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Short communication

Highly conducting divalent Mg^{2+} cation solid electrolytes with well-ordered three-dimensional network structure

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ABSTRACT

A three-dimensionally well-ordered NASICON-type Mg^{2+} cation conductor, $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$, was firstly developed by partial substitution of lower valent Mg^{2+} cation onto the Hf^{4+} sites in a $HfNb(PO_4)_3$ solid to realize high Mg^{2+} cation conductivity even at moderate temperatures. Due to the formation of well-ordered NASICON-type structure, both the high Mg^{2+} cation conductivity below 450 °C and the low activation energy for Mg^{2+} cation migration was successfully realized for the $(Mg_{0.1}Hf_{0.9})_{4/3.8}Nb(PO_4)_3$ solid. Pure Mg^{2+} cation conduction in the NASICON-type $(Mg_{0.1}Hf_{0.9})_{4/3.8}Nb(PO_4)_3$ solid was directly and quantitatively demonstrated by means of two kinds of dc electrolysis.

1. Introduction

Solid electrolytes are functional materials where single ion species generally migrate into the solid lattice as a charge carrier, which is quite different from liquid electrolyte solutions where cations and anions are simultaneously conducted. Based on such unique selective ion migration, solid electrolytes are applied to various electrochemical devices, such as rechargeable batteries and chemical sensors.

The conduction of various ions with valence states from monovalent to tetravalent has been observed in rigid crystal lattices; however, the ion conductivity is significantly dependent on the valence state and ionic size, i.e., lower valent or smaller sized ions can migrate in solids more readily than higher valent or larger sized ions. As a result, many researchers have paid an attention to the development of monovalent cation conductors, such as Li^+ and Na^+ conductors, to realize high-performance electrochemical devices in the 20th centuries. In the 21st century, there has been a strong demand for high-performance rechargeable batteries with high energy density, so that divalent cation conducting solid electrolytes have attracted much attention. Among them, Mg^{2+} cation conductors are believed to be suitable candidates for the electrolyte of next-generation batteries [1] due to advantages such as safety and low cost compared to the conventional Li-ion battery. However, most of the research on Mg^{2+} ion batteries has employed liquid or polymer electrolytes [2–4]. Consideration of features such as energy density, safety, and ease of fabrication concerns indicate that it is better to fabricate an all-solid-state battery with a Mg^{2+} cation conducting solid electrolyte.

Until now, there are few reports on Mg^{2+} cation conduction in crystalline solids [5–9]. Among them, $MgZr_4(PO_4)_6$ [5–8] with the β-$Fe_2(SO_4)_3$-type structure (monoclinic symmetry, $P2_1/n$), which is known to have a three-dimensional network linking ZrO_6 octahedra and PO_4 tetrahedra by corner-sharing, has been reported to exhibit high Mg^{2+} cation conductivity (1.4×10^{-3} S cm^{-1} at 800 °C), although its activation energy for Mg^{2+} ion conduction was extremely high (96–110 kJ mol^{-1}). Furthermore, improvement of the Mg^{2+} ion conductivity in the β-$Fe_2(SO_4)_3$-type $MgZr_4(PO_4)_6$ crystal structure was reported by the introduction of pentavalent Nb^{5+} cations to form the $Mg_{0.7}(Zr_{0.85}Nb_{0.15})_4P_6O_{24}$ solid [10]. Although the $Mg_{0.7}(Zr_{0.85}Nb_{0.15})_4P_6O_{24}$ solid possessed a Mg^{2+} cation conductivity of 7.7×10^{-4} S cm^{-1} at 600 °C, which was ca. 9 times higher than that of $MgZr_4(PO_4)_6$, the activation energy for Mg^{2+} cation migration was still high (92.0 kJ mol^{-1}), and therefore, its Mg^{2+} cation conductivity at lower temperatures was significantly reduced, which was attributed to the distortion behavior of the β-$Fe_2(SO_4)_3$-type structure.

Therefore, to obtain high Mg^{2+} cation conductivity even at moderate temperatures around 300 °C, we must select a more suitable structure for Mg^{2+} cation migration, such as the NASICON (Na^+ super ionic conductor [11])-type structure (rhombohedral symmetry with hexagonal setting, R_{-3c}), which is also a three-dimensional network structure similar to the β-$Fe_2(SO_4)_3$-type structure. Although the arrangement of $Zr_2P_3O_{18}$ (lantern) units in the β-$Fe_2(SO_4)_3$-type structure are distorted, the lantern units in the NASICON-type structure are well ordered. This provides an

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ordered ion conduction pathway surrounded by lantern units in the NASICON-type structure, so that smooth ion migration is expected with this NASICON-type structure, i.e., high ion conductivity is expected even at moderate temperatures of 300–500 °C due to lowering of the activation energy for ion migration. However, most of the solids that were synthesized at high temperature in an attempt to form the NASICON-type structure were obtained as β-$Fe_2(SO_4)_3$-type solids, which is speculated to be due to the small ionic radius of Mg^{2+}, so that the ordered NASICON-type crystal structure is not formed.

In the work reported here, we firstly succeeded to develop a series of NASICON-type Mg^{2+} cation conductors, $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$, by selecting $HfNb(PO_4)_3$ as the mother solid ($HfNb(PO_4)_3$ has been reported as a tetravalent Hf^{4+} cation conductor [12]), of which the lattice size is small compared to other NASICON-type solids, and we report its high Mg^{2+} cation conductivity at moderate temperatures.

2. Experimental

$(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ $(0.05 \leq x \leq 0.3)$ solids were synthesized using a co-precipitation method with high-purity $Mg(NO_3)_2$ (99.9%), $HfCl_4$ (99.9%), $NbCl_5$ (> 99.9%), and $(NH_4)_2HPO_4$ (> 99.9%) as starting materials. Appropriate quantities of $Mg(NO_3)_2$, $HfCl_4$, and $NbCl_5$ were dissolved in ethanol and then the $(NH_4)_2HPO_4$ nitric acid solution was dropped into the mixed ethanol solution to obtain a precipitation. After stirring the solution at 130 °C for 24 h, the samples were dried at 130 °C for several hours. The powders obtained were heated at 600 °C for 6 h in air, and then calcined at 1100 °C for 6 h, 1200 °C for 6 h, 1300 °C for 6 h, and 1300 °C for 6 h in synthetic air ($20\%O_2$–$80\%N_2$) with an intermediate grinding of the sample. The samples obtained were identified by X-ray powder diffraction (XRD) analysis (SmartLab, Rigaku) using Cu Kα radiation (40 kV, 40 mA). The XRD data were collected by a step-scanning method in the 2θ range between 10° and 70° with a step width of 0.04°. The lattice parameters and lattice volume were calculated from the XRD peak angles with respect to α-Al_2O_3 powder as an internal standard.

Electrical conductivity measurements of the samples were conducted using pellet samples sintered at 1300 °C for 12 h in air. After sputtering a Pt layer on the center of both sides of the sintered sample pellet, the ac conductivity was measured using a complex impedance method with an impedance analyzer (1260, Solartron) in the frequency region from 5 Hz to 13 MHz at temperatures between 300 and 600 °C in an air atmosphere. In order to identify the conducting species in the $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ solid, we investigated ac and dc conductivities at 600 °C in various oxygen partial pressure controlled by mixing O_2, He, synthetic air ($20\%O_2$–$80\%N_2$), $1\%CO$–$99\%CO_2$, and $99\%CO$–$1\%CO_2$. The oxygen partial pressure was monitored by using O_2 gas sensor based on yttria stabilized zirconia (YSZ). The dc electrolysis of the sintered $(Mg_{0.1}Hf_{0.9})_{4/3.8}Nb(PO_4)_3$ pellet was performed by applying a dc voltage of 4.0 V between ion-blocking Pt bulk electrodes at 900 °C for 7 days in an air atmosphere. The elemental distribution of the electrolyzed sample pellet was determined by cross-sectional line analysis using energy-dispersive X-ray spectroscopy (EDX; SSX-550, Shimadzu). Modified Tubandt electrolysis was conducted using three sample pellets at 800 °C with application of 4.0 V for 15 days. Because we investigate the ion conducting properties in atmospheric air and it is difficult to use Mg metal or its alloys as the anode at elevated temperatures in atmospheric air due to the oxidation of them. Therefore, we applied Pt bulk electrodes not only for cathode but also for anode.

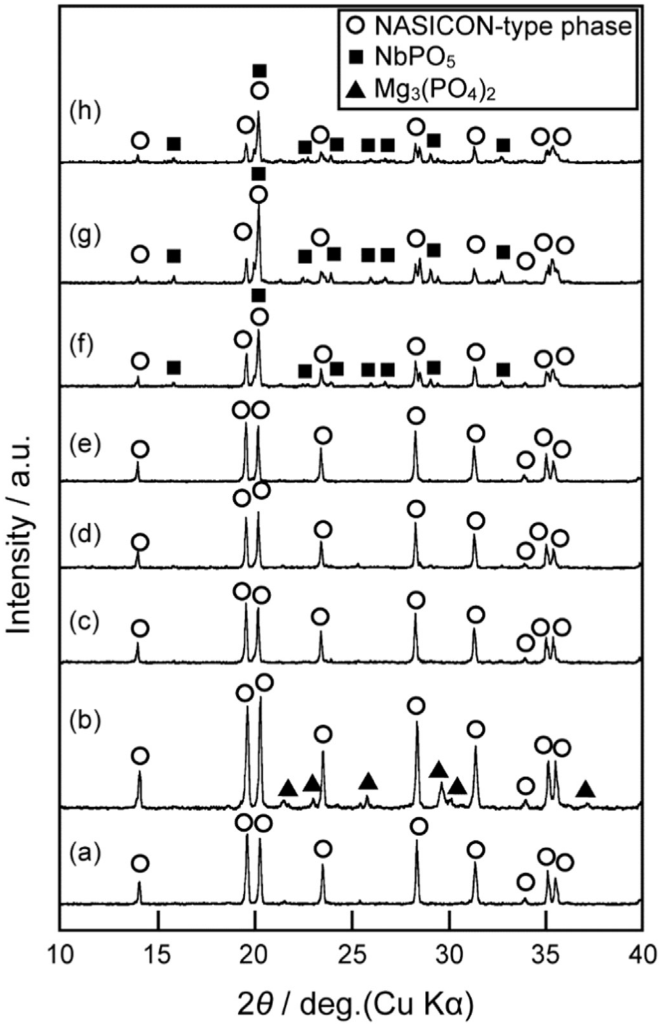

Fig. 1. XRD patterns for the $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ series; x=(c) 0.05, (d) 0.07, (e) 0.10, (f) 0.15, (g) 0.20, and (h) 0.30 with (a) the mother $HfNb(PO_4)_3$ and (b) the $HfNb(PO_4)_3$ mixed with 10 wt% $Mg_3(PO_4)_2$.

Table 1
Lattice parameters and unit cell volume of the NASICON-type phase for the prepared samples.

x in $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$	a/nm	c/nm	V/nm^3
0.00 ($HfNb(PO_4)_3$)	0.8729	2.240	1.4780
0.05	0.8725	2.242	1.4782
0.07	0.8755	2.227	1.4784
0.10	0.8734	2.238	1.4787
0.15	0.8754	2.228	1.4787
0.2	0.8708	2.252	1.4787
0.3	0.8726	2.243	1.4787

[*] Lattice parameters were calculated based on those for NASICON-type $NaZr_2(PO_4)_3$ (PDF# 00–023-1411).

3. Results and discussion

Fig. 1 shows XRD patterns of $(Mg_xHf_{1-x})_{4/(4-2x)}Nb(PO_4)_3$ after calcination at 1300 °C together with the corresponding patterns of mother $HfNb(PO_4)_3$, and Table 1 lists the lattice parameters and unit cell volume for the prepared samples which are calculated based on those for the NASICON-type $NaZr_2(PO_4)_3$ (rhombohedral symmetry with hexagonal setting, R_{-3c}) (PDF# 00–023-1411). In order to confirm that the present samples form the solid solution, we also investigated the XRD pattern for the $HfNb(PO_4)_3$ mixed