

CHEMISTRY OF MATERIALS

VOLUME 14, NUMBER 11

NOVEMBER 2002

© Copyright 2002 by the American Chemical Society

Communications

Extraordinary High Trivalent Al^{3+} Ion Conduction in Solids

Nobuhito Imanaka,* Yasunori Hasegawa, Misato Yamaguchi, Masaharu Itaya, Shinji Tamura, and Gin-ya Adachi

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

Received June 14, 2002

Revised Manuscript Received September 12, 2002

Solid electrolytes are one of the functional materials practically applied in industries, and their outstanding feature is that only a single ion species can migrate in the solid.^{1–3} Until recently most of the migrating ion species had been limited to only mono or divalent ions. In regard to trivalent ions, Al^{3+} ,⁴ In^{3+} ,⁵ and also rare earth ions^{6–10} have been just recently (since 1995) demonstrated to migrate macroscopically in solids. Among the trivalent cations, one of the most useful and commonly known ions in industries, and greatly ex-

pected to be applied soon, is the common metal ion of Al^{3+} , whose element has been widely applied such as a structural constituent and for beverage cans, etc. However, the trivalent Al^{3+} ion conductivity of the solid electrolyte first reported by us with $\text{Al}_2(\text{WO}_4)_3$ is as low as $3.2 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 600°C ,⁴ which is appreciably below the practical application range ($>10^{-3} \text{ S} \cdot \text{cm}^{-1}$) in comparison with the commercially available solid electrolytes of divalent ion series such as oxide anion conductors of yttria-stabilized zirconia (YSZ)¹¹ and calcia-stabilized zirconia (CSZ),¹¹ etc. For the purpose of realizing a reasonably high Al^{3+} ion conducting solid electrolyte whose ion conductivity reaches the region such as that of the typical divalent oxide (O^{2-}) ion series, the NASICON structure¹² which is an ideal structure, is selected because the structure is composed of three-dimensional ion pass ways suitable for such a bulky ion species. In addition, because the target migrating ion species is a trivalent Al^{3+} ion, the solid electrolyte should contain elements whose valency states are higher than the valency of the migrating ion (in this case, a trivalent state) to make a stronger electrostatic interaction with the counter lattice constituent anions such as O^{2-} and to realize the macroscopic Al^{3+} cation conduction in solids. In our previous studies^{13,14} we focused on the NASICON-type structure, for the above reason, and the $\text{M}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ series has been systematically prepared.

During the course of the preparation of the $\text{M}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ series, the synthesis of $\text{Al}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ was also examined. However, it was not successful because the Al^{3+} ion size (0.0675 nm)¹⁵ is too small to hold the

* Corresponding author. Telephone: +81-6-6879-7353. Fax: +81-6-6879-7354. E-mail: imanaka@chem.eng.osaka-u.ac.jp.

(1) Kudo, T.; Fueki, K. *Solid State Ionics*, Kodansha: Tokyo, 1990.

(2) Bruce, P. G. *Solid State Electrochemistry*, Cambridge University Press: Cambridge, 1995.

(3) Gellings, P. J.; Bouwmeester, H. J. M. *The CRC Handbook of Solid State Electrochemistry*, CRC Press: Boca Raton, FL, 1997.

(4) Kobayashi, Y.; Egawa, T.; Tamura, S.; Imanaka, N.; Adachi, G. *Chem. Mater.* **1997**, *9*, 1649.

(5) Köhler, J.; Imanaka, N.; Adachi, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1890.

(6) Imanaka, N.; Kobayashi, Y.; Fujiwara, K.; Asano, T.; Okazaki, Y.; Adachi, G. *Chem. Mater.* **1998**, *10*, 2006.

(7) Tamura, S.; Egawa, T.; Okazaki, Y.; Kobayashi, Y.; Imanaka, N.; Adachi, G. *Chem. Mater.* **1998**, *10*, 1958.

(8) Imanaka, N.; Hiraiwa, M.; Tamura, S.; Adachi, G.; Dabkowska, H.; Dabkowski, A.; Greedan, J. E. *Chem. Mater.* **1998**, *10*, 2542.

(9) Köhler, J.; Imanaka, N.; Adachi, G. *Chem. Mater.* **1998**, *10*, 3790.

(10) Imanaka, N.; Ueda, T.; Okazaki, Y.; Tamura, S.; Adachi, G. *Chem. Mater.* **2000**, *12*, 1910.

(11) Strickler, D. W.; Carlson, W. G. *J. Am. Ceram. Soc.* **1964**, *47*, 122.

(12) Goodenough, J. B.; Hong, H. Y. P.; Kafalas, J. A. *Mater. Res. Bull.* **1976**, *11*, 203.

(13) Tamura, S.; Imanaka, N.; Adachi, G. *Adv. Mater.* **1999**, *11*, 1521.

(14) Tamura, S.; Imanaka, N.; Adachi, G. *J. Alloys Cmpd.* **2001**, *323–324*, 540.

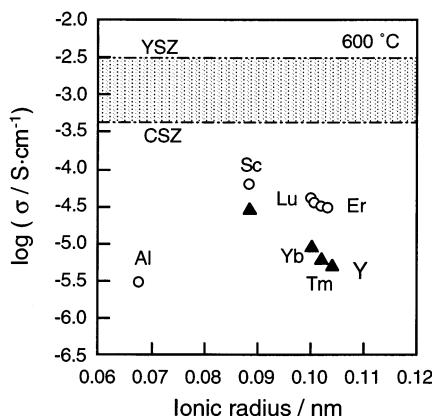


Figure 1. Trivalent ion conductivity at 600 °C for the M_2 (WO₄)₃ type and the $M_{1/3}$ Zr₂(PO₄)₃ type series (M = Al, Sc, Lu, Yb, Tm, or Er; M = Sc, Yb, Tm, or Y).

M_{1/3}Zr₂(PO₄)₃ type NASICON lattice structure. Here, for the purpose of realizing the formation of the NASICON structure with aluminum zirconium phosphate based series, the smaller pentavalent Nb cation (0.078 nm)¹⁵ was doped to partially replace the Zr⁴⁺ (0.086 nm)¹⁵ site in the M_{1/3}Zr₂(PO₄)₃ NASICON framework to shrink the NASICON crystal lattice to stabilize the NASICON structure.

In this communication, a new trivalent Al³⁺ ion conductor of (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ with the NASICON-type structure was successfully realized by applying pentavalent Nb⁵⁺ ion in addition to tetravalent Zr⁴⁺ and pentavalent P⁵⁺ ions as the constituent cations whose ion valencies are higher than trivalent state and tightly bond to counteranions of oxide anions, and an extraordinary high trivalent Al³⁺ ion conductivity which lies in the practical application region was intentionally achieved in solids.

The starting materials of Al(OH)₃, ZrO₂, Nb₂O₅, and (NH₄)₂HPO₄ were mixed in a stoichiometric ratio and then mixed in an agate mortar. The pulverized powder was pelletized and heated at 1000 °C for 12 h, 1200 °C for 12 h, and then 1300 °C for 12 h in air. The obtained (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ powder was made into pellets and sintered at 1300 °C for 12 h in air.

Platinum was sputtered on both center surfaces of the pellet as the electrode. The ac conductivity (σ_{ac}) was measured by a complex impedance method with the Precision LCR meter (Hewlett-Packard) in the frequency range from 20 Hz to 1 MHz at the temperature region from 300 to 600 °C in air. The dc conductivity (σ_{dc}) was obtained from the voltage generated by passing the dc current of 1 μ A between the two platinum electrodes sandwiching the pellet. The polarization behavior was measured by investigating the time dependence of the σ_{dc}/σ_{ac} ratio in air. The electrolysis was carried out by applying a dc voltage of 3 V at 800 °C for 240 h for the purpose of determining the conducting species, and the investigation of the cathodic surface of the pellet after the electrolysis was performed by SEM (SEM, S-800, Hitachi) and EPMA (EPMA-1500, Shimadzu). The experiment details were described in our previous papers.⁶⁻⁸

Figure 1 shows the trivalent ion conductivity at 600 °C for the Sc₂(WO₄)₃ type and the M_{1/3}Zr₂(PO₄)₃ type

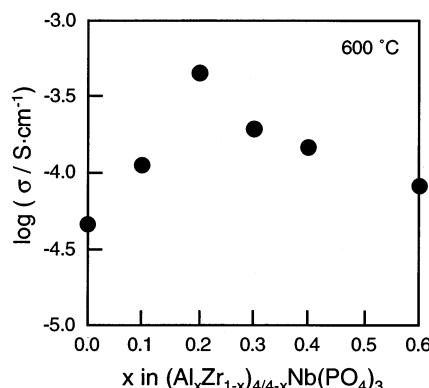


Figure 2. Al³⁺ ion conductivity changes with the Al content for (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃.

series. With the decrease in the ionic radius of migrating trivalent cations, the ion conductivity increases and shows the highest value in the case of Sc³⁺(0.0885 nm)¹⁵ ion in both series. However, the trivalent ion conductivity is still appreciably lower than 10⁻⁴ S·cm⁻¹ at 600 °C and the trivalent ion conducting solid electrolyte whose ion conductivity is comparable to that of the commercially produced stabilized zirconias (shaded area) such as YSZ¹¹ and CSZ¹¹ is strongly requested. In the case for Al³⁺, the Al₂(WO₄)₃ solids show a considerable low ion conductivity and the ionic size of Al³⁺ is too small to form the NASICON-type Al_{1/3}Zr₂(PO₄)₃ phase as described above for the M_{1/3}Zr₂(PO₄)₃ series.

The relationship between the electrical conductivity and the Al content in (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ is presented in Figure 2. The highest Al³⁺ ion conductivity was obtained for (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ among the (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ series with the NASICON-type structure (The demonstration of the Al³⁺ ion conduction in (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ is described below). From the X-ray powder diffraction measurements, the NASICON type (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ single phase was obtained only for the (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ series of $x = 0.1$ and 0.2 , and the (Al_xZr_{1-x})_{4/(4-x)}Nb(PO₄)₃ series with x higher than 0.3 is in a two-phase mixture of the NASICON phase and NbPO₅. This NbPO₅ formation as the secondary phase appreciably decreases the conductivity.

The temperature dependence of the trivalent ion conductivity of (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ is depicted in Figure 3 with the data of the Al³⁺ ion conducting Al₂(WO₄)₃ with the Sc₂(WO₄)₃ type structure reported before by us.⁴ The conductivity data for Sc₂(WO₄)₃ and Sc_{1/3}Zr₂(PO₄)₃, which show the optimum ion conductivity among the series introduced in Figure 1, are also plotted. The Al³⁺ ion conductivity considerably enhances more than 2 orders of magnitude compared with those of the Al³⁺ ion conducting Al₂(WO₄)₃ solid electrolyte. The Al³⁺ ion conductivity of (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ exceeds more than 1 order of magnitude in comparison to the similar phosphate-based Sc_{1/3}Zr₂(PO₄)₃ electrolyte which possess the optimum trivalent ion conductivity among the NASICON-type M_{1/3}Zr₂(PO₄)₃ series, and the Al³⁺ ion conductivity of (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ reaches the region of the typical oxide anion conductor series of YSZ¹¹ and CSZ¹¹.

The dc electrolysis was carried out by applying the dc voltage of 3 V, which is higher than the decomposition

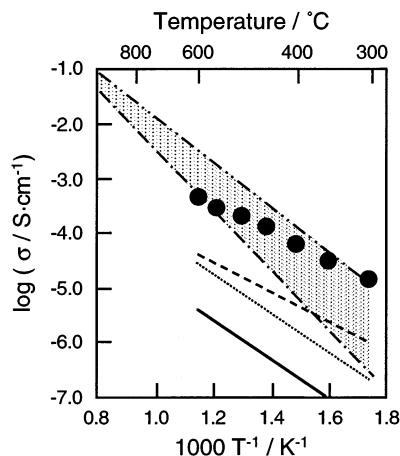


Figure 3. Temperature dependence of the Al^{3+} ion conductivity of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ (●) with the data of the Al^{3+} ion conducting $\text{Al}_2(\text{WO}_4)_3$ with the $\text{Sc}_2(\text{WO}_4)_3$ type structure (—) and the data for $\text{Sc}_2(\text{WO}_4)_3$ (---) and $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (···) which show the optimum trivalent ion conductivity among the series. The similar data for YSZ (···) and CSZ (···) are also plotted.

Table 1. Results of EPMA Spot Analyses on the Cathodic Surface Deposits after Electrolysis

element	before	atomic percent		
		after		
		cathode (area 1)	cathode (area 2)	cathode (area 3)
Al	4.1	88.8	82.6	81.3
Zr	16.7	0.2	0.2	0.4
Nb	19.8	6.1	7.8	11.2
P	59.4	4.9	9.4	7.1

voltage (ca. 1 V) of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$. After the electrolysis, precipitations were clearly observed on the cathodic surface. The EPMA spot analysis of the deposits was conducted and the results are listed in Table 1. Among the constituent elements, a considerable high Al segregation was clearly observed, and the Al content is more than 20 times that of the Al content before the electrolysis. In contrast, the other elements of Zr, Nb, and P appreciably decreased. The line EPMA measurements were also carried out for the electrolyzed pellet and the results are depicted in Figure 4. A high Al segregation was observed near the cathodic surface (shaded area), but no such segregation was recognized for Zr, Nb, or P. In addition, from the polarization analysis, the σ_{dc}/σ_{ac} ratio reduced less than 0.002 both in air and in helium, and it can be concluded that the

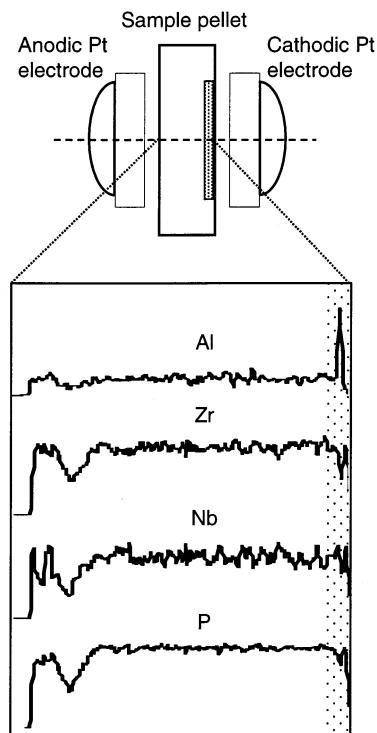


Figure 4. Results of the line EPMA measurements for the electrolyzed $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ pellet.

ion transference number is estimated to be higher than 0.998. From the results mentioned above, it becomes clear that the predominant migrating species in $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ is only the trivalent Al^{3+} ion.

In summary, an extraordinary high Al^{3+} ion conducting solid electrolyte was realized by successfully stabilizing the NASICON-type structure which has a suitable three-dimensional Al^{3+} ion pass way by applying not only Zr^{4+} and P^{5+} , but also Nb^{5+} , as another lattice constituent element. The Al^{3+} ion conductivity enhances more than 2 orders of magnitude in comparison with the Al^{3+} ion conducting $\text{Al}_2(\text{WO}_4)_3$ solid electrolyte reported so far. Because the Al^{3+} ion conductivity of the present solid electrolyte reaches the ion conductivity region of the well-known and commercially available oxide anion conducting solids, practical applications of the present Al^{3+} ion conducting $(\text{Al}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid for functional materials such as chemical sensors, rechargeable batteries, etc., are greatly expected.

CM020667F