Extraordinary High Tetravalent Cation Conducting Behaviors in Solid

Nobuhito Imanaka, Tomohiro Ueda, and Gin-ya Adachi*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

(Received March 1, 2001; CL-010172)

A tetravalent cation conductor whose ionic conductivity is extraordinary high and comparable to the conductivity range of the representative divalent oxide anion conductors, was artificially designed by strictly choosing the constituent elements and the structure of the solid. Promising applications such as rechargeable batteries and chemical sensors for a global environmental monitoring, are greatly expected.

Ionic conduction in solids is commonly well known such monovalent species as alkali metal cations. For multivalent ion species, divalent cations[1–4] and divalent oxide anions[5,6] and also trivalent,[7–9] tetravalent cations[10] have been reported. However, the ionic conductivity for the ion species higher than divalent state, is considerably low from a practical application point of view. Here, a tetravalent cation conductor whose ionic conductivity is extraordinary high and comparable to the conductivity range of divalent oxide anion conductors, was artificially designed by strictly choosing the constituent elements and the structure of the solid.[11]

The temperature dependencies of the ionic conductivity of the zirconium niobium phosphate ($ZrNb(PO_4)_3$) solid[12,13] are shown with the data of tetravalent ionic ($Zr_2O(PO_4)_2$) conductor reported previously[10] (Figure 1). (The demonstration of the Zr^{4+} ionic conduction is described below.) The first identification of the tetravalent cation conductor was reported for $Zr_2O(PO_4)_2$ with an orthorombic symmetry. However, the Zr^{4+} ionic conductivity is as low as below 10^{-5} $S{\cdot}cm^{-1}$ up to the temperature of 800 °C. The conductivities of the present $ZrNb(PO_4)_3$ solid electrolyte are more than two orders of magnitude and 30 times as high as that of $Zr_2O(PO_4)_2$ at 400 and 800 °C, respectively. In addition, the tetravalent Zr site substitution for Nb^{5+} was found to be effective enough to considerably reduce the activation energy for the Zr^{4+} ionic migration from 78.9 to 56.2 kJ/mol by the replacement, suggesting the efficient formation of the Zr^{4+} cation vacancies.

The phase transformation in the structure is one of conventional approaches to sharply enhance the ionic conductivity such ion species as oxide anion as demonstrated by the phase transition from the monoclinic to the cubic phase in $La_2Mo_2O_9$.[6] In the present case, the structure phase was intentionally modified from the orthorombic $Zr_2O(PO_4)_2$ phase to the monoclinic ß-$Fe_2(SO_4)_3$-type structure by partially substituting the Zr^{4+} site for higher valent Nb^{5+} ions with forming the Zr^{4+} ionic vacancies simultaneously. The Zr^{4+} ionic conductivity in $ZrNb(PO_4)_3$ is comparable to divalent oxide anion conductors of stabilized zirconias such as yttria stabilized zirconia(YSZ),[5] calcia stabilized zirconia(CSZ)[5] and the above described $La_2Mo_2O_9$.[6] Typical divalent oxide anion conductivity range is shown as a shaded area (Figure 1). The results described above explicitly indicate that $ZrNb(PO_4)_3$ holding the ß-$Fe_2(SO_4)_3$ type structure with Zr^{4+} vacancies, was artificially designed to show as high ionic conductivity as typically commercialized conductor series.

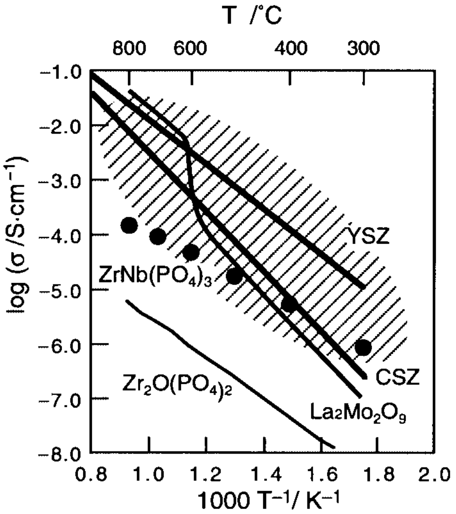

Figure 1. The temperature dependencies of the ion conductivity of the zirconium niobium phosphate ($ZrNb(PO_4)_3$) solid (●) with the data of tetravalent ion ($Zr_2O(PO_4)_2$) conductor reported previously[10] and the divalent oxide anion conductors of stabilized zirconias such as YSZ,[5] CSZ[5] and $La_2Mo_2O_9$.[6] Typical divalent oxide anion conductivity range is also shown as a shaded area.

The identification of the macroscopic tetravalent Zr^{4+} ionic migration is as follows. From the measurements of the electrical conductivity dependencies on the oxygen pressure for $ZrNb(PO_4)_3$,[14] the conductivity was almost constant in such a wide pressure range from 10^{-11} Pa to 10^{5} Pa, indicating that any hole or electron conduction does not appear in the above mentioned oxygen pressure region. In addition, polarization measurements[15] were also carried out by measuring the time dependencies of the dc to ac conductivity ratio (σ_{dc}/σ_{ac}) in both nitrogen (Po_2:50 Pa) and oxygen (Po_2:10^5 Pa) atmospheres. Because an abrupt reduction in the ratio was observed in both atmospheres, oxide ionic conduction in the zirconium niobium phosphate solid is denied as described in References 7 and 8. The proton (H^+) conduction was also excluded by the fact that the similar polarization phenomenon was recognized for the σ_{dc}/σ_{ac} ratio in both dry and wet (H_2O: 3.1 vol%) air atmospheres.[16] Therefore, the mobile ion species in the zirconium niobium phosphate is limited to the cationic species of Zr^{4+}, Nb^{5+} or P^{5+}.

For the purpose of directly identifying the migrating cation species, a dc electrolysis[17] was performed by sandwitching the zirconium niobium phosphate between two platinum electrodes as a similar manner as reported in our previous papers.[7–9] From the preliminary electrolysis experiment, the decomposition voltage of the sample was identified to be ca. 1.2 V. The higher voltage compared with the decomposition voltage was applied

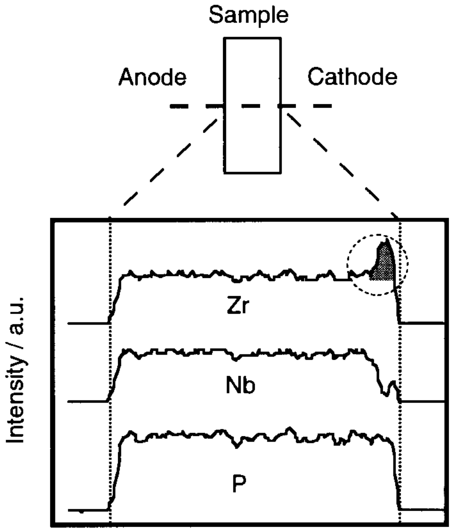

Figure 2. The EPMA line analysis results of the elements, Zr, Nb, and P. The Zr segregation is shown as a shaded area in the broken circle. The analysis was carried out from anode to cathode direction along the broken line.

so as to supply the migrating cation species at the anode and the macroscopic cation migration can proceed continuously. After the electrolysis, the deposits were clearly recognized on the cathodic surface of the $ZrNb(PO_4)_3$ electrolyte by mapping the surface by the electron probe micro analysis (EPMA). The Zr/Nb and Zr/P ratios in the deposits were found to be 4–6.5 and 0.53–0.60 by EPMA, while the ratios for $ZrNb(PO_4)_3$ without electrolysis were 1.2 and 0.30, respectively. In addition, the Nb/P ratio decreases from 0.25 to 0.09–0.13 by the electrolysis. These results clearly indicate the fact that a predominant element in the deposits is Zr and not Nb nor P. Furthermore, the cross-sectional line analysis of the electrolyzed pellet was also carried out (Figure 2) and a high amount of the Zr segregation was clearly identified near the cathodic surface as depicted as a shaded area, while any Nb^{5+} and P^{5+} increase in the content was not observed at all, showing that the predominant migrating cation species is only Zr^{4+} cation. The phenomena mentioned above, explicitly demonstrate that tetravalent Zr^{4+} ions migrate in the $ZrNb(PO_4)_3$ bulk by the electrolysis and deposit on the cathodic surface.

The realization of Zr^{4+} ionic conduction in solids which shows as high ionic conductivity as the typical O^{2-} ionic conductor series accelerates the practical application of the high multivalent ionic conductors such as the present Zr^{4+} ionic conducting $ZrNb(PO_4)_3$ as the component of rechargeable batteries and the global environmental gas monitoring tool useful in the future.

The present work was partially supported by a Grant-in-Aid for Scientific Research from The Ministry of Education, Science, Sports and Culture. This work was also supported by the "Research for the Future, Preparation and Application of Newly Designed Solid Electrolytes (JSPS-RFTF96P00102)" Program from the Japan Society for the Promotion of Science.

References and Notes

1 S. Ikeda, M. Takahashi, J. Ishikawa, and K. Ito, *Solid State Ionics,* **23**, 125 (1987).
2 K. Nomura, S. Ikeda, K. Ito, and H. Einaga, *Bull. Chem. Soc. Jpn.*, **65**, 3221 (1992).
3 K. Nomura, S. Ikeda, K. Ito, and H. Einaga, *Solid State Ionics,* **61,** 293 (1993).
4 N. Imanaka, Y. Okazaki, and G. Adachi, *J. Mater. Chem.,* **10,** 1431 (2000).
5 D.W. Strickler and W.G. Carlson, *J. Am. Ceram. Soc.*, **47**, 122 (1964).
6 P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux, and Y. Laligant, *Nature,* **404**, 856 (2000).
7 Y. Kobayashi, T. Egawa, S. Tamura, N. Imanaka, and G. Adachi, *Chem. Mater.*, **9**, 1649 (1997).
8 N. Imanaka, Y. Kobayashi, K. Fujiwara, T. Asano, Y. Okazaki, and G. Adachi, *Chem. Mater.*, **10**, 2006 (1998).
9 S. Tamura, N. Imanaka, and G. Adachi, *Adv. Mater.,* **11**, 1521 (1999).
10 N. Imanaka, T. Ueda, Y. Okazaki, S. Tamura, M. Hiraiwa, and G. Adachi, *Chem. Lett.*, **2000**, 452.
11 The NASICON(Na^+ Ion Super Ionic CONductors) type and the ß-$Fe_2(SO_4)_3$ type structure which is slightly distorted from the NASICON structure, have a rhombohedral and a monoclinic symmetry, respectively, and possess the three dimensional network ion pathway, which have been demonstrated to be one of suitable structures for multivalent ion migration such as divalent[1–4] and trivalent[9] cations. Here, the ß-$Fe_2(SO_4)_3$ structure was selected as the candidate structure. For the purpose of realizing the smoother multivalent cation migration, the higher electrostatic interaction between the lattice forming cations and anions is needed in comparison to the interaction between the mobile cations and the anions. In addition, the ion species migrate in solids is tetravalent, we must exclude the inclusion of lower valent cations than tetravalent state to eliminate the lower valent ionic conduction in solids. The needs described above mean that the solid should contain the elements which can stably hold the pentavalent state or higher. Also, solid electrolytes should be stable enough in various atmospheres to prevent the reduction of the constituent elements in solid which causes an electronic conduction. From a stability point of view, compounds commonly appear on earth and their stability has been already guaranteed, are the oxide based series. In this study, as the target tetravalent ion species, Zr^{4+} ion was selected. As the higher valent cation compared with Zr^{4+}, pentavalent Nb^{5+} was doped in the Zr^{4+} site to create Zr^{4+} cation vacancies. The formation of Zr^{4+} cation vacancies in the ß-$Fe_2(SO_4)_3$ type structure is greatly expected to enhance the Zr^{4+} ionic conduction with forming the Zr^{4+} ion three dimensional pathway. As the lattice forming cations whose valencies are higher than pentavalent state, P^{5+} as well as Nb^{5+} were selected to form a stable oxide solid and the compound we choose is the zirconium niobium phosphate.
12 Zirconium nitrate oxide dihydrate, diammonium hydrogenphosphate, and niobium oxide were mixed in a stoichiometric ratio. The mixture was firstly heated at 300 °C for 5 h, 1200 °C for 12 h and then 1300 °C for 12 h in air. The resulting zirconium niobium phosphate was pelletized and the pellets were sintered at 1300 °C for 12 h in air.
13 Electrical conductivity measurements were performed by an ac and a dc method, using the sintered ceramic pellet with two platinum electrodes. The ac conductivity measurements were done by an ac complex impedance method with Hewlett Packard precision LCR meter (4192A). Before the ac conductivity measurements, the pellets were pre-electrolyzed several times to remove the lower valent cation species which may exist in the starting materials as impurities and which may interfere the value of the conductivity. The termination of the pre-electrolysis was assured by ensuring the equivalent conductivity value before and after the electrolysis.
14 The oxygen pressure from 10^2 to 10^5 Pa and at 10^{-11} Pa were controlled by mixing Air–N_2 in an appropriate ratio or by using CO_2 gas.
15 The polarization measurements were carried out by passing the dc current of 1 μA between the two platinum electrodes sandwiching the pellet and the voltage was monitored as a function of time in oxygen (Po_2: 10^5 Pa) and in nitrogen (Po_2: 50 Pa).
16 Wet air atmosphere(3.1 vol%) was prepared by using a water vapor saturated air at 25 °C.
17 The dc electrolysis was carried out for the pre-electrolyzed pellet at 700 °C, 3 V for 21 days in air. The cathodic surface of the samples was analyzed by electron probe micro analysis (EPMA-1500, Shimadzu) after the electrolysis.