

Tetravalent Ion(Zr^{4+}) Conduction in Solids

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Tetravalent Zr^{4+} ion was directly demonstrated to migrate in zirconium oxide phosphate($Zr_2O(PO_4)_2$) solid in which pentavalent phosphorus ion forms PO_4^{3-} unit with bonding strongly to counter four oxygen ions, resulting in a released circumstance for the rest of the constituent tetravalent ion, Zr^{4+} , to migrate.

The ionic conduction of mono- or divalent ions in solids has been commonly encountered in the material science field, and some of these solid electrolytes have been already put on the market in a biomedical and industrial field.¹ In contrast, a trivalent cation had been considered to be extremely poor a migrant in solids because of its high electrostatic interaction with the surrounding structure of anions. For trivalent ion species, R^{3+} - β -Alumina²⁻⁴ ionically substituted for trivalent ions(R^{3+}) and β - $LaNb_3O_9$ ⁵ have been reported to be trivalent ion conductors from their electrical conducting behaviors. However, in both cases, any identification of the trivalent ion migration in solids was not performed at all. In 1995, Sc^{3+} ion in $Sc_2(WO_4)_3$ ⁶ was firstly demonstrated to be conducting in solid and in these years, various types of trivalent ions have been shown to migrate in solids⁷⁻¹¹ such as the quasi-layered $Sc_2(WO_4)_3$ -type structure series. The next forthcoming target is "tetravalent ion migrates in solids or not". Here, the ionic conduction of tetravalent Zr^{4+} ion was directly demonstrated in solids for the first time.¹²

The temperature dependencies of the electrical conductivity of the zirconium oxide phosphate($Zr_2O(PO_4)_2$) solid¹³ is shown in Figure 1 with the data of typical multivalent ion conductors.

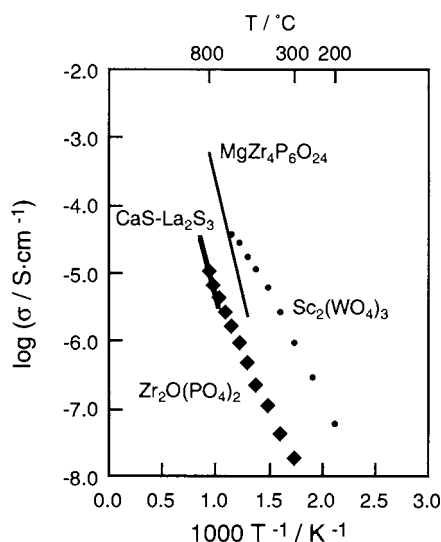


Figure 1. The temperature dependencies of the electrical conductivity of $Zr_2O(PO_4)_2$ (◆) with the data of divalent ion (Mg^{2+} ¹⁴ (thin solid), Ca^{2+} ¹⁵ (thick solid)) and trivalent ion (Sc^{3+})¹⁰ (●) conductors.

In comparison to divalent(Mg^{2+})¹⁴ and trivalent(Sc^{3+})¹⁰ ion conducting characteristics, the conductivity of $Zr_2O(PO_4)_2$ is lower than those of them, probably due to its higher valency state. However, the conductivity is similar to that of the Ca^{2+} ion conducting sulfide,¹⁵ indicating that a comparable high conductivity is obtained for zirconium oxide phosphate solid.

From the measurements of the electrical conductivity dependencies on the oxygen pressure for $Zr_2O(PO_4)_2$, the conductivity was found to be constant in the wide partial pressure range from 10^{-8} Pa to 10^5 Pa,¹⁶ showing that any hole or electron conduction does not appear in the above mentioned oxygen pressure region. In addition, polarization measurements¹⁷ were also conducted by measuring the time dependencies of the dc to ac conductivity ratio(σ_{dc}/σ_{ac}) in oxygen(P_{O_2} : 10^5 Pa) and helium(P_{O_2} :4 Pa) atmospheres. Because an abrupt decrease in the ratio was observed in both atmospheres, oxide ion conduction in the zirconium oxide phosphate solid is excluded as demonstrated in our previous paper.⁸ The proton (H^+) conduction was also denied by the fact that the similar polarization phenomenon was observed for the σ_{dc}/σ_{ac} ratio in both dry and wet(H_2O : 3.1 vol%) air. Therefore, the mobile species in the zirconium oxide phosphate is limited only to the cationic species of Zr^{4+} or P^{5+} .

For the purpose of directly identifying the migrating cation species, a dc electrolysis¹⁸ was carried out by sandwiching the oxide phosphate between two platinum electrodes as shown in Figure 2a. After the electrolysis, the deposits were clearly observed on the cathodic surface (shade part in Figure 2a) by mapping the electrolyte surface from the electron probe micro-analysis (EPMA). The Zr/P ratio in the deposit was found to be 14.8 by EPMA, while the ratio for $Zr_2O(PO_4)_2$ without electrolysis is 1.01, indicating a predominant element in the deposit is Zr and not P. Furthermore, from the X-ray powder diffraction analysis of the cathodic surface of the oxide phosphate (Figure 2b), ZrO_2 (★) was definitely identified in addition to the mother $Zr_2O(PO_4)_2$ phase (○). In contrast, on the anodic surface of the electrolyte, any ZrO_2 deposition was not observed at all. The phenomena described above clearly suggest that Zr^{4+} ion, which is discharged at the cathode to form the ZrO_2 deposit.

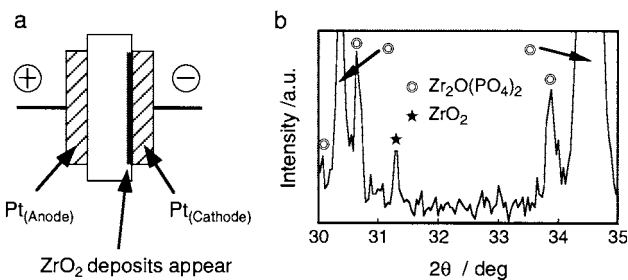


Figure 2. The dc electrolysis setup(Figure 2a) and the X-ray diffraction result(Figure 2b) on the cathodic surface(shade part in Figure 2a) of the electrolyte after electrolysis.

In order to definitely identify the macroscopic ion migration in the oxide phosphate solid, we constructed a test cell consisting of three electrolyte pellets of zirconium oxide phosphate (named A, B, and C from anodic side, middle, and cathodic side, respectively) and two Pt electrodes in a similar manner to that shown in Figure 2a. The weight change of the three pellets after the electrolyses is tabulated in Table 1. The weight of tablet C, which is

Table 1. The changes in weight after the electrolysis¹⁹

Tablet	Change in weight of tablet / mg	
	Run 1	Run 2
C + Pt (Cathode)	+0.371(32.2%)	+0.814(32.2 %)
B	- 0.167	- 0.162
A + Pt (Anode)	- 0.317(27.5 %)	- 0.861(34.1 %)

located to the cathode side, increases while similar weight loss is observed in tablet A (Runs 1 and 2). The weight change percentage calculated from the total coulomb current on the assumption that the deposit is ZrO_2 is presented in parenthesis. The lower Zr^{4+} ion transference number might be ascribed to the appearance of a leak current due to the considerable low ion conductivity. However, the detail is under investigation. Tablet B shows little weight change (± 0.02 wt%). The weight of tablet C (cathode side, C + Pt) increases while that of tablet A (anode side, A + Pt) decreases by a similar amount to that in (C + Pt). Such macroscopic mass changes clearly indicate that Zr^{4+} ions migrate from the anode side to the Pt cathode to deposit ZrO_2 by the discharge reaction ($Zr^{4+} + 4e^- + O_2 = ZrO_2$). Hence, it is confirmed that $Zr_2O(PO_4)_2$ is a Zr^{4+} conductor.

The fact that "*tetravalent ion really migrates in solids*" seems to be an extraordinary phenomenon at the first glance. However, by strictly selecting the constituent elements from the consideration of their valencies and by choosing the component of the material from their stability, "*tetravalent ion migration in solid*" is clearly demonstrated for the first time. Tetravalent ion conduction in solids expands migrating ion species in addition to mono-, di-, and also trivalent states and this constitutes a unique way of obtaining new advanced characteristics applicable for Materials Chemistry.

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- 12 The most important issue to be kept in mind for the realization of the tetravalent ion conduction is to exclude the mobile mono-, di-, and also trivalent ion species from the candidate solid component. In addition, the solid material should be stable enough and any ion species which exists in solid, should not be reduced to a lower valence state because the reduction causes the electron conduction at the operating temperature and its ion conducting properties were greatly inhibited by the reduction. However, the above two criteria are not still satisfactory. The additional tactics for the realization of the tetravalent ion conduction is that solids must contain the cation species whose valency is higher than tetravalent state to make the tetravalent ions migrate in solids. Here, as the mobile tetravalent ion candidate, Zr^{4+} , was selected, since the stability of the oxide has been already guaranteed as stabilized zirconia in various material science fields (e.g., sensors), and as the higher valent cation in comparison to tetravalent Zr^{4+} , pentavalent P^{5+} was chosen since the phosphate is also very stable in various atmospheres. Phosphorus which holds a pentavalent state works as the host ion to strongly bond the counter oxide(O^{2-}) ions, as a result, the tetravalent zirconium ions are expected to be left in such a circumstance to migrate smoothly in solid. The material obtained from zirconium oxide and phosphate is zirconium oxide phosphate ($Zr_2O(PO_4)_2$) and the oxide phosphate was chosen as the candidate for the tetravalent ion conducting solid electrolyte.
- 13 Zirconium oxide and ammonium dihydrogenphosphate, or diammonium hydrogenphosphate were mixed in a stoichiometric ratio. The mixture was firstly heated at 1000 °C for 12 h and then 1400 °C for 12 h in air. The resulting zirconium oxide phosphate was pelletized and the pellets were heated at 1400 °C for 12 h in air (Relative density 98.7%). The obtained white samples were identified by X-ray powder diffraction analysis(Mac Science M18XHF diffractometer) using Cu-K α radiation. Electrical conductivity measurements were carried out by an ac and a dc method, using the sintered ceramic pellet with two platinum plate and net electrodes, respectively in the temperature between 300 and 800 °C. The ac conductivity was measured by an ac complex impedance method in the frequency range from 5 Hz to 13 MHz with Hewlett Packard precision LCR meter (4192A).
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- 16 The oxygen pressure of 10^2 to 10^5 Pa and 10^{-8} Pa were controlled by mixing Air-N $_2$ in an appropriate ratio or by using CO $_2$.
- 17 The polarization measurements were performed by passing the dc current of 1 μ A between the two platinum electrodes sandwiching the pellet and the voltage generated was monitored as a function of time in oxygen (P_{O_2} : 10^5 Pa) and in helium (P_{O_2} : 4 Pa).
- 18 The dc electrolysis was done at 800 °C in air for 17 days. The applied voltage was 8 V, which was higher than the decomposition voltage of 5.5 V for $Zr_2O(PO_4)_2$ determined from the I-V characteristics. After the electrolysis, the cathodic surface of the sample was analyzed by scanning electron microscope (SEM, S-800, Hitachi), and electron probe microanalysis (EPMA-1500, Shimadzu).
- 19 The electrolyses of Runs 1 and 2 were carried out at 800 °C with 18 V for 34 days and at 1000 °C with 18 V for 11 days in air, respectively. In addition, monovalent sodium ion which is a typical impurity appearing in starting materials was intentionally mixed with the zirconium oxide phosphate to investigate the possible migration of Na $^+$ impurity in zirconium oxide phosphate. After the $Zr_2O(PO_4)_2$ electrolysis with Na $_2$ O in 1 mol%, NASICON($NaZr_2(P_2O_7)_3$) deposits were clearly observed, indicating that the present $Zr_2O(PO_4)_2$ does not contain any sodium species because of no peak identified to the NASICON phase on the surface of the pellet (shade part in Figure 2a).