Divalent Sr$^{2+}$ Cation Conducting Solid Electrolyte with NASICON-type Structure

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ABSTRACT

A divalent strontium cation highly conducting solid was successfully developed by introducing Sr$^{2+}$ cations into the NASICON-type HfNb(PO$_4$)$_3$ solid together with W$^{6+}$ ions. The (Sr$_{0.05}$Hf$_{0.95}$)$_{4-x}$Nb$_{1-x}$W$_x$$_{2/3}$($5+y$)/($3+y$)PO$_4$ solid exhibited Sr$^{2+}$ conductivity that was 3300 times higher than that of previously reported NASICON-type Sr$^{2+}$ conductors, which was caused by the effective reduction of electrostatic interaction between conducting Sr$^{2+}$ and surrounding O$^{2-}$ ions due to the existence of high valent Nb$^{5+}$ and W$^{6+}$ cations in the structure.

Keywords : Solid Electrolyte, NASICON-type Structure, Strontium

1. Introduction

In the field of solid state ionics, ion conduction is generally influenced by the crystal structure, ionic size of the migrating ion, and the strength of interactions between the migrating ion and surrounding counter ions. Therefore, small size and low valence cations such as H$^+$ and Li$^+$ ions have been reported to migrate easily in various solid materials. In contrast, ions with large ionic size or high valence state are regarded to be poor migrating species in solids compared with small-size monovalent cations. However, divalent cation conductors are considered as candidates for next-generation electrical devices, such as rechargeable batteries and chemical sensors.

To date, some solids in which divalent cations can migrate have been reported, but most of them are limited to solids where the conducting cation is small sized, such as Mg$^{2+}$. This is because small cation can migrate more easily among the cations holding the same valence state, even in a rigid crystal lattice, which means that higher ion conductivity can be generally obtained for smaller cations. While other divalent cation conducting solids have been developed by selecting the $\beta$-Fe$_2$(SO$_4$)$_3$ type structure, in which three-dimensional large open spaces exist to realize fast ion conduction, their conductivities were still lower than those for Mg$^{2+}$ ion conductors, due to bottlenecks of the ion conduction pathway caused by distortion of the $\beta$-Fe$_2$(SO$_4$)$_3$ type structure. To obtain high ion conductivity for large-size divalent cations, it requires an expanded open space with a three-dimensional well-ordered conduction pathway in the crystal structure and effective reduction of the electrostatic interactions between conducting ions and surrounding counter anions. One of the promising candidate structures is the NASICON (Na$^+$ super ionic conductor)-type structure, which is similar to the $\beta$-Fe$_2$(SO$_4$)$_3$-type structure. High divalent cation conduction would be expected to occur in a well-ordered NASICON-type structure, even for large-size divalent cations such as Sr$^{2+}$; however, Sr$^{2+}$ ion conductivity in the NASICON-type Sr$_{0.5}$Zr$_{2}$($PO_4$)$_3$ was considerably lower than that for smaller divalent cations. Therefore, it is necessary to realize optimal conditions for smooth ion migration in a crystal lattice; reduction of the electrostatic interactions between Sr$^{2+}$ and surrounding counter anions and/or suitably sized conduction pathways in the NASICON-type structure.

Here, we have focused on HfNb(PO$_4$)$_3$ as a mother solid, which has been reported as a tetravalent Hf$^{4+}$ ion conductor with the NASICON-type structure. Sr$^{2+}$ ions are also expected to migrate smoothly in the NASICON-type structure by the introduction of Sr$^{2+}$ ions into the Hf$^{4+}$ sites in the HfNb(PO$_4$)$_3$ solid, considering that lower valence cations can migrate more easily in a solid lattice than higher valence cations.

In this study, the highly Sr$^{2+}$ ion-conducting solid electrolyte (Sr$_{x}$Hf$_{(1-x)}/(4-2x)$)Nb(PO$_4$)$_3$ was developed. In addition, the effect of hexavalent W$^{6+}$ ion doping into the (Sr$_{x}$Hf$_{(1-x)}/(4-2x)$)Nb(PO$_4$)$_3$ solid on the Sr$^{2+}$ ion conduction properties was investigated.

2. Experimental

(Sr$_{x}$Hf$_{(1-x)}/(4-2x)$)Nb(PO$_4$)$_3$ solids were synthesized from Sr(NO$_3$)$_2$, (NH$_4$)$_2$HPO$_4$, HfCl$_4$, and NbCl$_4$ starting materials. After mixing Sr(NO$_3$)$_2$ and (NH$_4$)$_2$HPO$_4$ nitric acid solutions with ethanol solutions of HfCl$_4$ and NbCl$_4$, the mixed solution was stirred at 130°C for 24 h. To prepare (Sr$_{0.05}$Hf$_{0.95}$)$_{4-x}$Nb$_{1-x}$(5+y)/(3+y)PO$_4$ solids, an aqueous solution of (NH$_4$)$_2$WO$_4$ was also added to the mixed solution. The precipitates obtained were successively calcined at 600, 1000, 1200, and 1300°C, each for 12 h in air. After pulverizing the samples into powders, pellets were formed and sintered at 1300°C for 12 h in air. The synthesized samples were identified using X-ray powder diffraction (XRD; Rigaku, SmartLab) analysis with Cu Kα radiation in the 2θ range between 10° and 70°.

AC conductivities of the sintered sample pellets were measured using the complex impedance method with an impedance/gain phase analyzer (Solartron, 1260) in the frequency range from 5 Hz to 13 MHz at 600–900°C in air. Both AC and DC conductivities were measured at various oxygen partial pressures from 10$^{-15}$ to 10$^0$ Pa at 900°C to identify the conducting species in the samples. Furthermore, DC electrolysis of sample pellets sandwiched with Pt bulk electrodes was performed at 900°C in air to directly demonstrate Sr$^{2+}$ ion migration in the (Sr$_{0.05}$Hf$_{0.95}$)$_{4-x}$Nb$_{1-x}$(5+y)/(3+y)- (PO$_4$)$_3$ solids.
3. Results and Discussion

From the XRD analyses of the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{Nb}(\text{PO}_4)_3\) solids, the NASICON-type structure was clearly observed for all the prepared samples, while a NbPO\(_5\) impurity appeared in the solids with \(x > 0.05\) (Fig. 1). Furthermore, the cationic ratio in the samples were confirmed to be the same as the mixing one by the fluorescent X-ray analysis. Figure 2 shows that the lattice volume of the NASICON-type phase increased linearly with increasing \(x\) up to 0.05, because the ionic size of Sr\(^{2+}\) (ionic radius: 0.132 nm\(^{-1}\)) is larger than that of Hf\(^{6+}\) (0.085 nm\(^{-1}\)), whereas a constant value was maintained for the solids with \(x > 0.05\). The change in lattice volume for the solids with \(x \leq 0.05\) obeys Vegard’s law; therefore, it is considered that the samples with \(x \leq 0.05\) form a solid solution, in which large Sr\(^{2+}\) ions partially replace the Hf\(^{6+}\) sites in the \(\text{Hf}(\text{PO}_4)_2\) solid. The electrical conductivity of the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{Nb}(\text{PO}_4)_3\) solids measured at 900°C is also depicted in Fig. 2. In the single phase region of the NASICON-type structure (\(x \leq 0.05\)), the conductivity increased monotonically and the highest conductivity \((2.5 \times 1.0^{-4}\text{S cm}^{-1})\) at 900°C was obtained for the solid solution composition of \(x = 0.05\), due to the increase of Sr\(^{2+}\) in the solid. On the other hand, the conductivity of the solids containing the NbPO\(_2\) secondary phase was significantly decreased because this phase may inhibit Sr\(^{2+}\) ion conduction in the solids. Such enhancement of Sr\(^{2+}\) ion conductivity (Sr\(^{2+}\) ion conduction in the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{Nb}(\text{PO}_4)_3\) solid is demonstrated by the same manner described below) is considered to be by the presence of pentavalent Nb\(^{5+}\) cations in the NASICON-type structure, which effectively reduces the electrostatic interaction between Sr\(^{2+}\) ions and surrounding O\(^{2-}\) ions; therefore, it can be expected that much higher Sr\(^{2+}\) conductivity could be realized by reducing the interactions more effectively, and hexavalent W\(^{6+}\) ions were introduced into the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{Nb}(\text{PO}_4)_3\) solid by the partial substitution of Nb\(^{5+}\) sites with W\(^{6+}\) ions.

Similar to the case for the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{Nb}(\text{PO}_4)_3\) solids, the \((\text{SrHf}_{1-x})_{4}(4-2x)\text{NbHf}(\text{PO}_4)_3\) solids formed a solid solution with single phase NASICON-type structures for \(y \leq 0.15\), whereas the solids with \(y > 0.15\) were a two-phase mixture of NASICON-type solid and \(\text{HfP}_2\text{O}_7\). The lattice volume of the samples with \(y \leq 0.15\) decreased linearly with increasing content of the small ionic size W\(^{6+}\) (0.074 nm\(^{-1}\)) at Nb\(^{5+}\) (0.078 nm\(^{-1}\)) sites, as shown in Fig. 3. Furthermore, an increase in conductivity with increased W\(^{6+}\) content was observed for the single phase samples (Fig. 3), while the lattice volume was reduced. The reason for the increase in conductivity for the solids with \(y \leq 0.15\), regardless of lattice volume contraction, is the effective reduction of the electrostatic interactions between Sr\(^{2+}\) and surrounding O\(^{2-}\) ions caused by the presence of high valence W\(^{6+}\) ions in the structure. In contrast, the solids with \(y > 0.15\) exhibited lower conductivity, although the lattice volumes were the same as that for \(y = 0.15\). In this compositional region, the amount of the \(\text{HfP}_2\text{O}_7\) insulator increases with \(y\), so that the conductivity of these samples is reduced.

To identify the conducting species in the \((\text{SrHf}_{0.95})_{4}(5-1.5)\text{Nb}(\text{PO}_4)_3\) \((\text{NbHf}_{0.5})_{4}(5-1.5)\text{W}(\text{PO}_4)_3\) solid, which had the highest conductivity among this series, the AC and DC conductivities were measured under various oxygen partial pressures from 10\(^{-12}\) to 10\(^{0}\) Pa. The \((\text{SrHf}_{0.95})_{4}(5-1.5)\text{Nb}(\text{PO}_4)_3\) solid had constant AC conductivity above \(P_{\text{O}_2} = 10^{-8}\) Pa, indicating no electronic conduction in the sample. Furthermore, oxide anion conduction was also eliminated by investigation of the DC to AC conductivity ratio (\(\sigma_{\text{dc}}/\sigma_{\text{ac}}\)) in an \(O_2\) atmosphere, and the cation transference number was identified to be smaller than 0.09. These results suggest that the cations in the \((\text{SrHf}_{0.95})_{4}(5-1.5)\text{Nb}(\text{PO}_4)_3\) solid do not exhibit valence change over a wide range of oxygen partial pressures.
although Nb and W ions are known to easily change their valence state.

DC electrolysis was performed under an air atmosphere to elucidate which cation (Sr$^{2+}$, Hf$^{4+}$, Nb$^{5+}$, P$^{5+}$, or W$^{6+}$) is the migrating species in the (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid. If the conducting species in (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ is only Sr$^{2+}$, then the sample will decompose at the anodic side to produce Sr$^{2+}$ cations by application of a higher DC voltage than the decomposition voltage (1.6 V) of the sample. The Sr$^{2+}$ cations generated should migrate in the sample pellet toward the cathode side according to the potential gradient, and be reduced to the metallic state at the cathodic surface in contact with the ion-blocking Pt electrode. When DC electrolysis is conducted in atmospheric air, metallic Sr should be immediately oxidized, so that evidence for Sr$^{2+}$ conduction can be obtained by investigating the cathodic surface. EDX line analysis result for the electrolyzed (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid after application of a DC voltage of 6 V at 900°C for 7 days is depicted in Fig. 4. A clear Sr segregation was observed at the cathodic surface that contacts with the ion-blocking Pt electrode. When DC electrolysis is conducted in atmospheric air, the metallic state at the cathodic surface in contact with the ion-blocking Pt electrode, whereas other cations are homogeneously distributed over the sample pellet. This result indicates that only Sr$^{2+}$ ions migrated into the (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid. The divalent Sr$^{2+}$ ion conductivity of the (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid is shown in Fig. 5 together with the corresponding data for the Sr$_{0.5}$Hf$_{2}$(PO$_4$)$_3$ and M$_{0.5}$Zr$_{2}$(PO$_4$)$_3$ (M = Mg (- - -), Ca ( ), Sr ( --)).

4. Conclusions

High Sr$^{2+}$ cation conduction was successfully realized in the (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid having the NASICON-type structure with a well-ordered three-dimensional network. The introduction of high valence cations such as Hf$^{4+}$, Nb$^{5+}$, P$^{5+}$, and W$^{6+}$ into the structure enables Sr$^{2+}$ cations to easily migrate in the rigid crystal lattice; the (Sr$_{0.05}$Hf$_{0.95}$)$_{4/3}$($\text{Nb}_{0.85}$W$_{0.15}$)$_{5/15}$(PO$_4$)$_3$ solid exhibited an extraordinarily high divalent cation conductivity comparable to the Mg$^{2+}$ cation conductor of Mg$_{0.5}$Zr$_{2}$(PO$_4$)$_3$ with the same NASICON-type structure.

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