MICROSTRUCTURE OBSERVATION AND ELECTRICAL CONDUCTIVITIES OF PROTON-CONDUCTING $\text{TiO}_2\text{-P}_2\text{O}_5$ GLASS-CERAMIC SOLID ELECTROLYTES

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Abstract: A new, fast proton-conducting $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic was developed and investigated through microstructure observation and electrical conductivity measurements. $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic samples were prepared by a sol-gel method and post-annealing heat treatment. With an increase in the post-annealing temperature, growth of TiP_2O_7 crystals in the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase was observed. In addition, a tenfold enhancement in maximum conductivity was observed after post-annealing heat treatment compared with the as-prepared sample and polycrystalline TiP_2O_7 . The interfacial layer between the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase and the TiP_2O_7 crystal phase may act as a fast proton-conducting path, thereby improving the total conductivity. This hypothesis is discussed using the brick layer model.

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INTRODUCTION

The development of alternative power sources is an increasingly important issue for the establishment of a sustainable society with low greenhouse gas emissions. Fuel cell technology is one of the key technologies currently available for power generation systems. Among the various types of fuel cells, solid oxide fuel cells (SOFCs) have the advantage of power generation efficiency. To diminish degradation of the cell and stack due to a high-temperature operation and to achieve long lifetime, lowering the operation temperature of SOFC systems is important. Inorganic proton conductors have high ion conductivity at intermediate temperatures (300–600 °C) and can provide a solution for the development of next-generation fuel cell systems using proton-conducting electrolytes operating at intermediate temperature (p-ITFC: proton-conducting solid electrolyte intermediate temperature fuel cell). p-ITFCs can be used to realize robust systems with high energy conversion efficiency¹. Therefore, the development of proton-conducting materials is very important. However, as yet, a suitable proton-conducting material has not been developed and currently much effort is directed to developing a new proton-conducting electrolyte¹⁻³.

In this study, we focus on a phosphorous-oxide based proton conductor. Phosphate glasses have been studied because of their relatively high proton conductivities⁴⁻⁸ and are considered as excellent candidate materials for p-ITFC electrolytes. In recent studies, glass-ceramics of phosphorous-oxide materials were also investigated in terms of the

influence of the interface between the glassy and crystalline phases on ionic conductivity⁹⁻¹¹. To improve ion conductivity, controlling the microstructure of the ion conductors, especially the interfacial structure, may be an effective approach⁹⁻¹³. We have previously taken this approach to investigate the enhancement of interfacial ion conductivity. In our previous study¹¹, we investigated proton conductivity in a mixture of phosphorous-oxide glass and pyrophosphate ($\text{ZnO-P}_2\text{O}_5$ glass and TiP_2O_7 crystal) and observed an improvement of proton conductivity, which may have been due to an acceleration effect at the interface between the glassy and crystalline phases. The interfacial proton diffusion paths around pyrophosphate particles may also contribute to the improvement in proton conductivity¹¹.

In the present study, we prepared proton-conducting glass-ceramics from $\text{TiO}_2\text{-P}_2\text{O}_5$ glass, controlling crystal growth in the glassy phase by post-annealing heat treatment. Through appropriate heat treatment, we demonstrate the formation of the TiP_2O_7 crystal phase in the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase and the effect of crystal formation on the enhancement of electrical conductivity. We also show that the maximum conductivity is obtained by controlling the microstructure of the glass-ceramics. In the previous studies, phosphate glasses were prepared by a melt-quenching technique^{9,10}, which are performed at relatively high temperature and thereby proton will desorb *via* dehydration. To keep high proton concentration in prepared glasses, we employed a sol-gel method, which enables us to

lower temperature in the sample preparation. The present study provides the fundamental information about proton conductivity at interface with controlling the microstructure, considering the application as solid electrolyte working at intermediate temperature in p-ITFC.

MATERIALS AND METHODS

The following reagents were purchased commercially for the sol-gel synthesis of $\text{TiO}_2\text{-P}_2\text{O}_5$ glasses and were used as received: titanium tetra-*i*-propoxide ($\text{Ti}(\text{OPr}^i)_4$, TTIP) (Kanto Chemical, Japan, purity > 97.0%), titanium tetra-*sec*-butoxide ($\text{Ti}(\text{OBu}^{\text{sec}})_4$, TTSB) (Kojundo Chemical Laboratory, Japan, purity > 99.999%), an approximately 1:1 molar mixture of mono- ($\approx 45\text{--}55\%$) and di-substituted ($\approx 45\text{--}55\%$) *n*-butyl phosphate ($\text{PO}(\text{OH})(\text{OBu}^n)_2$, $\text{PO}(\text{OH})_2(\text{OBu}^n)$, P-Bu) (Santa Cruz Biotechnology, USA), super dehydrated isopropanol (Pr^iOH) (Wako Pure Chemical Industries, Japan, purity > 99.5% or Kanto Chemical, Japan, purity > 99.7%), and 2-butanol ($\text{Bu}^{\text{sec}}\text{OH}$) (Wako Pure Chemical Industries, purity > 99.0%).

The desired amount of TTIP was initially dissolved in super dehydrated Pr^iOH , typically with a molar ratio of 1:14. P-Bu was then added dropwise and the solution was stirred with a magnetic stirrer for 1 h. The resulting mixture was hydrolyzed by adding an aqueous solution consisting of Pr^iOH and $\text{Bu}^{\text{sec}}\text{OH}$ dropwise. The typical molar ratio of TTIP : H_2O : Pr^iOH : $\text{Bu}^{\text{sec}}\text{OH}$ was 1:4:2.7:2.9. Mixing was performed in a glovebox under a dry nitrogen flow. The prepared sol was poured into a polystyrene case in the glovebox and gelation was allowed to occur at room temperature in air. The resulting gel was aged at room temperature for $\approx 3\text{--}7$ weeks. After drying, the gel was placed into an alumina tube and further heated under a pure oxygen flow at 165 °C for 5 h and then 295 °C for 2 h before being sintered at 480 °C for 4 h. This heating process was conducted under a pure oxygen flow. During the heating process, solvent, water, and organic compounds were removed. The obtained samples were white, glassy, and lustrous thin pieces (typical size of one edge: $\approx 2\text{--}3$ mm; thickness: 0.5–1 mm). The samples were then mechanically ground to powder in an agate mortar for 15 min. The obtained powdered samples were pressed at 5.6 t cm^{-2} to form dense pellets (diameter: 10 mm, thickness: ca. 1 mm). Finally, the pellets were calcined at $\approx 480\text{--}700$ °C in air. Au electrodes were attached to both sides of the pellets using a quick coater (SC-701; Sanyu Denshi, Tokyo, Japan).

The pellet samples were placed in a quartz tube and dry Ar gas was supplied through the tube at atmospheric pressure. Conductivity measurements

were obtained using ac impedance spectroscopy with a Hewlett Packard 4192A impedance analyzer in the frequency range from 10 MHz to 10 Hz.

To characterize the specimens, X-ray diffraction (XRD) (Rigaku SmartLab, Tokyo, Japan) patterns were recorded at room temperature using a $\text{Cu K}\alpha$ radiation source. Raman spectroscopy was also conducted for the $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic samples using a micro-Raman spectrometer (LabRAM1B; Horiba-JobinYvon, Kyoto, Japan) with a continuous wave He-Ne laser beam at 632 nm and a CCD detector. Microstructures of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass and the glass-ceramics after post-annealing heat treatment were observed by transmission electron microscopy (TEM) (JEOL-2100; JEOL Ltd., Tokyo, Japan) and energy dispersive X-ray spectroscopy (TEM-EDX) (JEOL-2010F; JEOL Ltd.).

RESULTS AND DISCUSSION

Characterization of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics

Typical XRD patterns after heat treatment at different temperatures are shown in Fig. 1. The as-prepared sample that was heated at 480 °C was mostly amorphous, although small amounts of titanium pyrophosphate, TiP_2O_7 , also formed. The broad peak between 15–35°, i.e., halo peak, may originate from phosphate glass.

FIGURE 1. XRD patterns of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic samples after various heat treatments. a) as-prepared (480 °C); and after post-annealing heat treatment at b) 590 °C and c) 700 °C.

Increasing the post-annealing temperature up to 700 °C, the TiP_2O_7 peak became larger: TiP_2O_7 crystal phase was grown in $\text{TiO}_2\text{-P}_2\text{O}_5$ glass. This result shows that $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics (i.e., the

composite of the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase and the TiP_2O_7 crystal phase) can be successfully prepared under these conditions.

Raman spectra of the samples heat treated at 550, 560, 580, and 600 °C are shown in Fig. 2. As the temperature increases, the broad signal becomes sharp. The Raman bands were assigned based on previous studies¹⁴⁻¹⁷. The main bands are attributed to TiP_2O_7 ¹⁴. In addition, very weak signals originating from anatase TiO_2 ^{15,16} were observed at around 520 and 650 cm^{-1} at temperatures higher than 580°C. The observed spectra suggest that TiP_2O_7 crystal growth mainly occurs through annealing of the $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics accompanied by the formation of a small amount of TiO_2 .

FIGURE 2. Raman spectra of the $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic samples after post-annealing heat treatment at: a) 550 °C, b) 560 °C, c) 580 °C, and d) 600 °C.

Microstructure of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics

To observe the microstructural changes of the $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics subjected to different heat treatment conditions, TEM images were analyzed and are shown in Fig. 3. For the as-prepared sample treated at 480 °C without post-annealing treatment, a small crystal, less than 5 nm in diameter, is observed in the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase (Fig. 3a). Considering the XRD patterns, these small particles can be assumed to be TiP_2O_7 . After post-annealing treatment at 600 °C, significant crystal growth was observed. The diameter of the TiP_2O_7 particles reached approximately 100 nm. These TEM images clearly show that the TiP_2O_7 crystal phase is surrounded by the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase. To investigate the details of the composite structure, TEM-EDX measurements

were performed, in particular, focusing on the interface between the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase and the TiP_2O_7 crystalline phase. Elemental analysis was conducted by line-scanning from point A to point B, as shown in Fig. 4, which marks the transition from the glassy phase to the crystalline phase. The boundary between the two phases was analyzed by the morphological change in the image. As previously discussed, if the interfacial layer between the glassy and crystalline phases acts as a fast proton-conducting path, spatial deviation of elements such as Ti, P, and O around the interfacial layer might occur. The present elemental analysis of Ti, P, and O suggests that there was no deviation of the elements or segregation between the glassy and crystalline phases.

FIGURE 3. TEM images of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramic samples after heat treatment at different temperatures: a) as-prepared sample (480 °C) scale bar: 5 nm; b) post-annealing heat treated at 600 °C, scale bar: 100 nm.

FIGURE 4. TEM-EDX analysis of the interface between the $\text{TiO}_2\text{-P}_2\text{O}_5$ glassy phase and the TiP_2O_7 crystalline phase after post-annealing heat treatment at 600 °C. a) TEM images. Line-scanning was conducted from point A to point B. The broken line represents the boundary between the glassy and crystalline phases. b) EDX signals obtained by line-scanning from point A to point B. The broken line represents the boundary position.

Electrical conductivities in $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics

The influence of post-annealing heat treatment on electrical conductivity in the $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-

ceramics was investigated (Fig. 5). The electrical conductivity was found to be significantly influenced by the post-annealing temperature, whereas the activation energy, ΔE_a , was not influenced by the post-annealing temperature. The values of ΔE_a in Fig. 5 were approximately 65 kJ/mol. According to previous studies, the values of ΔE_a for phosphate glasses, $\text{MO-P}_2\text{O}_5$ ($M = \text{Ca}, \text{Mg}, \text{Be}, \text{Ba}$ and Sr), which were prepared by a melt-quenching technique, were 105-125 kJ/mol^{4,8}, while the value of ΔE_a for polycrystalline 2% Al-doped TiP_2O_7 was 68 kJ/mol¹⁸. The present value is rather close to that of Al-doped TiP_2O_7 . The value indicates the barrier of proton diffusion process. The results suggest that ΔE_a depends on preparation method, heat treatment and resultant microstructure of the samples. Because the electrical conductivity is expected to have a maximum value under optimum conditions, this was measured as a function of post-annealing temperature to further investigate the effect of heat treatment; the results are shown in Fig. 6.

FIGURE 5. Temperature dependence of the electrical conductivity (measured in a dry Ar flow) of $\text{TiO}_2\text{-P}_2\text{O}_5$ glass-ceramics subjected to post-annealing heat treatment at different temperatures: $\square$: 480 °C; $\bullet$: 550 °C; $\blacklozenge$: 595 °C. Solid line: reported value of polycrystalline TiP_2O_7 ¹⁴.

The electrical conductivity is plotted in Fig. 6 as a function of post-annealing temperature at a fixed measurement temperature of 450°C. The electrical conductivity increases with an increase in post-annealing temperature, reaching a maximum at $\approx 530\text{--}550^\circ\text{C}$. At higher temperatures, the conductivity decreases. The conductivity measured for a post-annealing temperature of 600°C

approximates the reported value for polycrystalline TiP_2O_7 ¹⁸. The maximum conductivity was approximately ten times higher than that of the as-prepared sample and TiP_2O_7 . The result suggests that an optimum microstructure of the TiO_2 - P_2O_5 glass-ceramic exists, at least in terms of its conductive properties. We suggest, based on these results that the formation of TiP_2O_7 particles in TiO_2 - P_2O_5 glass may contribute to the improvement of proton conductivity. Additionally, the relatively high conductivity observed in this work may also be realized by a sol-gel method. The present samples were prepared at lower temperatures in comparison with a melt-quenching technique. Although any direct evidences are not obtained, such low preparation temperature can contribute to retain high proton concentration in the present samples.

FIGURE 6. Electrical conductivity of TiO_2 - P_2O_5 glass-ceramics as a function of post-annealing temperature. The electrical conductivity was measured at a fixed temperature of 450 °C and under Ar flow.

A plausible explanation for the improvement of proton conductivity is the fast proton transport along the interface between the TiO_2 - P_2O_5 glassy phase and the TiP_2O_7 crystalline phase. A recent study¹⁸ has rejected fast proton transport in polycrystalline TiP_2O_7 . During heat treatment, the interface is generated by crystal growth of the TiP_2O_7 grains. We roughly evaluated the influence of interfacial conductivity in TiO_2 - P_2O_5 glass-ceramic on the total conductivity using a brick layer model¹⁹. The interfacial admittance, $\hat{Y}_i$, can be estimated by the following equation.

$$\hat{Y}_i = \hat{Y}_{\text{glass-ceramics}} - \hat{Y}_{\text{bulk}} = \hat{\sigma}_i \left\{ \frac{(2D+d)d}{D+d} \right\} f_i, \quad (1)$$

$$1/\hat{Y}_{\text{bulk}} = \hat{Z}_{\text{bulk}} = (1-x)\hat{Z}_{\text{glass}} + x\hat{Z}_{\text{ceramics}}, \quad (2)$$

FIGURE 7. Estimated interfacial conductivity in TiO_2 - P_2O_5 glass-ceramic as a function of the thickness of the interfacial layer. The sample was subjected to post-annealing heat treatment at 550 °C and measurements were conducted at 450 °C. The volume fraction of crystallite: $x = 0.32$.

The glass-ceramic consists of glass and crystalline grains with diameter, D , and an interfacial layer between the glass and crystal phases of thickness, d . In Eq. 1, $\hat{\sigma}_i$ represents the interfacial ac conductivity. The volume fraction, x , in Eq. 2 was determined by crystallinity estimated by XRD peak intensity. If it is supposed that the real part of the impedance at 1 kHz corresponds to dc conductivity, $\hat{Z}_{\text{bulk}}$ can be calculated from the conductivity of TiO_2 - P_2O_5 glass and TiP_2O_7 ceramics to obtain a value of interfacial conductivity. Figure 7 shows the interfacial conductivity according to Eq. 1 as a function of the thickness of the interfacial layer for the sample heat treated at 550°C. Assuming d is between 1 and 20 nm, $\hat{\sigma}_i$ is $\approx 10^{-2.5}$ – 10^{-4} S/cm, which is ≈ 10 –400 times higher than that of the TiP_2O_7 ceramic. In previous studies^{18,20}, there is discordance in the reported values for proton conductivity in polycrystalline TiP_2O_7 . Thus, in light of our results, this discordance might be because of surface or interfacial proton diffusion on TiP_2O_7 particles. Although the model of Eq. 1 is one possible mechanism of conductivity enhancement, the microstructural observations (in terms of the spatial elemental distribution) of the glass-ceramics do not provide clear evidence for fast proton transport in the interfacial layer. If segregation at the interfacial layer, e.g., formation of phosphorus-rich layer between glassy and crystal phases, would occur, fast proton transport can be induced. In that case, however, the interfacial layer might be finer than the resolution of the present microstructural observation. Further fine microstructural observation

will be needed. As another possibility, the change of Ti-O-P bonding structure in the interfacial layer can influence proton conductivity. In fact, it has been suggested that proton conductivity in phosphate glasses strongly depends on the state of non-bridging oxygen of P=O⁸. Thus, there is a possibility that non-bridging oxygen can be modulated in the interfacial layer when creation of crystalline grains proceeds in the glass-ceramics, thereby increasing proton conductivity. Such hypothesis should be investigated in detail through the observations of proton concentration and Ti-O-P bonding structure in the interfacial layer. This will be the focus of our future research.

CONCLUSION

Proton-conducting TiO₂-P₂O₅ glass-ceramics were prepared by a sol-gel method and subsequent post-annealing heat treatment. The microstructure of the TiO₂-P₂O₅ glass-ceramics was investigated by TEM, which revealed that TiP₂O₇ crystal grains were surrounded by a TiO₂-P₂O₅ glassy phase. Elemental analysis of Ti, P, and O was also performed using TEM-EDX. The result suggested that there was no deviation of the elements or segregation between the glassy phase and the crystalline phase. The electrical conductivity in the TiO₂-P₂O₅ glass-ceramics was examined under dry conditions and was found to be strongly influenced by the post-annealing temperature. The maximum conductivity value was observed for the sample treated at around 530 °C. To understand the conductivity enhancement, the brick layer model was employed with the assumption that the interface between the TiO₂-P₂O₅ glassy phase and the TiP₂O₇ crystalline phase plays a key role in the highly proton-conducting layer. The brick layer model was found to be valid when an appropriate thickness of the interfacial layer was assumed. Although the detailed mechanism remains unclear, the obtained results provide a strategy for the fabrication of fast proton-conducting materials.

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