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Enhancement of Hf^{4+} Ion Conductivity in a NASICON-Type Solid

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Tetravalent hafnium ion conducting solid electrolytes with a NASICON-type structure, $HfNbP_{3-x}V_xO_{12}$ and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$, were developed by partially replacing the P^{5+} site in a $HfNb(PO_4)_3$ solid with larger V^{5+} or W^{6+} ions. Although the Hf^{4+} ion conductivity monotonically increased with increasing V content in the $HfNbP_{3-x}V_xO_{12}$ solids, the electronic conduction appeared to be due to the valence change of V^{5+}. In contrast, the $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ series maintained a high ionic transference number, above 0.995 for single-phase NASICON-type samples ($y \leq 0.15$). The optimum lattice volume for Hf^{4+} conduction was determined to be 1.482 nm^3, which was obtained for samples with $x = 0.1$ or $y = 0.05$. The $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid, which contains the higher valence W^{6+} ion rather than the V^{5+} ion, showed the highest conductivity of 2.8×10^{-4} S cm^{-1} at 600 °C, approximately 2.5 times that of $HfNb(PO_4)_3$.

Solid electrolytes are unique functional materials, in that the solid generally conducts only a single ionic species and shows no electron or hole conduction. Some solid electrolytes have already been commercialized as components of battery and chemical sensing devices.[1,2] In these electrolytes, it is believed that the ion conduction in the solids greatly depends on their valence state. For example, ion conductivity decreases with increasing valence of the conducting ion. While ion conductivities high enough for practical application have been obtained for various mono-, di-, and trivalent ions, higher valence tetravalent cations have been regarded as extremely poor migrating species in solids, due to the extraordinarily strong electrostatic interaction between the tetravalent cation and the surrounding anions, which inhibits ionic conduction in the solid lattice. To realize tetravalent cationic conduction in a solid requires not only a suitable crystal structure, but the constituent ions must also be able to reduce the strong electrostatic interaction. One effective method of weakening this interaction is the introduction of pentavalent or higher valence cations into the structure. Such cations may attract anions more strongly than the tetravalent cations, enabling tetravalent cation migration in the solid lattice.

In our previous work, we successfully developed pure Zr^{4+} or Hf^{4+} ion conducting $MNb(PO_4)_3$ (M = Zr, Hf)[3–6] solids based on the above concept. These solids contained pentavalent Nb^{5+} and P^{5+}, and had a NASICON (Na^+ super ionic conductor)-type structure, which is well known to be a three-dimensional network suitable for ion migration.[7] Furthermore, we have also demonstrated that the Hf^{4+} ion conductivity was higher than the Zr^{4+} ion conductivity in NASICON-type $MNb(PO_4)_3$ (M = Zr, Hf) solids.

In this study, the tetravalent Hf^{4+} ion conductivity in a NASICON-type solid was enhanced by an intentional expansion of the lattice volume of the $HfNb(PO_4)_3$ solid by doping large cations into the structure. This expanded the conducting pathway, which improved the ion conduction in the solid. We selected V^{5+} (ionic radius: 0.050 nm [coordination number (CN) = 4][8]) and W^{6+} (0.056 nm [CN = 4][8]) as the large cation for the partial replacement of the P^{5+} (0.031 nm [CN = 4][8]) sites, and investigated the electrical conductivity of $HfNbP_{3-x}V_xO_{12}$[9] and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids.

Experimental

A conventional solid-state reaction was applied to prepare $HfNbP_{3-x}V_xO_{12}$ and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids. $HfNbP_{3-x}V_xO_{12}$ was synthesized by heating a stoichiometric mixture of HfO_2, Nb_2O_5, V_2O_5, and $(NH_4)_2HPO_4$ at 1100 °C for 12 h and then 1200 °C for 12 h in synthetic air (N_2:O_2 = 79:21).[9] For $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids, stoichiometric amounts of $Hf(SO_4)_2$, Nb_2O_5, WO_3, and $(NH_4)_2HPO_4$ powders were mixed in an agent pot at a rotation speed of 300 rpm for 3 h using a planetary ball milling apparatus (Pulverisette 7, FRITSCH GmbH). The mixed powder was calcined at 600 °C for 6 h, 1200 °C for 12 h, and 1300 °C for 12 h in synthetic air. The samples obtained were identified by X-ray powder diffraction (XRD) analysis using Cu Kα radiation (MultiFlex, Rigaku). The XRD data were collected by step scanning in the 2θ range from 10 to 70° with a step width of 0.04°. The lattice volume of the samples was calculated from the XRD peak angles, which were refined using α-Al_2O_3 as a standard. After identifying the crystal phase of the samples, the sample powders were pressed into a pellet and sintered at 1200 °C ($HfNbP_{3-x}V_xO_{12}$) or 1300 °C ($Hf_{1-y/4}NbP_{3-y}W_yO_{12}$) for 12 h in air.

The AC conductivity (σ_{AC}) of the sintered sample pellets with a platinum layer sputtered on both center surfaces was measured by complex impedance method in the frequency region from 5 Hz to 13 MHz (precision LCR meter 4192A, Hewlett Packard) at temperatures between 300 and 600 °C in an air atmosphere (oxygen pressure $[Po_2] = 2.1 \times 10^4$ Pa). The ionic transference number (t_{ion}) in air was calculated from the equation, $t_{ion} = 1 - (\sigma_{DC}/\sigma_{AC})$. Here, the DC conductivity (σ_{DC}) was measured from the DC voltage over the sample generated by passing a DC current of 1 µA between platinum electrodes sandwiching the sintered pellet. The DC electrolysis of the sintered $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ pellet was carried out by applying a DC voltage of 4 V between ion-blocking platinum bulk electrodes at 800 °C for 336 h in atmospheric air. The cathodic surface of the electrolyzed sample pellet was analyzed by electron probe microanalysis (EPMA-1500, Shimadzu).

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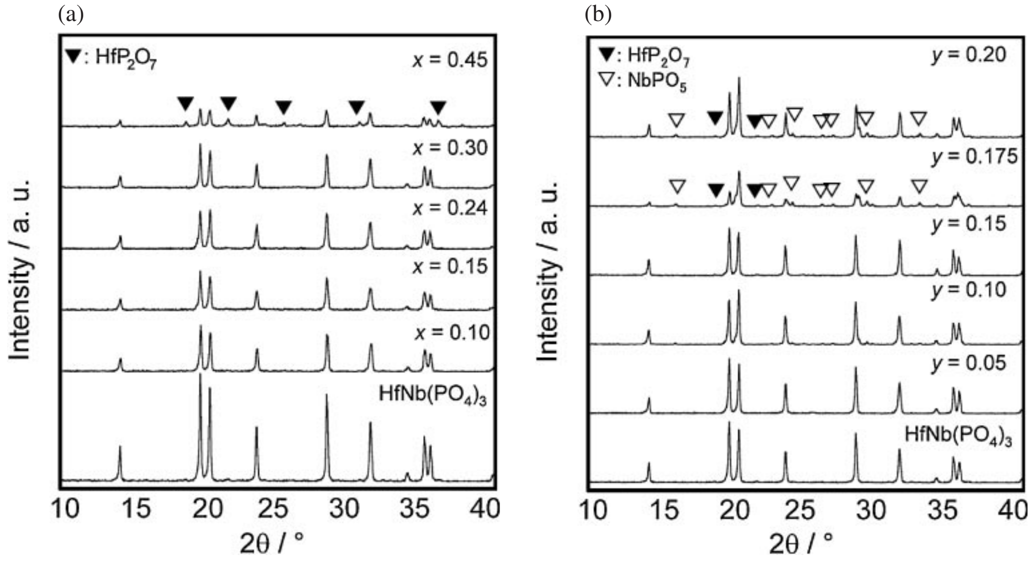

Figure 1. XRD patterns of (a) $HfNbP_{3-x}V_xO_{12}$[9] and (b) $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$.

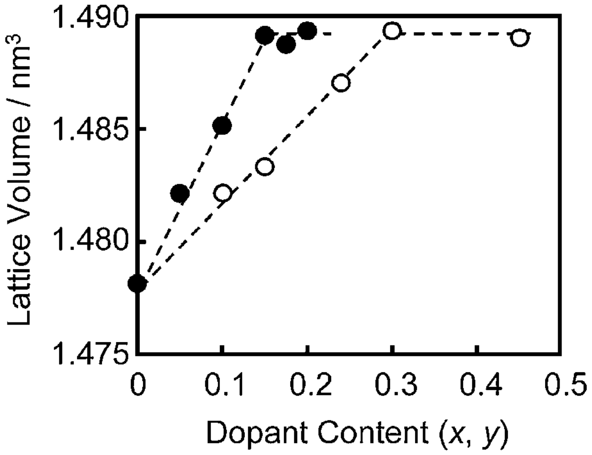

Figure 2. Lattice volume variation of the NASICON-type phase in $HfNbP_{3-x}V_xO_{12}$ ($0 \leq x \leq 0.45$) (○) and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ ($0 \leq y \leq 0.2$) (●) solids.

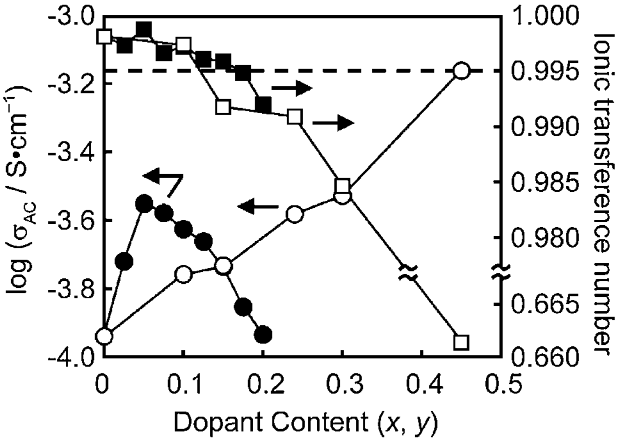

Figure 3. Compositional dependencies of the AC conductivity and the ionic transference number at 600 °C for $HfNbP_{3-x}V_xO_{12}$ (○, □)[9] and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids (●, ■).

The relative density of the sintered sample was measured by pycnometer (AccuPyc 1330, Shimadzu).

Results and Discussion

XRD patterns of the $HfNbP_{3-x}V_xO_{12}$[9] and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids are shown in Figure 1. Although samples with $x \leq 0.3$ maintained a single phase of NASICON-type structure in $HfNbP_{3-x}V_xO_{12}$ solids, the sample with $x = 0.45$ was a two-phase mixture of NASICON-type phosphate and HfP_2O_7. On the other hand, the $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids possessed a single phase of NASICON-type structure in the compositional region of $y \leq 0.15$, while samples with $y > 0.15$ had a multi-phase mixture of NASICON-type phosphate, HfP_2O_7, and $NbPO_5$. Figure 2 depicts the compositional dependence of the lattice volume of the NASICON-type phase in the prepared samples. A linear lattice expansion of the NASICON-type phase was clearly observed within the single-phase regions of both series ($x \leq 0.3$ or $y \leq 0.15$). No meaningful lattice expansion of the NASICON-type phase for samples with $x > 0.3$ or $y > 0.15$ was observed, compared with the lattice volume of samples with $x = 0.3$ or $y = 0.15$, respectively. Furthermore, the lattice volume of the $HfNbP_{2.7}V_{0.3}O_{12}$ ($x = 0.3$) and $Hf_{385/400}NbP_{2.85}W_{0.15}O_{12}$ ($y = 0.15$) solids, with compositions at the solid solubility limit for each series, were nearly identical (ca. 1.489 nm^3). These results clearly indicate that larger V^{5+} (ionic radius: 0.050 nm [CN = 4][8]) or W^{6+} (0.056 nm [CN = 4][8]) ions successfully replaced the P^{5+} (0.031 nm [CN = 4][8]) sites in the $HfNb(PO_4)_3$ solid when $x \leq 0.3$ or $y \leq 0.15$, respectively.

Figure 3 presents the compositional dependencies of the AC conductivity and the ionic transference number ($t_{ion} = 1 - (\sigma_{DC}/\sigma_{AC})$) at 600 °C for the $HfNbP_{3-x}V_xO_{12}$ ($0 \leq x \leq 0.45$)[9] and $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ ($0 \leq y \leq 0.2$) solids in an air atmosphere ($P_{O_2} = 2.1 \times 10^4$ Pa). The ion transference number was estimated from the σ_{DC}/σ_{AC} ratio after 30 min. In the single-phase region of NASICON-type $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ ($0 \leq y \leq 0.15$), the conductivity increased with the W content (y) up to 0.05, due to expansion of the lattice volume, in other words, the Hf^{4+} conducting pathway (Hf^{4+} ion conduction is demonstrated below). Although the lattice volume of samples with $y > 0.05$ expanded linearly up to $y = 0.15$, the conductivity decreased because a lattice volume too large for Hf^{4+} ion conduction was reached. If a solid has a larger than optimal lattice volume for Hf^{4+} ion conduction, the Hf^{4+} ion cannot be located at the center of the ideal Hf site while surrounded by O^{2-} ions, because of the resulting elongation of Hf^{4+}–O^{2-} bonds. Therefore, Hf^{4+} ions will be preferentially situated near certain O^{2-} ions, generating strong electrostatic interactions which prevent smooth Hf^{4+} migration. Figure 3 indicates that the lattice volumes of $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids with $y > 0.05$ were too large to realize smooth Hf^{4+} ion conduction, and that the optimum lattice volume (ca. 1.482 nm^3) for Hf^{4+} ion conduction in NASICON-type solids was obtained in $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ ($y = 0.05$). If the suitable lattice volume for Hf^{4+} ion conduction in a NASICON-type structure is ca. 1.482 nm^3, then $HfNbP_{2.9}V_{0.1}O_{12}$ ($x = 0.1$) with a lattice volume of 1.482 nm^3 should have the highest conductivity of the $HfNbP_{3-x}V_xO_{12}$ series. However, the conductivity of $HfNbP_{3-x}V_xO_{12}$ increased monotonically with increasing vanadium content (x). Since the ionic transference number of $HfNbP_{3-x}V_xO_{12}$ monotonously decreased with x, the linear enhancement of AC conductivity by $HfNbP_{3-x}V_xO_{12}$ solids was caused by electronic conduction because of the valence change of V^{5+}. On the other hand, the $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ solids maintained high ionic transference numbers, above 0.995 for single phase NASICON-type samples with $y \leq 0.15$, while the ionic transference number of $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ ($y > 0.05$) slightly decreased with increasing y. This reduction of ionic transference number in the $Hf_{1-y/4}NbP_{3-y}W_yO_{12}$ ($y > 0.05$) solids was mainly due to the decrease of ionic conductivity caused by having a lattice size too large for ion conduction.

In order to directly demonstrate Hf^{4+} ion conduction in a $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid, which had the highest conductivity and the highest ionic transference number of the prepared solids, DC electrolysis was carried out by applying a DC voltage of 4 V for 336 h at 800 °C, as shown in Figure 4a. From preliminary investigation of the *I–V* relationship of the sample, it was found that the DC current abruptly increased over ca. 1.2 V, suggesting that the sample began to decompose around 1.2 V. When applying a DC voltage higher than the decomposition voltage, conducting cations generated by sample decomposition on the anodic side should migrate toward the cathode along the potential gradient. Since the cationic species cannot enter the ion-blocking Pt bulk electrode, they should segregate on the cathodic surface of the sample pellet. After DC electrolysis, electron probe microanalysis (EPMA) line measurement was performed for electrolyzed $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solids (Figure 4b). Only Hf segregation was clearly observed near the cathodic surface, although the other cationic elements were homogeneously distributed within the sample, even after the DC electrolysis. This strongly indicates that only Hf^{4+} was conducted by the sample, and that the present $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid is a pure Hf^{4+} ion conductor ($t_{ion} = 0.999$).

The temperature dependence of tetravalent Hf^{4+} ion conductivity in $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid ($t_{ion} = 0.999$) is presented in Figure 5, along with the corresponding data for $HfNb(PO_4)_3$ ($t_{ion} = 0.998$) and $HfNbP_{2.9}V_{0.1}O_{12}$ ($t_{ion} = 0.997$). Although the Hf^{4+} ion conductivity of $HfNbP_{2.9}V_{0.1}O_{12}$ and $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$, whose lattice volumes (1.482 nm^3) were larger than that (1.478 nm^3) of $HfNb(PO_4)_3$, were successfully enhanced by lattice expansion, the $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid exhibited a higher Hf^{4+} ion conductivity. Because the valence of the V^{5+} ion is the same as that of the P^{5+} ion in the $HfNb(PO_4)_3$ solid, the enhancement in conductivity of the $HfNbP_{2.9}V_{0.1}O_{12}$ solid must have been mainly because of the expansion of the conducting pathway for Hf^{4+} ions into the NASICON-type structure. Therefore, the further enhancement of conductivity realized in $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ was most likely due to the effective reduction of the electrostatic interaction between the conducting Hf^{4+} cation

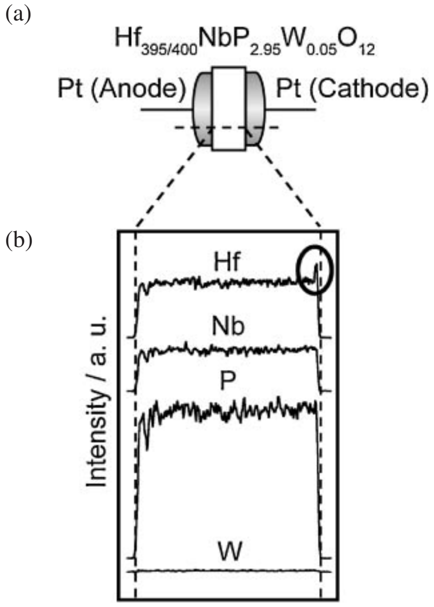

Figure 4. EPMA line analysis results for the electrolyzed $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid.

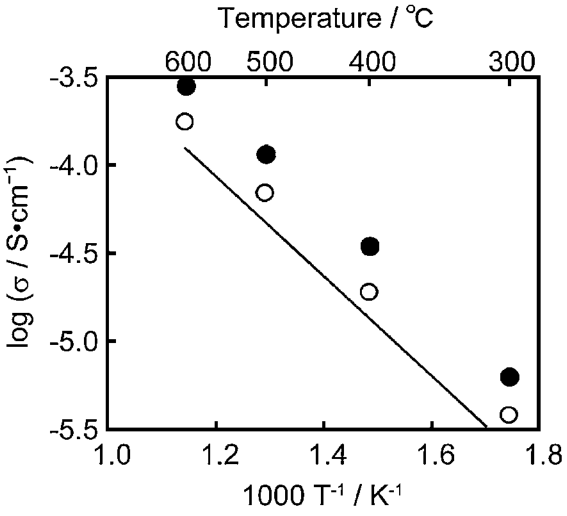

Figure 5. Temperature dependencies of the ionic conductivity for the $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ (●), $HfNbP_{2.9}V_{0.1}O_{12}$ (○), and $HfNb(PO_4)_3$ (–) solids.

and the surrounding O^{2-} anions, which was caused by the higher valence of the W^{6+} ion compared to the V^{5+} ion. Although it is well known that the ion conduction is also influenced by the sample sinterability for the polycrystalline sample, the relative density of both samples are the same (0.99), suggesting that the main factor for higher conductivity of the $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ is the higher valence state of W^{6+} compared to V^{5+}. From these results, it is clear that the hexavalent W^{6+} ion is a suitable dopant into the P^{5+} site for the realization of pure, high Hf^{4+} ion conduction in NASICON-type $HfNb(PO_4)_3$. The conductivity of $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ was approximately 2.5 times that of $HfNb(PO_4)_3$ at 600 °C.

Conclusion

Highly Hf^{4+} ion conductive solid electrolytes were successfully developed by intentionally expanding the Hf^{4+} ion conducting pathway in a NASICON-type solid by the partial substitution of the P^{5+} site in $HfNb(PO_4)_3$ by larger W^{6+} or V^{5+} ions. Although the Hf^{4+} ion conductivities for both $HfNbP_{2.9}V_{0.1}O_{12}$ and $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solids, which had the optimal lattice volume ($1.482\,nm^3$) for Hf^{4+} ion migration, were higher than that of $HfNb(PO_4)_3$, $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid in which the P^{5+} site was partially replaced with higher valence W^{6+} ions possessed the highest ionic transference number and the highest Hf^{4+} ion conductivity of the samples prepared. This was due to an effective reduction of the electrostatic interaction between Hf^{4+} cations and the surrounding O^{2-} anions. As a result, the W^{6+} ion is a superior dopant cation for the enhancement of Hf^{4+} ion conductivity in NASICON-type $HfNb(PO_4)_3$, which has no electronic conduction, and the $Hf_{395/400}NbP_{2.95}W_{0.05}O_{12}$ solid was about 2.5 times as conductive as $HfNb(PO_4)_3$.

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