% H_2O. The reversibility of CsH_2PO_4 dehydration was also demonstrated, i.e., the conductivity of CsH_2PO_4, after decreasing by dehydration under a dry condition, completely recovered in a 30% H_2O/Ar-balance ambient atmosphere at 250 °C. The phase diagram of CsH_2PO_4 as a function of water partial pressure and temperature was drawn, which showed the region of superprotonic phase and suggested conditions for fuel cell operation. The protonic transport number of CsH_2PO_4 was evaluated by measuring electromotive force, revealing that the protonic transport number is almost unity. The results indicate the applicability of the CsH_2PO_4 solid electrolyte to intermediate temperature fuel cells. An MEA made of CsH_2PO_4 electrolyte was operated at 250 °C with a supply of 30 mol% H_2O/70 mol% H_2 and of 30 mol% H_2O/70 mol% O_2 for the anode and cathode, respectively. This demonstrated that the CsH_2PO_4 electrolyte was stable in fuel cell operation with appropriate humidity.

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