



Divalent Ni^{2+} cation conduction in NASICON-type solid

Wonrak Lee, Shota Yamauchi, Shinji Tamura, Nobuhito Imanaka *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Suita, Osaka 565-0871, Japan

ARTICLE INFO

Article history:

Received 18 July 2018

Received in revised form 13 September 2018

Accepted 17 September 2018

Available online 18 September 2018

Keywords:

Solid electrolyte

Divalent

NASICON-type structure

Electroceramics

Functional

ABSTRACT

Divalent Ni^{2+} cation-conducting solid electrolytes, $(\text{Ni}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$, were successfully developed by introducing Ni^{2+} cations into a $\text{HfNb}(\text{PO}_4)_3$ solid exhibiting a three-dimensional NASICON-type structure. Although the $\text{HfNb}(\text{PO}_4)_3$ solid has been reported to be purely a Hf^{4+} ion conductor, the conducting species was changed to the divalent Ni^{2+} cation upon Ni^{2+} doping, due to the facile migration of lower-valence ions in the rigid crystal lattice. In addition, by selecting the well-ordered NASICON-type structure as the mother crystal, the $(\text{Ni}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$ solid electrolytes exhibited lower activation energies and higher Ni^{2+} cation conductivities than a previously reported $\text{NiZr}_4(\text{PO}_4)_6$ solid with the $\beta\text{-Fe}_2(\text{SO}_4)_3$ -type structure. Among the $(\text{Ni}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$ solids, $(\text{Ni}_{0.06}\text{Hf}_{0.94})_{4/3.88}\text{Nb}(\text{PO}_4)_3$ ($x = 0.06$) showed the highest Ni^{2+} ion conductivity, of $2.27 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 600°C , which is ca. 23 times higher than that of the $\text{NiZr}_4(\text{PO}_4)_6$ solid.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Solid electrolytes, in which ions migrate macroscopically in solids as charge carriers, are promising candidate materials for components of electrochemical devices such as batteries, fuel cells, chemical sensors, and others, due to their favorable thermal and mechanical properties which realize high performance and long-term stability. Specifically, solid electrolytes whose conducting species are Li^+ , H^+ , or O^{2-} ions are extensively studied for their potential applications in electrochemical energy storage devices [1–4].

In the field of solid electrolytes, it is generally accepted that ion migration is strongly influenced by the valence state of the conducting ion species, where conducting ion species with higher valence number exhibit stronger electrostatic interactions with surrounding anions; thus, the migration of high-valence ions is regarded to be poor in solids [5]. Based on this theory, many researchers have focused on monovalent ions such as Li^+ , H^+ , and Na^+ , which interact with the surrounding counter anions in weaker electrostatic interactions.

Recently, however, the demand for next-generation batteries with high energy density is gradually increasing due to the high power requirements of devices like mobile phones and portable computers, and divalent-cation conductors are promising candidate component materials because they can theoretically carry twice the amount of electricity that monovalent cations can. Several divalent cations, such as Mg^{2+} , Ca^{2+} , Sr^{2+} , Pb^{2+} , and Ba^{2+} ,

have been reported to conduct in β -alumina- and $\beta\text{-Fe}_2(\text{SO}_4)_3$ -type structures [6–10]. However, their ion conductivities were too low for commercialization, mainly because the large ionic size limits migration in rigid crystal lattices, or because the crystal structures were unsuitable for smooth ion migration.

Therefore, we focused on the Ni^{2+} ion as the migrating cation species because the ionic radius of Ni^{2+} is relatively small in comparison to those of other divalent cations. While the $\text{NiZr}_4(\text{PO}_4)_6$ [9] solid with $\beta\text{-Fe}_2(\text{SO}_4)_3$ -type structure has been studied as a Ni^{2+} cation conductor, the activation energy (123 kJ mol^{-1}) for Ni^{2+} conduction in the $\text{NiZr}_4(\text{PO}_4)_6$ solid was extraordinarily high because of a bottle-neck for ion conduction caused by distortion of the crystal structure, resulting in low Ni^{2+} conductivity even at an elevated temperature (600°C). In order to achieve high Ni^{2+} ion conductivity, it is essential to select a crystal structure that is conducive to ion migration. We selected the NASICON-type structure, which comprises a well-ordered three-dimensional conducting pathway.

In this study, we successfully achieved high Ni^{2+} ion conduction in NASICON-type $(\text{Ni}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$ solids by selecting $\text{HfNb}(\text{PO}_4)_3$ [11] as the mother solid. By selecting NASICON-type $\text{HfNb}(\text{PO}_4)_3$, Ni^{2+} ions were able to migrate smoothly through the solid with the help of high-valence cations such as Nb^{5+} , P^{5+} , and Hf^{4+} present in the structure, which effectively diminished the electrostatic interaction between Ni^{2+} and surrounding oxide anions.

2. Experimental

$(\text{Ni}_x\text{Hf}_{1-x})_{4/(4-2x)}\text{Nb}(\text{PO}_4)_3$ ($0.03 \leq x \leq 0.10$) solids were synthesized using a conventional co-precipitation method. The detail

* Corresponding author.

E-mail address: imanaka@chem.eng.osaka-u.ac.jp (N. Imanaka).