Phase Relationship of CsH₂PO₄–CsPO₃ System and Electrical Properties of CsPO₃

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The dehydration behavior of the paraelectric phase of CsH₂PO₄ was investigated by thermogravimetric and X-ray diffraction analyses, and then the phase diagrams of CsH₂PO₄–CsPO₃ system were established. The relationship between the onset temperature of dehydration (Tdehy/K) and the partial pressure of water (pH₂O/atm) is given by

\[ \log_{10} p_{H_2O} = -2370.7 + 0.976 T_{dehy} \]

The thermodynamically stable phase just above Tdehy is the fully dehydrated product CsPO₃(s), although partially dehydrated products transiently appeared in the course of the dehydration to CsPO₃.

Such developments allowed us to complete the temperature-humidity phase diagram and to regard the composition-temperature phase diagram as the eutectic type. This paper also reports the phase transition and electrical properties of CsPO₃ examined by differential thermal analysis, ac impedance spectroscopy, and dc polarization measurement. The thus-synthesized CsPO₃ showed the relatively high electrical conductivity in unhumidified Ar. Ionic conductivity as high as 5 x 10⁻⁴ S cm⁻¹ was observed on heating from 150 to 450°C. Such high ionic conductivity disappeared after first heating up to 620°C and was explained by the proton diffusion through the absorbed H₂O. At around 600°C, a high-temperature phase of CsPO₃ showed the electrical conductivity as high as 10⁻³ S cm⁻¹. However, this conductivity was not purely ionic.

In this study, for a comprehensive understanding of the dehydration behavior of CsH₂PO₄, we investigate the dehydration reaction from the paraelectric phase of CsH₂PO₄ [CsH₂PO₄(s,pe); paraelectric phase] at temperatures lower than 228°C. On the basis of the results of this study as well as those in previous reports, the composition-temperature phase diagram of CsH₂PO₄ is completed and a composition-temperature phase diagram of CsH₂PO₄–CsPO₃ system is developed. These phase diagrams are useful for researchers developing CsH₂PO₄-type fuel cells. As far as we know, there is no report about the electrical properties of CsPO₃, which is the final dehydration product. The just synthesized CsPO₃ showed relatively high electrical conductivity. Thus, the thermal and electrical properties of CsPO₃ are also investigated in detail.

Experimental

Dehydration behavior of CsH₂PO₄—Polycrystalline powder of CsH₂PO₄ was prepared from Cs₂CO₃–H₃PO₄ aqueous solutions by the introduction of methanol. X-ray powder diffraction (XRD) was utilized to confirm that the desired phase had been obtained. In addition, the ratios of phosphorus (P) and cesium (Cs) in the powder were checked using inductively coupled plasma atomic emission spectrometry and an atomic adsorption spectrophotometer, respectively.

A thermogravimetric (TG) analysis (TGA) of CsH₂PO₄ powder was carried out using a Rigaku TG-DTA/HUM with the platinum sample container. The weight of the sample was ~25 mg. pH₂O around the sample was controlled by flowing humidified Ar-gas at the rate of ~400 mL min⁻¹.

Phase identification was carried out via XRD analysis on a Rigaku 2200 using Cu Kα radiation. The diffraction pattern of the sample at various levels of dehydration was collected at room temperature.

Thermal and electrical properties of CsPO₃—Polycrystalline powder of CsPO₃, which is the final dehydration product, was prepared by the dehydration reaction from CsH₂PO₄ polycrystalline powder. CsH₂PO₄ powder in a silica glass crucible was kept at 190°C for 62 h in Ar or at 220°C for 72 h in air. In each case, the final weight change was ~7.7 ± 0.2%, which is evidence of the formation of CsPO₃ because the theoretical weight change for the dehydration reaction from CsH₂PO₄ to CsPO₃ is ~7.84%.

A differential thermal analysis (DTA) of CsPO₃ powder was carried out using a Rigaku TG-DTA/HUM utilizing platinum as the reference. The sample in a platinum container was heated and cooled at the rate of 5 K min⁻¹ from 200 to 800°C. Ar-gas with pH₂O = 0.0085 atm was flowed at the rate of ~400 mL min⁻¹.

The electrical conductivity of CsPO₃ was examined by ac impedance spectroscopy and dc polarization measurement. The details of the experimental apparatus were shown previously. For the electrical measurements, CsPO₃ powder was pressed uniaxially at 3 ton cm⁻² for 10 min to form the pellets (diameter 1.11 cm, thick-
ness ~ 1 mm). Prior to forming pellets, CsPO₃ powder was heated at 550°C for 12 h in air to minimize the effect of absorbed H₂O and to eliminate the possibility of partial rehydration of CsPO₃. Silver electrodes were attached on both sides of the pellet with silver paint (Fujikura Kasei, D-550). The temperature dependence of conductivity was measured by ac impedance spectroscopy using a Solartron 1260 in the frequency range from 1 to 1 MHz with voltage amplitude of 500 mV. The CsPO₃ pellet was heated and cooled at 1 K min⁻¹ in the temperature range from 150 to 620°C. The measurements were performed under flowing unhumidified Ar gas. Collected impedance data were analyzed using the commercial software package Z-View. The dc polarization measurement was performed using a Solartron 1278 potentiostat. DC voltage was applied under flowing unhumidified Ar gas.

Results

Dehydration behavior of CsH₂PO₄.— TGA of CsH₂PO₄.— Figure 1 shows the results of weight change on heating at the three different rates of 2, 5, and 10 K h⁻¹ under pH₂O = 0.022 ± 0.009 atm. Figure 1a and b shows the weight change against temperature (TG curve) and the differential values of weight change [differential TG (DTG) curve], respectively. The theoretical weight changes to form CsPO₃ (−7.84%) and CsHPO₃.₅ (−3.92%) are also plotted as dotted lines in Fig. 1a. The TG and DTG curves revealed an onset temperature of dehydration of CsH₂PO₄ (Tdehy in Fig 1), a local minimum of weight loss (Tₛ in Fig. 1), and subsequent completion of the reaction. A similar profile was observed in the dehy under CsH₂PO₄(s,sp), where the dehydration temperature is in the range from 228 to 260°C.⁷

The phase-boundary between CsH₃PO₄(s,pe) and CsHPO₃.₅ and CsPO₃. The phase-boundary between CsH₂PO₄ and CsHPO₃.₅ was determined by the value of Tdehy. Tdehy in Fig. 1 is an apparent value because it increases with a rise in heating rate. True Tdehy was estimated by the extrapolation against the square root of heating rate.⁸ Figure 2a shows the extrapolation of the apparent Tdehy under pH₂O = 0.022 ± 0.009 atm to zero heating rate. This extrapolation is reasonable because a linear relationship can clearly be seen. Similar measurements were repeated under four different pH₂O. The results are summarized in the Arrenius form in Fig. 2b. A good linear relationship between the inverse temperature and log(pH₂O) is evident by the dotted line. The resultant relationship between pH₂O(atm) and Tdehy(K) is described by

\[
\text{log}(pH₂O) = 7.62(±1.18) - 4.42(±0.56)\frac{1000}{T_{dehy}} \tag{2}
\]

The total weight loss at the end of the reaction as seen in Fig. 1a was in excellent agreement with the theoretical weight loss to form CsPO₃ for all heating rates. The sample after TGA remained in the form of loose powder. Thus, the dehydration from CsH₂PO₄(s,pe) to CsPO₃(s) was not through the liquid phase.

Figure 3 shows the results of isothermal TGA. Figure 3a and b are TG/DTG curves at 190°C under pH₂O = 0.0085 ± 0.0003 atm and at 218°C under pH₂O = 0.0354 ± 0.0015 atm. These temperatures are slightly higher than the equilibrium Tdehy implied by Eq. 2. That is, with the given pH₂O, CsH₂PO₄ should dehydrate at 183 ± 3 and 214 ± 3°C, respectively. In either condition, final weight losses were in excellent agreement with the theo-

Figure 1. TGA of CsH₂PO₄ powder at three heating rates of 2, 5, and 10 K h⁻¹ under pH₂O = 0.022 ± 0.009 atm. (a) Temperature dependence of weight change (TG curve). Dotted lines indicate the theoretical weight changes to form CsHPO₃ (CsPO₃ for all heating rates. The sample after TGA remained in an apparent value because it increases with a rise in heating rate. True Tdehy was estimated by the extrapolation against the square root of heating rate.Fig. 2a shows the extrapolation of the apparent Tdehy under pH₂O = 0.022 ± 0.009 atm to zero heating rate. This extrapolation is reasonable because a linear relationship can clearly be seen. Similar measurements were repeated under four different pH₂O. The results are summarized in the Arrenius form in Fig. 2b. A good linear relationship between the inverse temperature and log(pH₂O) is evident by the dotted line. The resultant relationship between pH₂O(atm) and Tdehy(K) is described by

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retical value to form the fully dehydrated product of CsPO₃. Partially dehydrated products, such as CsHPO₃, could not be obtained as a stable phase. However, a local minimum of weight loss appeared at a time of τₚ in Fig. 3, where the weight loss almost coincided with the theoretical value to form CsHPO₃.

X-ray diffraction analysis of dehydration products.— Figure 4 shows the XRD patterns of samples at various levels of dehydration. The diffraction pattern of nondehydrated CsH₂PO₄ (s,pe) is shown in Fig. 4a, which agreed with the diffraction pattern for paraelectric phase of CsH₂PO₄ provided in the JCPDS database, and the impurity phases were not seen. The diffraction pattern of fully dehydrated CsPO₃ (s) is shown in Fig. 4d. Fully dehydrated CsPO₃ was prepared by heating CsH₂PO₄ at 215 °C for 94 h under unhumidified Ar gas. The weight change of ~7.9% agreed with the theoretical weight change to form CsPO₃ (~7.84%). In addition, the pattern in Fig. 4d was in excellent agreement with the diffraction pattern for CsPO₃, which we reported previously. Meanwhile, Fig. 4b and c show the diffraction pattern of the partially dehydrated sample where weight changes are ~0.4 and ~1.6%, respectively. In Fig. 4b, CsH₂PO₄ (s,pe) was kept for 2.5 h at 217 °C and pH₂O = 0.036 atm, where the temperature was 3 °C higher than Tdehy. Weight change was ~0.4%. (c) Partially dehydrated sample. CsH₂PO₄ (s,pe) was kept for 1 h at 220 °C in air (pH₂O = about 0.016 atm). Fixed temperature was ~25 °C higher than Tdehy. Weight change was ~1.6%. Arrowed line indicates typical peak of unknown phase. (d) Fully dehydrated CsPO₃, which was prepared by keeping CsH₂PO₄ (s,pe) at 215 °C for 94 h in unhumidified Ar.

Thermal and electrical properties of CsPO₃.— Figure 5 shows the DTA profile of CsPO₃ powder at the heating/cooling rate of 5 K min⁻¹. Two endothermic peaks and two exothermic peaks were seen on heating and cooling, respectively.

Figure 3. TGA of CsH₂PO₄ powder at the constant temperature of (a) 190 °C under pH₂O = 0.0085 ± 0.0003 atm and (b) 218 °C under pH₂O = 0.0354 ± 0.0015 atm.

Figure 4. XRD patterns of samples at the various extent of dehydration. The diffraction patterns were collected at room temperature. The positions of diffraction peaks from CsHPO₃, are also shown. (a) Nondehydrated CsH₂PO₄. (b) Partially dehydrated sample. CsH₂PO₄ (s,pe) was kept for 2.5 h at 217 °C and pH₂O = 0.036 atm. Fixed temperature was 3 °C higher than Tdehy. Weight change was ~0.4%. (c) Partially dehydrated sample. CsH₂PO₄ (s,pe) was kept for 1 h at 220 °C in air (pH₂O = about 0.016 atm). Fixed temperature was ~25 °C higher than Tdehy. Weight change was ~1.6%. Arrowed line indicates typical peak of unknown phase. (d) Fully dehydrated CsPO₃, which was prepared by keeping CsH₂PO₄ (s,pe) at 215 °C for 94 h in unhumidified Ar.

Figure 5. DTA of CsPO₃ powder at the heating/cooling rate of 5 K min⁻¹ under pH₂O = 0.0085 ± 0.0003 atm. Tc and Tm mean the transition temperature to the high-temperature phase and melting point of CsPO₃, respectively.
The sample shape after DTA suggested melting in the course of the temperature sweep. Onset temperatures of two endothermic peaks on heating were 467°C ($T_{m1}$ in Fig. 5) and 735°C ($T_{m2}$ in Fig. 5), respectively. It was reported that CsPO$_3$ exhibits a phase transition to high temperature phase at $\sim$480°C and melts at $\sim$735°C. Thus, the endothermic and exothermic peaks at the higher temperature side around 700°C indicate the melting and freezing of CsPO$_3$. Thus, the endothermic and exothermic peaks at the higher temperature for two heating/cooling cycles. The conductivity of CsH$_3$PO$_4$ is also represented as a solid line. On first heating, CsPO$_3$ showed the relatively high conductivity of about $5 \times 10^{-3}$ S cm$^{-1}$ at the intermediate temperature from 150 to 450°C. However, this high conductivity at the intermediate temperature disappeared after first heating. The conductivity at 300°C on second heating was about three orders of magnitude lower than the value on first heating. Furthermore, the conductivity at 300°C on second heating was about four orders of magnitude lower than the value on first heating. The conductivity at 300°C on first cooling and second heating were not large, even though an abrupt small change of conductivity existed at the phase transition on heating.

The conductivity jumps at the transition temperature [CsPO$_3$(s) $\leftrightarrow$ CsPO$_3$(l)], at 467°C on first heating ($\rho_{\text{electrolyte}}$) was evaluated by the intersection between the arc and the real axes, as indicated in Fig. 6a. The straight line can be explained by the polarization phenomena at the electrolyte/electrode interfaces. Large polarization at the interfaces with Ag electrodes suggests that ionic conduction exists in CsPO$_3$. At 499°C on first heating (Fig. 6a), where CsPO$_3$ shows high-temperature phase, one arc and deviated semicircle were seen in the higher and lower frequency regions, respectively. The resistivity of CsPO$_3$ was evaluated by the intersection between the arc at higher frequency and the real axes, as indicated in Fig. 6a. The semicircle at the lower frequency region was probably attributed by the electrolyte/electrode interfaces. Meanwhile, the impedance spectrum collected at 297°C on second heating showed two distinct semicircles. It was estimated that the clear semicircle at the higher frequency region and the deviated semicircle at the lower frequency region corresponded to the CsPO$_3$ electrolyte and the electrolyte/electrode interfaces, respectively.

Figure 7 shows the conductivity of CsPO$_3$ as a function of temperature for two heating/cooling cycles. The conductivity of CsH$_3$PO$_4$ is also represented as a solid line. On first heating, CsPO$_3$ showed the relatively high conductivity of about $5 \times 10^{-3}$ S cm$^{-1}$ at the intermediate temperature from 150 to 450°C. However, this high conductivity at the intermediate temperature disappeared after first heating. The conductivity at 300°C on first cooling and second cooling was about three orders of magnitude lower than the value on first heating. Furthermore, the conductivity at 300°C on second cooling was about four orders of magnitude lower than the value on first heating. At $\sim$600°C, CsPO$_3$ in the high-temperature phase exhibited conductivity as high as $10^{-3}$ S cm$^{-1}$ in any heating/cooling cycle. It is also noteworthy that the conductivity jumps at the transition temperature [CsPO$_3$(s) $\leftrightarrow$ CsPO$_3$(s,ht), at 467°C on heating] were not large, even though an abrupt small change of conductivity existed at the phase transition on heating.

**Figure 6.** Typical impedance spectra of CsPO$_3$. (a) At 297 and 499°C on first heating and (b) at 298°C on second heating.

**Figure 7.** (Color online) Temperature dependence of electrical conductivity of CsPO$_3$ in unhumidified Ar. CsPO$_3$ pellet was heated and cooled at the rate of 1 K min$^{-1}$. The results of two heating and cooling cycles are presented.

Conductivity change of CsH$_3$PO$_4$ on heating under $p_{H_2O} = 0.3$ atm is also plotted as a solid line.

DC polarization measurement of CsPO$_3$.— DC polarization measurements were performed at two different temperatures in Ar (not humidified). Figure 8 shows the change of current with time and the relationship between steady current and voltage at 250 ± 2°C and at 543 ± 2°C. Prior to the measurements, CsPO$_3$ pellets were not treated at high temperature.
polarization measurements correspond to those of first heating of conductivity measurement, as Fig. 7 shows. At 250°C, dc voltages of 0.1, 0.2, and 0.3 V were each applied for 600 s. DC current rapidly decreased with time, as seen in Fig. 8a. The dc current at 600 s is plotted as a function of applied dc voltage in Fig. 8b. An obvious linear relationship was obtained (shown as the dotted line).

Meanwhile, at 543°C, dc voltages of 0.1, 0.2, 0.3, 0.4, and 0.5 V were each applied for 600 s. DC current rapidly decreased with time, as seen in Fig. 8c. As seen in Fig. 8c, the transference number for ion conduction at 8.5 s, as shown in Fig. 8d. The transference number, $TN_{dc}$, was evaluated based on the dc current at 0.1, 0.2, 0.3, 0.4, and 0.5 V were each applied for 600 s. At this temperature, $TN_{dc}$ showed the high-temperature phase. Compared to the current change with time at 250°C in Fig. 8a, the reduction rate of dc current was small at 543°C, as seen in Fig. 8c. $TN_{dc}$ was evaluated based on the dc currents at 8.5 s, as shown in Fig. 8d. $TN_{dc}$ and $TN_{electrolyte}$ at 543°C are also summarized in Table I. At 543°C, $TN_{dc}$ (1.10 $\times$ 10$^8$ Ω cm) did not show a large difference from $TN_{electrolyte}$ (6.59 $\times$ 10$^7$ Ω cm) and was about half the time of $TN_{electrolyte}$.

### Discussion

**Mechanism of dehydration reaction**.— The weight change at iso-temperatures in Fig. 3 indicated that the stable dehydration phase just above $T_{dehy}$ is CsPO$_3$(s). However, CsHPO$_{3.5}$(s) appeared as a transient phase in the course of dehydration as seen in the XRD analysis. This situation is the same as we found in our experiments of dehydration in the temperature range from 228 to 260°C.10 The existence of a transient phase complicates the thermodynamic analysis and reaction mechanism. There are two possibilities for the thermodynamic meaning of the $T_{dehy}$ in Eq. 2: constant temperature of the dehydration from CsH$_2$PO$_4$ to CsHPO$_{3.5}$ and that from CsH$_2$PO$_4$ to CsPO$_3$. Considering each equilibrium (or quasi-equilibrium) at a given temperature, $P_H_2O$ can be written as

$$2\text{CsH}_2\text{PO}_4(s,pe) = 2\text{CsHPO}_3.5(s) + \text{H}_2\text{O}(g)$$

$$\ln p_{H_2O}^{(3)} = \frac{-\Delta_{dehy}G_{(3)}(T)}{RT}$$

$$\text{CsH}_2\text{PO}_4(s,pe) = \text{CsPO}_3(s) + \text{H}_2\text{O}(g)$$

$$\ln p_{H_2O}^{(4)} = \frac{-\Delta_{dehy}G_{(4)}(T)}{RT}$$

where $\Delta_{dehy}G_{(i)}$ is the standard Gibbs energy of the dehydration reactions of Eq. 3 and 4 at Kelvin temperature $T$, $R$ is the gas constant, and $p_{H_2O}^{(i)}$ is the partial pressure of water in equilibrium Eq. 3 or 4. It is assumed that we take pure substances as standard state, and the reactant CsH$_2$PO$_4$ and the products CsHPO$_{3.5}$ and CsPO$_3$ do not have mutual solubility. In Eq. 3, quasi-equilibrium is established between CsH$_2$PO$_4$ and CsHPO$_{3.5}$.

Because CsPO$_3$ is a thermodynamically stable phase just above $T_{dehy}$, the mixture of CsH$_2$PO$_4$ and CsPO$_3$ is more stable than CsHPO$_{3.5}$.
2CsHPO₄(s) → CsH₂PO₄(s,pe) + CsPO₄(s)  \[ \Delta G_\text{r}^\circ(T) < 0 \]  \[5\]

Therefore

\[ \ln p_{\text{H}_2\text{O}}^{(\text{eq})} - \ln p_{\text{H}_2\text{O}}^{(\text{eq})} = -\frac{\Delta G_\text{r}^\circ(T)}{RT} \]

\[6\]

Equation 6 means that, at a fixed temperature, the \( p_{\text{H}_2\text{O}}^{(\text{eq})} \) quasi-equilibrating CsH₂PO₄ with CsHPO₄ is lower than that equilibrating CsH₂PO₄ with CsPO₄. Furthermore, at a given \( p_{\text{H}_2\text{O}}^{(\text{eq})} \), the following relationships exist

\[ T^{(7)} = \frac{-\Delta_{\text{dehy}} G^{(7)}_\text{r}}{R \ln p_{\text{H}_2\text{O}}} \]

\[7\]

\[ T^{(8)} = \frac{-\Delta_{\text{dehy}} G^{(8)}_\text{r}}{R \ln p_{\text{H}_2\text{O}}} \]

\[8\]

\[ \Delta_{\text{dehy}} G^{(7)}_\text{r} - \Delta_{\text{dehy}} G^{(8)}_\text{r} = -[T^{(8)} - T^{(7)}] \Delta_{\text{dehy}} S^{(3)} \]

\[9\]

where it is reasonable to assume that the standard enthalpy change, \( \Delta_{\text{dehy}} H^{\circ} \), and the standard entropy change, \( \Delta_{\text{dehy}} S^{\circ} \), for Reactions 3 and 4 are constant in the considered temperature range. Subtracting Eq. 8 from Eq. 7, we obtain

\[ T^{(7)} - T^{(8)} = \frac{-\Delta_{\text{dehy}} G^{(7)}_\text{r}}{R \ln p_{\text{H}_2\text{O}}} \]

\[10\]

Then, we substitute Eq. 9 into Eq. 10 for \( \Delta_{\text{dehy}} G^{(7)}_\text{r} \) to come out. The result is

\[ T^{(7)} - T^{(8)} = \frac{-\Delta_{\text{dehy}} G^{(7)}_\text{r}}{R \ln p_{\text{H}_2\text{O}}} - \Delta_{\text{dehy}} S^{(3)} \]

\[11\]

Or, \( \Delta_{\text{dehy}} S^{(3)} \) is a positive value because the reaction is a gas evolution reaction, and \( R \ln p_{\text{H}_2\text{O}} \) is a negative value, which means \( T^{(7)} - T^{(8)} > 0 \). This implies that the dehydration reaction from CsH₂PO₄ to CsPO₄ occurs at lower temperature on heating than the dehydration reaction from CsH₂PO₄ to CsHPO₄, thermodynamically. Therefore, we can regard \( T^{(8)} = T_{\text{dehy}} \) (the value determined by experiment). Meanwhile, we observed formation of CsHPO₄, at the initial stage even at just above \( T_{\text{dehy}} \) (43°C), as seen in Fig. 4b. This suggests that the difference between \( T^{(7)} \) and \( T^{(8)} \) is very small.

As a result, the driving force of the dehydration reaction from CsH₂PO₄ to CsPO₄, as well as the driving force of the dehydration reaction from CsH₂PO₄ to CsHPO₄, are generated at a slightly higher temperature than \( T_{\text{dehy}} \). Kinetically speaking, the rate of the dehydration reaction from CsH₂PO₄ to CsPO₄ should be much smaller than that from CsH₂PO₄ to CsHPO₄ because the former is a polymerization reaction of PO₄³⁻ anion and the latter is a reaction of dimer formation of PO₄²⁻ anion. For this reason, CsHPO₄ appears as a transient phase. The transient appearance of CsHPO₄ probably explains the local minimum in the weight change profile (\( T_p \) in Fig. 1, \( T_e \) in Fig. 3), where the weight loss is in good agreement with the theoretical value to form CsHPO₄. It is also notable that an unknown product was detected by XRD analysis in Fig. 4c when CsH₂PO₄ (s,pe) partially dehydrates at a much higher temperature than \( T_{\text{dehy}} \). It is possible that the driving force to form other partially dehydrated species are generated at much higher temperature than \( T_{\text{dehy}} \).

### Table II. Standard enthalpy, entropy, and Gibbs energy of the formation of CsPO₄ at 298 K. Estimated values were compared to the reported values.⁷,8,10

<table>
<thead>
<tr>
<th>Source</th>
<th>( \Delta H^{\circ} ) (kJ mol⁻¹)</th>
<th>( \Delta S^{\circ} ) (J mol⁻¹ K⁻¹)</th>
<th>( \Delta G^{\circ} ) (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>-1238 (±11)</td>
<td>-324 (±23)</td>
<td>-1141 (±18)</td>
</tr>
<tr>
<td>Ref. 10</td>
<td>-1242 (±9)</td>
<td>-330 (±17)</td>
<td>-1144 (±14)</td>
</tr>
<tr>
<td>Ref. 17</td>
<td>-1241.4</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Thermodynamic evaluation for onset temperature of dehydration.**—Thermodynamical properties of CsPO₄(s) are re-evaluated by the relationship between \( T_{\text{dehy}} \) and \( p_{\text{H}_2\text{O}}^{(\text{eq})} \) in Eq. 2. The detailed evaluation procedure was shown previously.⁷ We can regard \( T_{\text{dehy}} \) in Eq. 2 as \( T^{(8)} \) in Eq. 8. Inserting the numeric values yields

\[ \Delta_{\text{dehy}} H^{\circ} = 84.6 ± 10.7 \text{ kJ mol}^{-1} \]

\[12\]

We assume that \( \Delta_{\text{dehy}} H^{\circ} \) and \( \Delta_{\text{dehy}} S^{\circ} \) are constant in the temperature range to 298 K. On the basis of the standard enthalpy and entropy of formation of CsH₂PO₄(s,pe) and H₂O(g) at 298 K,¹⁷ as well as Eq. 12, thermodynamic properties of formation of CsPO₄(s) can be calculated as shown in Table II. Table II also shows the values in the literature and those evaluated in our previous study,¹⁰ where the dehydration from the superprotonic phase was investigated above 228°C. The values evaluated in this study are self-consistent with previous results.

**Electrical conduction in CsPO₂.**—The final dehydration product of CsPO₄ showed relatively high electrical conductivity in two conditions: (i) at an intermediate temperature anywhere between 150 and 450°C only during first heating and (ii) at around 600°C, where CsPO₄ is in the high-temperature phase for any heating/cooling cycles. Thus, we discuss the mechanism of high electrical conduction in CsPO₄.

Conductivity as high as 5 × 10⁻⁴ S cm⁻¹ was seen at intermediate temperatures in the range from 150 to 450°C on first heating as seen in Fig. 7. DC polarization measurement showed that \( \rho_{\text{dc}} \) was about two orders of magnitude higher than \( \rho_{\text{Pb elec}} \). A high conduction electron/hole flow provides electron, but it is quite difficult for the Ag electrode in humidified Ar to work for ionic species such as protons and oxide ions. That is, the Ag electrode is considered to be a blocking electrode for ionic conductors. We can regard that the current in steady state, when dc voltage is applied, is due to the current flow by electrons or holes. Thus, \( \rho_{\text{dc}} \) corresponds to the resistivity of electron/hole flow. Meanwhile, \( \rho_{\text{Pb elec}} \), obtained by ac impedance spectroscopy should correspond to the resistivity of diffusion of all mobile carriers (i.e., the sum of ion, electron, and hole diffusion). As a result, the transference numbers of ions (\( T_f \)) and sum of those of electrons and holes (\( T_N \)) can be estimated from \( \rho_{\text{dc}} \) and \( \rho_{\text{Pb elec}} \), while the estimated values are preliminary ones. The estimated transference numbers are shown in Table I. At 250°C, \( T_f \) was 0.99 and the type of conduction of CsPO₄ was ionic. Although the mobile ion and its conduction mechanism are still unclear, we speculate that proton diffusion occurs through the absorbed H₂O on the surface and interface. CsPO₄ powder kept in a dry desiccator was pelletized at ambient temperature under atmospheric conditions. We believe that some amount of H₂O in air was absorbed during pelletizing. It is also noteworthy that it was difficult to detect further weight changes when CsPO₄ powder, which was dehydrated at above 200°C and, subsequently quenched, was kept at the ambient temperature under atmospheric conditions. Thus, the amount of ab-
absorbed H₂O should be very small. The disappearance of high ionic conductivity after first heating can be explained by desorption of H₂O.

Meanwhile, at around 600°C, CsPO₃ exhibited high conductivity of ~10⁻³ S cm⁻¹ for all heating/cooling cycles as seen in Fig. 7. TNₙ and TNₐ at 543°C can be defined as 0.40 and 0.60, respectively, as listed in Table I. Thus, CsPO₃ was estimated to be a mixed conductor at 543°C on first heating. We speculate that residual H₂O sorbed on the CsPO₃ surface is the origin of ionic conduction at this temperature. When CsPO₃ is kept at a higher temperature than 543°C, ionic conduction probably disappears and almost pure liquid phase.

Preliminary composition-temperature phase diagram of the CsH₂PO₄–CsPO₃ system estimated based on Fig. 9a. The melting point of CsH₂PO₄ is 345°C based on the data reported by Rapoport et al.³⁴ CsPO₃ exhibits phase transition to high-temperature phase at 467°C and melts at 733°C, as seen in Fig. 5. CsHPO₄·xH₂O line. Each line explains the three types of dehydration pathway depending on humidity and temperature. Lines I and II are the dehydration pathways from CsH₂PO₄(s,sp) to CsPO₃(s), and from CsH₂PO₄(s,sp) to CsPO₃(s), respectively. Line III is the dehydration pathway from CsH₂PO₄(s,sp) to CsPO₃(s) through liquid phase.

In the previous study, phase boundaries were determined based on the conductivity and weight changes on heating. In this diagram, we can see that CsH₂PO₄ electrolyte in a practical application must be kept in regions 1 and 2. Meanwhile, Fig. 9b shows the preliminary composition-temperature phase diagram of the CsH₂PO₄–CsPO₃ system estimated based on Fig. 9a. The melting point of CsH₂PO₄ can be estimated at ~345°C based on the data reported by Rapoport et al.³⁴ CsPO₃ exhibits phase transition to high-temperature phase at 467°C and melts at 733°C, as seen in Fig. 5. CsHPO₄·xH₂O line. Each line explains the three types of dehydration pathway depending on humidity and temperature. Lines I and II are the dehydration pathways from CsH₂PO₄(s,sp) to CsPO₃(s), and from CsH₂PO₄(s,sp) to CsPO₃(s), respectively. Line III is the dehydration pathway from CsH₂PO₄(s,sp) to CsPO₃(s) through liquid phase.

The onset temperatures of dehydration of various alkali metal dihydrogen phosphates (MH₂PO₄, M = Na, K, Cs) are compared in Fig. 10a. Kiehl and Wallace³⁹ reported the values for NaH₂PO₄ and KH₂PO₄. Figure 10b shows the Pauling electronegativity of alkali metals and the stability against dehydration of CsH₂PO₄ is improved on decreasing electronegativity. Dehydration temperatures of MH₂PO₄ (M = Na, K, Cs) at pH₂O = 0.05 and 0.15 atm are also summarized.
sidering solid acids, which have a strong ionic nature, a cation with smaller electronegativity makes the net charge of oxygen negatively larger. As a result, the binding of proton and oxide ion (O⁻–H⁻O) between phosphate anions probably becomes stronger, which increases the dehydration temperature. Meanwhile, Boysen reported that ion size plays a key role in the appearance of superprotonic transition. Superprotonic phases exist in RbH₂PO₄ and CsH₂PO₄, which have smaller ratios of cation and oxy-anion, but are absent in NaH₂PO₄ and KH₂PO₄, which have smaller ratios of cation and oxy-anion. These two kinds of empirical knowledge will become a hint to find new solid acids, which have higher chemical stability against dehydration while keeping their appearance of superprotonic phase.

Conclusion

At temperatures lower than 228°C, the relationship between the onset temperature of dehydration \( T_{dehy} \) of CsH₂PO₄(s,pe) and the partial pressure of water \( (p_{H₂O}/atm) \) is expressed by

\[
\log p_{H₂O} = 7.62(±1.18) - 4.42(±0.56) - 1000 \frac{T_{dehy}}{T_{dehy}}
\]

The stable phase just above \( T_{dehy} \) is the fully dehydrated product of solid CsPO₃. However, partially dehydrated products, such as solid CsH₂PO₄ and an unknown phase, appeared as transient phases in the course to complete dehydration. The dehydration mechanism from CsH₂PO₄(s,pe) was explained by thermodynamic considerations. The findings in this study allowed us to complete the temperature-humidity phase diagram of CsH₂PO₄, which is important information for its stable operation as a fuel cell electrolyte. Moreover, the composition-temperature phase diagram of the CsH₂PO₄-CsPO₃ system was estimated to be of the eutectic type with no intermediate compound of solid.

The final dehydration product of CsPO₃ showed relatively high electrical conductivity in unhumidified Ar. In the intermediate temperature range from 150 to 450°C, CsPO₃ exhibited ionic conductivity as high as \( 5 \times 10^{-4} \) S cm⁻¹ with a property to disappear after first heating. This high ionic conductivity was probably caused by the proton diffusion through the absorbed \( H₂O \) on the surface and interface. At \( -600°C \), after the transition to the high-temperature phase, CsPO₃ exhibited high conductivity of \( -10^{-3} \) S cm⁻¹. This conductivity was not pure ionic and did not change by heating/cooling cycles.

Acknowledgments

This work was financially supported by Superprotonic, Inc. (California, USA). The authors thank Professor Sossina M. Haile and Ayako Ikeda (California Institute of Technology) for useful discussions.

Kyoto University assisted in meeting the publication costs of this article.

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