Proton Conduction in In$^{3+}$-Doped SnP$_2$O$_7$ at Intermediate Temperatures

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SnP$_2$O$_7$-based proton conductors were characterized by Fourier transform infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), X-ray diffraction (XRD), and electrochemical techniques. Undoped SnP$_2$O$_7$ showed overall conductivities greater than $10^{-2}$ S cm$^{-1}$ in the temperature range of 75–300°C. The proton transport numbers of this material at 250°C under various conditions were estimated, based on the ratio of the electromotive force of the galvanic cells to the theoretical values, to be 0.97–0.99 in humidified H$_2$ and 0.89–0.92 under fuel cell conditions. Partial substitution of In$^{3+}$ for Sn$^{4+}$ led to an increase in the proton conductivity (from 5.56 $\times$ $10^{-2}$ to 1.95 $\times$ $10^{-1}$ S cm$^{-1}$ at 250°C, for example). FTIR and TPD measurements revealed that the effects of doping on the proton conductivity could be attributed to an increase in the proton concentration in the bulk Sn$_{1-x}$In$_x$P$_2$O$_7$. The deficiency of P$_2$O$_7$ ions in the Sn$_{1-x}$In$_x$P$_2$O$_7$ bulk decreased the proton conductivity by several orders of magnitude, which was explained as due to a decrease in the proton mobility rather than the proton concentration. The mechanism of proton incorporation and conduction is examined and discussed in detail.


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Nafion is widely viewed as the most important proton-conducting electrolyte material in polymer electrolyte fuel cells. In recent years, however, there has been considerable interest in the development of alternative materials with high proton conductivities at operating temperatures of 150°C or more. At intermediate temperatures, CO poisoning of the platinum catalyst becomes less serious compared to lower temperatures, so that the fuel cell system does not require a CO removal unit (water-gas shift and CO preferential oxidation reactors). In addition, the electrode reaction kinetics is enhanced, and water is easily desorbed from the cathode.

Several approaches have been proposed for the design of intermediate-temperature proton conductors. Although a number of hydrous proton conductors have been developed, most of them require highly humid conditions to achieve sufficient proton conductivities. Anhydrous proton conductors, at least in principle, do not require the presence of water as the charge carrier, because protons migrate via jumps between adjacent oxide ions by a series of making and breaking of hydrogen bonds (Grotthuss or hopping mechanism). However, the proton conductivities reported so far were in the range of $10^{-2}$ S cm$^{-1}$, which is not sufficiently high to provide good fuel cell performance.

We have recently reported that an anhydrous proton conductor, 10 mol % In$^{3+}$-doped SnP$_2$O$_7$ (Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$), shows high proton conductivities $>10^{-1}$ S cm$^{-1}$ between 150 and 350°C under water-free conditions.13 Attempts to apply this material as an electrolyte in some electrochemical devices were also made. A fuel cell using the 0.35 mm thick Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ electrolyte membrane yielded a power density of 264 mW cm$^{-2}$ under unhumidified H$_2$/air conditions.14 In addition, an electrochemical reactor using the Sn$_{0.9}$In$_{0.1}$P$_2$O$_7$ electrolyte membrane with a PtBa/C cathode reduced NO$_2$ to N$_2$ with a current efficiency of 5.81% at 250°C in oxidizing atmospheres (pO$_2$ = 0.02–0.09 atm).14 This material also had the potential to be used for NO$_2$ and other gas sensor applications.15 However, a detailed mechanism of the incorporation of protons in the bulk is still unclear. Moreover, the migration of protons through the electrolyte is not well understood.

The purpose of this study was to attempt to address the above questions and clarify the mechanisms. Proton conduction in undoped SnP$_2$O$_7$ was first characterized by impedance spectra, the H/D isotope effect, and galvanic cell measurements. The effects of In$^{3+}$ doping and P$_2$O$_7$ deficiency on the proton conductivity were then clarified by Fourier transform infrared spectroscopy (FTIR) and temperature-programmed desorption (TPD) techniques. A mechanism of proton incorporation and conduction is proposed on the basis of these results.

Experimental

M$_x$P$_{2-x}$O$_{3+2x}$ (M = Si, Ge, Sn, and Ti) was prepared as follows. The corresponding oxide (SiO$_2$, GeO$_2$, SnO$_2$, or TiO$_2$) was mixed with 85% H$_3$PO$_4$ and then held with stirring at 300°C until it formed a paste with a high viscosity. The pastes were calcined in an alumina pot at 650°C for 2.5 h and then ground with a mortar and pestle. Sn$_{1-x}$In$_x$(P$_2$O$_7$)$_{y-}$ was also synthesized in a similar manner from SnO$_2$, In$_2$O$_3$, and 85% H$_3$PO$_4$. In this case, the x and y values were changed by varying the molar ratio of the raw materials. The preparation of layered SnP$_2$O$_7$ and amorphous Sn$_{1-x}$In$_x$P$_2$O$_7$ has been described in the literature. The final P/M or P/(Sn + In) molar ratio of the compounds was confirmed to be 2.0 (±0.02) from X-ray fluorescence (XRF) measurements. The crystalline structure of the compounds was measured using X-ray diffraction (XRD). The lattice constant measurements for SnP$_2$O$_7$ and Sn$_{1-x}$In$_x$P$_2$O$_7$ were made using an Si internal standard.

For electrochemical measurements, the compound powders were pressed into pellets (diameter 12 mm, thickness 1.0–1.2 mm) under a pressure of $2 \times 10^3$ kg cm$^{-2}$. The ac conductivity values of the pellets were measured by the standard four-probe method in different atmospheres ($p_{O_2}$ = 0.0008–0.12 atm; $p_{O_2}$ = $10^{-27}$–1 atm). The frequency range was 0.1–10$^6$ Hz, and the ac amplitude was 10 mV. The dc conductivity values were also estimated from the IR drop of the pellet measured by current interruption method. Two types of galvanic cells, a H$_2$ concentration cell and a H$_2$/air fuel cell, were fabricated using the pellet (thickness ~1.2 mm, diameter 12 mm) as the electrolyte membrane. Both anode and cathode (area 0.5 cm$^2$) were made from the catalyst (10 wt % Pt/C, E-TEK) and carbon paper (Toray TGP-H90), wherein the Pt loading was 0.6 mg cm$^{-2}$. The electromagnetic forces (emfs) of the galvanic cells were monitored as a function of the gas concentration or temperature.

FTIR spectra of SnP$_2$O$_7$ and Sn$_{0.9}$In$_{0.1}$(P$_2$O$_7$)$_{0.9}$ powders were measured in the range of 400–4000 cm$^{-1}$ in a JASCO FT/IR-460 Plus spectrometer. FTIR measurements were performed in the transmission mode by the KBr pellet technique. Data points were obtained in 60 scans with a resolution of 4 cm$^{-1}$.
Figure 1. Temperature dependence of the conductivity of MP$_2$O$_7$ (M = Si, Ge, Sn, and Ti) in unhumidified air ($p_{H_2}O = \sim 0.0075$ atm). Symbols as noted in figure.

TPD spectra of the Sn$_0.9$In$_{0.1}$P$_{2}$O$_{7}$ powders were measured in a conventional TPD apparatus with an on-line mass spectrometer. Sample powder (4 g) was heated in a stream of humidified Ar at 200°C for 2 hours. After purging with dry Ar, the sample powder was heated at a rate of 5°C min$^{-1}$ until the evolution of gases was completed.

Results and Discussion
Proton conduction in undoped SnP$_2$O$_7$.—Figure 1 shows the temperature dependence of the conductivity of cubic MP$_2$O$_7$ (M = Si, Ge, Sn, and Ti) in unhumidified air ($p_{H_2}O = \sim 0.0075$ atm). The conductivity increased in the order of Ge$^{4+} < $Si$^{4+} < $Ti$^{4+} < $Sn$^{4+}$, which agreed with the closely related order of electron-hole conductivity for the species (as discussed later). However, Matsui et al. reported conductivities of SiP$_2$O$_7$ and TiP$_2$O$_7$ much lower than those shown in Fig. 1. The dc conductivity measurements for SnP$_2$O$_7$, TiP$_2$O$_7$, and SiP$_2$O$_7$ were made to prove the validity of our results. The conductivities measured at 250°C were $4.7 \times 10^{-1}$, $4.6 \times 10^{-2}$, and $1.7 \times 10^{-3}$ S cm$^{-1}$ for SnP$_2$O$_7$, TiP$_2$O$_7$, and SiP$_2$O$_7$, respectively, which were in agreement with their ac conductivities shown in Fig. 1. As mentioned later, the conductivity of MP$_2$O$_7$ was significantly decreased by the deficiency of P$_2$O$_7$ ions in the lattice. It is thus speculated that the samples prepared by Matsui et al. may lose a slight amount of P$_{2}$O$_{7}^{4-}$ ions by the vaporization of phosphorus species during the preparation process at 700°C, resulting in the low conductivities of SiP$_2$O$_7$ and TiP$_2$O$_7$.

Other P$_2$O$_7$-based tin phosphates are known, including layered SnP$_2$O$_7$ and amorphous Sn$_3$P$_2$O$_7$. As can be seen from Fig. 1, the conductivities of these materials were higher than those of PO$_2$-based SnHPO$_3$, but lower than those of cubic SnP$_2$O$_7$, indicating the importance of the crystalline structure, not only based on the P$_2$O$_7$ groups but also on cubic symmetry. These results also suggest that the conductivity of SnP$_2$O$_7$ is related to bulk conduction rather than surface conduction, because the former is more strongly influenced by structural characteristics than the latter.

Comparison of the emf values of the following galvanic cells calculated from Nernst’s equation was performed to estimate the proton transport number of SnP$_2$O$_7$, under various conditions:

\[ H_2(1 \text{ atm}), \text{Pt/C}|\text{SnP}_2\text{O}_7|\text{Pt/C}, H_2 + \text{Ar}(0.1 \text{ atm}) \]

\[ H_2, \text{Pt/C}|\text{SnP}_2\text{O}_7|\text{Pt/C}, \text{air} \]  

It can be seen from Fig. 2 that all the emf values observed for cell 1 between 100 and 250°C were very close to the corresponding theoretical values. From the ratio of the emf value to the theoretical value, the proton transport number of SnP$_2$O$_7$ was calculated to be in the range 0.97–0.99, which means that this material is substantially a pure proton conductor in H$_2$ atmospheres. Cell 2 showed emf values deviating from the theoretical values (proton transport number = 0.89–0.92), although the EMF values were as high as $~920$ mV. This deviation was due to electron holes in the SnP$_2$O$_7$ bulk (as described later). However, mechanical leakage of gas through the electrolyte may also be responsible for the lower emf values compared to the theoretical values, because the EMF value was affected by the thickness of the electrolyte used. For example, the EMF value increased from 922 to 934 mV with increasing electrolyte thickness from 1.2 to 2.6 mm.

SnP$_2$O$_7$ nominally does not contain protons in the bulk. Therefore, we attempted to clarify how this material is protonated. The dependence of the overall conductivity of SnP$_2$O$_7$ on the partial pressure of oxygen ($p_{O_2}$) was investigated at various $p_{H_2}O$ values. As shown in Fig. 3, at $p_{H_2}O = 0.0008$ atm, a large increase in conductivity with increasing $p_{O_2}$ was observed under oxidizing conditions ($p_{O_2} = 0.21$–1 atm), indicating that this material shows mixed
Here, h. and H. denote an electron hole and a proton, respectively. It is proposed that protons migrate via dissociation of O-H bonds in water vapor and electron holes. The following mechanism has been proposed as a mechanism of proton incorporation in perovskite oxides such as SrCe0.9Yb0.05O3-

\[ H_2O + 2 h. \rightarrow 2H^+ + \frac{1}{2} O_2 \]  
\[ (H_2O + 2 O_2 + 2h. \rightarrow 2H_2O + \frac{1}{2} O_2) \]  

[3]

Here, h and H denote an electron hole and a proton, respectively. It is reasonable to consider that protons are formed in the SnP2O7 bulk through Reaction 3. We similarly measured the electron-hole conductivity for other MP2O7 and found it to be an order of magnitude, in agreement with the proton conductivity measurements. This result supports the validity of Reaction 3. Another important result in Fig. 3 is that almost no variation of the conductivity with \( p_{H_2O} \) under reducing conditions (\( p_{H_2O} \approx 10^{-20} \) atm) was observed, excluding the reduction of Sn7+ and P5+ to lower valences.

We also attempted to develop a more detailed explanation for proton conduction in the SnP2O7 bulk. An H/D isotope effect on conductivity is helpful to clarify this point, and the results are shown in Fig. 4. SnP2O7 yielded a 1.06–1.44 times higher conductivity and a lower activation energy of 0.03 eV for H2O-containing atmospheres than for D2O-containing atmospheres. This result can be interpreted by a nonclassical H/D isotope effect. When the dissociation of the O-H bond is a rate-determining step for proton conduction, the activation energy for D+ is higher than that for H+ by a difference in zero point energy of 0.05 eV, which is near the difference in activation energy shown above. It is thus proposed that protons migrate via dissociation of O-H bonds (hopping mechanism).

Effect of In3+ doping in Sn1−xInxP2O7 on proton conduction.—Figure 5 shows typical XRD patterns of undoped and In3+-doped SnP2O7 measured at room temperature. The peaks observed for SnP2O7 were almost identical to those reported in the literature. SnP2O7 has a cubic or pseudocubic structure, with SnO6 octahedra and P2O7 units at the corners and the edges, respectively. Sn1−xInxP2O7 with In3+ content of not more than 10 mol % shows the same patterns as those of SnP2O7 and an increasing lattice constant with increasing In3+ content, 7.945 Å for SnP2O7 and 7.950 Å for Sn0.9In0.1P2O7. Sn1−xInxP2O7 with In3+ contents of 20 and 30 mol % contained some other unidentified peaks. It seems that the In3+ content of 10 mol % is the limit of substitution for In3+.

Proton conductivities for undoped and In3+-doped SnP2O7 at different temperatures in unhumidified air (\( p_{H_2O} \approx 0.0075 \) atm) are shown in Fig. 6. The conductivity of Sn1−xInxP2O7 increased with increasing In3+ content and reached a maximum at Sn4+ = 10 mol %. This In3+ content of 10 mol % corresponded well with the substitution limit for In3+ estimated from the XRD measurements. Therefore, it is concluded that the doping of In3+ for Sn4+ plays an important role in the enhancement of proton conductivity. It should be noted here that the conductivities of undoped and In3+-doped SnP2O7 increased monotonously with increasing temperature, which was different from “superprotonic” behavior that shows a sharp increase in the conductivity of some orders of magnitude by a structural transition from a low- to a high-temperature phase. This is because SnP2O7 does not show such a structural transition in the temperature range of interest. The IR spectrum of Sn0.9In0.1P2O7 with the highest conductivity of 1.95 × 10−1 Sc m−1 at 200°C was used in subsequent experiments.

To better understand the effects of In3+ doping, the environment of the protons in the bulk Sn0.9In0.1P2O7 was observed by FTIR. An IR spectrum of Sn0.9In0.1P2O7 is shown in Fig. 7 along with the spectrum for undoped SnP2O7 for comparison. In both IR spectra, some absorption bands appeared from 1560 to 3720 cm−1, with large differences in the absorbance between the two materials. The wide absorption bands centered at 1655 and 3410 cm−1 are evidence

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**Figure 4.** Isotope effect on conductivity of SnP2O7. The data were obtained in argon saturated with H2O or D2O vapor at 20°C. The transient change in ohmic resistance was measured at 50°C.

**Figure 5.** XRD patterns of Sn1−xInxP2O7.

**Figure 6.** Temperature dependence of the conductivity of Sn1−xInxP2O7. The samples were maintained in unhumidified air (\( p_{H_2O} \approx 0.0075 \) atm).

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The TPD spectra are shown in Fig. 8. Water vapor and a small amount of H₂ were evolved from 260 to 1050°C. The evolution of water vapor from water adsorbed on the sample surface, these results at least suggest that the absorption bands are mainly attributable to protons incorporated in the bulk. It is also likely that the protons interact with the lattice oxide ions to form hydrogen bonds.

A more quantitative measurement of the proton concentration in Sn₀.₉In₀.₁P₂O₇ and SnP₂O₇ was made by TPD of hydrogen species. The TPD spectra are shown in Fig. 8. Water vapor and a small amount of H₂ were evolved from 260 to 1050°C. The evolution of water vapor from water adsorbed on the surface of the samples cannot be neglected, especially for data at relatively low temperatures. However, we determined the proton concentrations in Sn₀.₉In₀.₁P₂O₇ and SnP₂O₇ by assuming that all the evolved water vapor and H₂ can be attributed to the incorporated protons. The resulting proton concentration values were 10.4 and 2.5 mol % for Sn₀.₉In₀.₁P₂O₇ and SnP₂O₇, respectively. Note that the former value was in good agreement with the proton concentration predicted from the In³⁺ content of 10 mol %. It thus appears that the protons were fully introduced as point defects by the substitution of In³⁺ for Sn⁴⁺.

Electron holes and oxygen vacancies are considered to be original positive defects in the Sn₀.₉In₀.₁P₂O₇ bulk. As described previously, protons are incorporated into the bulk according to Reaction 3. Another possible reaction is the following interaction between water vapor and an oxygen vacancy:

\[
H₂O(g) + V₀ \rightarrow 2H⁺ + O_²⁻
\]

Here, V₀ and O_²⁻ denote an oxygen vacancy and a lattice oxide ion, respectively. The degree of Reaction 4 cannot be entirely demonstrated at this stage. However, when the proton conductivity of Sn₀.₉In₀.₁P₂O₇ was measured at different P₁₀.₀ values at 250°C, it slightly increased with increasing P₁₀.₀. This result is associated with the process of proton incorporation through Reaction 4 rather than 3, because the order of mobility is oxygen vacancy < proton < electron hole. Therefore, Reaction 4 as well as Reaction 3 are possible mechanisms of proton incorporation.

Effects of P₂O₇ deficiency in Sn₀.₉In₀.₁P₂O₇ on proton conductance.— P₂O₇-deficient Sn₀.₉In₀.₁(P₂O₇)₁₋ₓ with y values of 0.0–0.15 was synthesized. Figure 9 shows the results of XRD measurements for Sn₀.₉In₀.₁(P₂O₇)₁₋ₓ with the amount of P₂O₇ deficiency. For example, the fwhm’s for the (200) reflection of Sn₀.₉In₀.₁P₂O₇ and Sn₀.₉In₀.₁(P₂O₇)₀.₃₋ₓ were 0.192–0.200°, respectively. These results suggest substantial distortion and disorder of the crystalline structure of Sn₀.₉In₀.₁(P₂O₇)₁₋ₓ. A significant decrease in the conductivity with P₂O₇ deficiency can be seen in Fig. 10. The proton conductivity of Sn₀.₉In₀.₁(P₂O₇)₀.₃₋ₓ was about 2 orders of magnitude lower than that of Sn₀.₉In₀.₁P₂O₇, indicating that the conductivity is strongly affected by the number of P₂O₇²⁻ ions in the lattice.

IR measurements of Sn₀.₉In₀.₁(P₂O₇)₀.₃₋ₓ were conducted to clarify the effect of P₂O₇ deficiency on the proton conductivity. As shown in Fig. 11, the IR spectrum showed large peaks at almost the same wave numbers as those observed for Sn₀.₉In₀.₁P₂O₇. The absorbance ratios of Sn₀.₉In₀.₁P₂O₇ to Sn₀.₉In₀.₁(P₂O₇)₀.₃₋ₓ were 1.4 and 1.5 for ν(OH) and δ(OH), respectively, which are much smaller than their conductivity ratio shown in Fig. 10. A similar behavior was observed for the TPD spectra, as shown in Fig. 12. The proton concentration in Sn₀.₉In₀.₁(P₂O₇)₀.₃₋ₓ was estimated to be about 8.1 mol % per unit, which is not significantly different from the value of 10.4 mol % observed for Sn₀.₉In₀.₁P₂O₇. Therefore, it is suggested that the large difference in proton conductivity between

Figure 7. IR spectra of SnP₂O₇ and Sn₀.₉In₀.₁P₂O₇.

Figure 8. TPD spectra of SnP₂O₇ and Sn₀.₉In₀.₁P₂O₇.

Figure 9. XRD patterns of Sn₀.₉In₀.₁(P₂O₇)₁₋ₓ.
The samples were maintained in unhumidified air. The proton mobilities in Sn0.9In0.1P2O7 and Sn0.9In0.1P2O7 volume of Sn0.9In0.1P2O7, respectively. The proton mobilities in Sn0.9In0.1P2O7 and Sn0.9In0.1P2O7 were calculated to be 1.49 × 10\(^{-3}\) and 6.3 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) V\(^{-1}\), respectively. Considering the results from the XRD and FTIR measurements, it is assumed that the extremely low proton mobility in Sn0.9In0.1P2O7 is not associated with the local environment of the protons in the crystalline lattice but is correlated with the long-range nature for the proton transfer between the crystalline lattices. This assumption is supported by the strong dependence of the proton conductivity on the crystalline structure of the P2O7-based tin phosphates with different types of P2O7 networks shown in Fig. 1. Thus, a possible speculation on the proton mobility of Sn0.9In0.1P2O7 is that the P2O7 deficiency causes a partial disconnection of the P2O7 network for proton conduction, resulting in a large energy barrier for proton jumps between sites.

Conclusions

Proton conduction in In\(^{3+}\)-doped SnP2O7 was investigated by controlling the In\(^{3+}\) and P2O7 content in the bulk. SnP2O7 had an ionic transport number of ~1 and exhibited a large H/D isotope effect on conductivity, which demonstrates that the protons are migrating via a hopping mechanism. The substitution of In\(^{3+}\) for Sn\(^{4+}\) increased the proton concentration in the bulk, resulting in an increase in proton conductivity. The P2O7 deficiency caused extremely low proton conductivity, which was explained by a large increase in energy barrier for proton conduction due to partial disconnection of the P2O7 network for proton conduction.

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