Highly Tetravalent Hafnium Ion Conducting Solids with a NASICON-Type Structure

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1. Introduction

Solid electrolytes are unique functional materials in which, generally, only a single ionic species acts as the conductor and no electron or hole conduction occurs. Some solid electrolytes have already been commercialized as a component in batteries and chemical sensing devices.1,2 In the solid electrolyte field, it is accepted that ion conduction in solids greatly depends on their valence state, e.g., ion conductivity decreases with an increase in the valence state of the conducting ion. While ion conductivity high enough for practical applications has been obtained for various types of mono-, di-, and trivalent ions, higher valence tetravalent cations have been believed to be extremely poor migrating species in solids due to their strong electrostatic interaction with surrounding anions, which prevents smooth ionic migration in the rigid crystal lattice. To realize smooth tetravalent cation conduction in solids, it is necessary to carefully select not only the crystal structure, but also the constituent ions that can weaken the strong electrostatic interaction. One of the effective ways to reduce the interaction is via the introduction of higher valence cations compared to the conducting tetravalent cation into the structure, because such higher valence cations may attract anions more strongly than the tetravalent cation, thus enabling tetravalent cation migration in the solid lattice.

Based on the above-described concept, pure Zr4+ and Hf4+ ion conducting MNb(PO4)3 (M = Zr, Hf) solids were successfully developed12-14. These solids contain pentavalent Nb5+ and P5+ and have a NASICON (Na+ super ionic conductor)-type structure,5 which holds a three-dimensional framework built up by corner-shared NbO6 octahedra and PO4 tetrahedra. Furthermore, it was demonstrated that the ion conductivity of the Hf4+ cation was higher than that of the Zr4+ cation in MNb(PO4)3 (M = Zr, Hf) solids. Recently, in order to enhance the Hf4+ ion conductivity in HfNb(PO4)3 solid, the P5+ (ionic radius: 0.031 nm [coordination number (CN) = 4])15 sites in HfNb(PO4)3 solid were partially substituted with larger size and higher valence W6+ ions (0.056 nm [CN = 4])15 to intentionally expand the crystal lattice and reduce the electrostatic interaction between the Hf4+ cation and the surrounding O2– anions. As a result, it was demonstrated that the Hf1–x/y(Nb1–yWx)0.5/yP3–yW0.5xO12 (x = 0.05)16 solid showed the highest conductivity among reported Hf4+ ion conductors.

In this study, to further enhance the Hf4+ ion conductivity, Hf1–x/y(Nb1–yWx)0.5/yP3–yW0.5xO12 solids were developed, where not only the P5+ sites, but also the Nb5+ sites, were partially substituted by higher valence W6+ ions, in order to weaken the Hf4+–O2– bonds more effectively, and the Hf4+ ion conducting properties were investigated.

2. Experimental

Hf1–x/y(Nb1–yWx)0.5/yP3–yW0.5xO12 solids were synthesized using a conventional solid-state reaction with Hf(SO4)2, Nb2O5, WO3, and (NH4)2HPO4 as the starting materials. After mixing these materials 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 6 h, and 1300°C for 6 h in an air atmosphere. The obtained samples were identified by X-ray powder diffraction (XRD) analysis using Cu Kα radiation (SmartLab, Rigaku). The XRD data were collected using a step scanning method in the 2θ range from 10 to 40° 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-Al2O3 as a standard. After identifying the crystal phase of the samples, the mixed powder was pressed into a pellet shape and sintered at 1300°C for 12 h in an air atmosphere.

The AC conductivity of a sintered sample pellet with a platinum layer sputtered on both center surfaces was measured using the complex impedance method in the frequency region from 5 to 13 MHz (1260 Impedance/Gain-Phase Analyzer, Solartron) at temperatures between 300 and 600°C in an air atmosphere.

DC electrolysis was carried out by applying a DC voltage of 6 V to a sample pellet sandwiched by Pt bulk electrodes at 800°C for 336 h. After DC electrolysis, the elemental distribution in the electrolyzed sample was examined by energy dispersive X-ray spectroscopy (EDX; SSX-550, Shimadzu).
3. Results and Discussion

From the XRD measurements of the Hf1−x+y(Nb1−x−y)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solids, it was found that a single-phase of a NASICON-type structure was obtained for the samples with \([y = 0.1; \ 0 \leq x \leq 0.2]\), \([y = 0.2; \ 0.05 \leq x \leq 0.25]\), and \([y = 0.3; \ 0.1 \leq x \leq 0.3]\). In order to confirm the partial substitution of the W⁶⁺ ions in both the Nb⁵⁺ and P⁵⁺ sites, the lattice volume of the NASICON-type structure was calculated for the single-phase samples (Fig. 1).

For each series with the same W⁶⁺ ion content \((y)\) at the Nb⁵⁺ sites, a linear lattice expansion of the NASICON-type phase was observed with an increase in the W⁶⁺ ion content \((x)\) at the P⁵⁺ sites, suggesting that the P⁵⁺ (0.031 nm [CN 4])³(5) sites in the Hf(Nb1−x−y)5+yP3−2x−yP3−x−yO12 solids were partially substituted with larger W⁶⁺ ions (0.056 nm [CN = 4]).³(5) On the other hand, with an increase in the W⁶⁺ content \((y)\) at the Nb⁵⁺ sites in the Hf1−x+y(Nb1−x−y)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solids, the lattice volume monotonically decreased due to the replacement of the Nb⁵⁺ (0.078 nm [CN = 6])³(5) sites by the smaller W⁶⁺ (0.074 nm)³(5) ions.

Because the solid solubility limit of the W⁶⁺ ion content \((x)\) at the P⁵⁺ sites holding the same lattice volume increased with an increase in the W⁶⁺ ion concentration \((y)\) at the Nb⁵⁺ sites, it was concluded that the total amount of W⁶⁺ ions in the Hf1−x+y(Nb1−x−y)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solids can be intensively varied by partial substitution of both the Nb⁵⁺ and P⁵⁺ sites.

Furthermore, it is clear that the lattice volume that can hold the NASICON-type phase for the Hf1−x+y(Nb1−x−y)5+yP3−2x−yP3−x−yO12 solids is between 1.476 and 1.489 nm³.

Figure 2 shows the lattice volume dependence of the AC conductivity at 600°C for the Hf1−x+y(Nb1−x−y)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solids. The conductivity increased with an increase in the lattice volume up to 1.482 nm³ due to the expansion of the Hf⁴⁺ ion conductivity pathway in the crystal structure. In contrast, the case for the solids whose lattice volume was larger than 1.482 nm³, the conductivity decreased because the lattice expanded beyond the limit for Hf⁴⁺ ion conduction. This result clearly indicates that a suitable lattice volume exists for Hf⁴⁺ ion conduction, and it is 1.482 nm³ for the NASICON-type solid.

Figure 3 presents the total W⁶⁺ ion concentration dependence of the AC conductivity and the activation energy for ion conduction for the Hf1−x+y(Nb1−x−y)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solids \((y = 0; \ x = 0.05\), \([y = 0.1; \ x = 0.1]\), \([y = 0.2; \ x = 0.15]\), and \([y = 0.3; \ x = 0.2]\) with an optimum lattice volume (1.482 nm³). An increase in conductivity and a decrease in activation energy were clearly observed with an increase in the W⁶⁺ ion concentration in the solid up to 2.0% due to the successful reduction of the electrostatic interaction between the Hf⁴⁺ cation and the O⁵⁻ anions, because the O⁵⁻ anions are more strongly attracted to the high-valence W⁶⁺ ions. In contrast, the sample with \([y = 0.3; \ x = 0.2]\) showed a lower conductivity and a higher activation energy compared to those with \([y = 0.2; \ x = 0.15]\), because the W⁶⁺ ion content was too high in the crystal lattice. The introduction of W⁶⁺ ions into the Hf(NbO₃)₃ structure leads to the shrinkage of the NbO₆ octahedra and the expansion of the PO₄ tetrahedra caused by the differences in the ionic sizes (W⁶⁺: 0.078 nm [CN = 6]; Nb⁵⁺: 0.031 nm [CN = 4]); and therefore, the replacement of too many Nb⁵⁺ and P⁵⁺ sites by W⁶⁺ ions results in a greater than optimum content and further distortion of the network structure built by the NbO₆ octahedra and PO₄ tetrahedra, which has a negative effect on the smooth Hf⁴⁺ ion migration.

For the purpose of directly identifying the migrating ion species in the Hf1−x+y(Nb0.8W0.2)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solid that exhibited the highest conductivity in the prepared samples, DC electrolysis was performed by applying a DC voltage of 6 V, which is higher than the decomposition voltage (the decomposition voltage at 800°C was preliminarily determined by our experiment to be ca. 1.2 V from the current-voltage relationship). After the electrolysis, energy dispersive X-ray spectroscopy (EDX) line analysis was performed for the electrolyzed Hf1−x+y(Nb0.8W0.2)5+yP3−2x−yW6(3+y)P3−x−yW6O12. (Fig. 4).

Only Hf segregation was observed near the cathodic surface, while such segregation was not recognized for the other cations (Nb, P, and W). This result clearly indicates that the predominant conducting species in the Hf1−x+y(Nb0.8W0.2)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solid is only the Hf⁴⁺ cation, which is similar to the case for the Hf(NbO₃)₃ solid that was demonstrated to be a pure Hf⁴⁺ ion conductor.

The temperature dependence of the Hf⁴⁺ ion conductivity in the Hf1−x+y(Nb0.8W0.2)5+yP3−2x−yW6(3+y)P3−x−yW6O12 solid is presented in Fig. 5 with...
Among the samples prepared, the Hf$_3.85$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid, which possessed the optimum lattice volume (1.478 nm$^3$), exhibited 2.8 times higher conductivity than that of the Hf$_{3.85}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid previously reported, exhibited the highest Hf$_{4+}$ ion conductivity due to the more effective reduction of the activation energy (53.9 kJ·mol$^{-1}$) for Hf$^{4+}$ ion conduction in the NASICON-type structure compared to the Hf$_{3.95}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid at 600°C. Furthermore, the Hf$_{3.95}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid exhibited 2.8 times higher conductivity than that of the HfNb(PO$_4$)$_3$ solid at 600°C.

4. Conclusion

Highly Hf$_{4+}$ ion conducting solid electrolytes were successfully developed by the partial replacement of not only P$^{5+}$ sites, but also Nb$^{5+}$ sites, in HfNb(PO$_4$)$_3$, solid with high-valence W$^{6+}$ ions. Among the samples prepared, the Hf$_{3.85}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid, which possessed the optimum lattice volume (1.482 nm$^3$) for Hf$^{4+}$ ion migration, exactly the same as that for the Hf$_{3.95}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid previously reported, exhibited the highest Hf$^{4+}$ ion conductivity due to the more effective reduction of the Hf$^{4+}$O$^{2-}$ interaction in the Hf$_{3.95}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid, where the W$^{6+}$ ion content is seven times greater than that in the Hf$_{3.85}$/4(Nb$_{0.8}$W$_{0.2}$)$_5$P$_{2.85}$W$_{0.15}$O$_{12}$ solid.

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References