

Tetravalent Tellurium Ion Conducting Solid Electrolyte
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In the solid electrolyte field, while the cations whose valence states are less than +4 are widely reported for the migrating cation species in solids, the tetravalent cations are regarded as an extremely poor conducting species due to the high electrostatic interaction between the tetravalent cation and the surrounding anion species. Recently, although we have succeeded in developing some solid electrolytes whose conducting tetravalent cations are Zr^{4+} [1, 2], Hf^{4+} [3], Ti^{4+} [4], Ge^{4+} [5], and Sn^{4+} [6] by selecting the three-dimensional skeleton network with a NASICON-type structure, other tetravalent cations are not demonstrated to conduct in solids yet.

In this study, we focused on tellurium ion (Te^{4+}) as a new candidate for the conducting tetravalent cation species in solids, and we successfully demonstrated a tetravalent Te^{4+} ion conduction in the α - Te_2MoO_7 solid with two-dimensional layered structure [7].

α - Te_2MoO_7 solid was synthesized by a conventional solid-state reaction method. TeO_2 and MoO_3 powders were mixed in a molar ratio of 1.8:1 by using a planetary ball milling apparatus (Pulverisette 7, FRITTSCH GmbH) at a rotation speed of 300 rpm for 3 h. The mixture was pressed into a pellet form and calcined at 500 °C for 12 h in synthetic air. After identifying the sample obtained by XRD analysis, the sample powder was pressed into a pellet and sintered at 500 °C for 12 h in air. The AC conductivity of the sintered sample pellet was measured by a complex impedance method in the frequency region from 5 to 13M Hz (precision LCR meter 4192A, Hewlett Packard) at temperatures between 300 °C and 530 °C in the air atmosphere. For identifying the Te^{4+} ion migration in the α - Te_2MoO_7 solid, the modified Tubandt electrolysis of the sintered α - Te_2MoO_7 pellets was carried out by applying a DC voltage of 4 V between ion-blocking Pt bulk electrodes at 400 °C for 7 days in the air atmosphere.

From the XRD analysis of the prepared sample, it was confirmed that the sample possessed a crystalline α -phase. Figure 1 shows the temperature dependence of the electrical conductivity for the α - Te_2MoO_7 solid on heating with the corresponding data for typical solid electrolytes. The conductivity of the α - Te_2MoO_7 solid above 500 °C was higher than that of both O^{2-} ion conducting yttria-stabilized zirconia (YSZ), which has been utilized for practically applications in automotive oxygen sensing devices, and Zr^{4+} conducting $Zr_{39/40}TaP_{2.9}W_{0.1}O_{12}$ solid [2], which has the highest conductivity among the tetravalent ion conductors. Furthermore, the conductivity of the α - Te_2MoO_7 solid at 530 °C reached the minimum threshold value of $10^{-2} S \cdot cm^{-1}$ required for practical applications.

In order to directly demonstrate the Te^{4+} ion migration in the α - Te_2MoO_7 solid, modified Tubandt DC electrolysis was performed by sandwiching three sintered sample pellets between ion-blocking Pt electrodes. The observed mass changes for the pellets are tabulated in Table 1 along with the theoretical changes calculated from the current flow through the samples. The actual mass changes observed in anodic pellet (A) and cathodic pellet (C) are almost identical to the theoretical ones estimated by considering Te^{4+} ion migration. Furthermore, we have also confirmed an increase and a decrease in Te concentration in the cathodic and anodic pellets, respectively, by X-ray fluorescence analysis. These

results in which Te concentration changes along with theoretical mass changes were observed, strongly indicate that the conducting species in the α - Te_2MoO_7 solid is only tetravalent Te^{4+} ions.

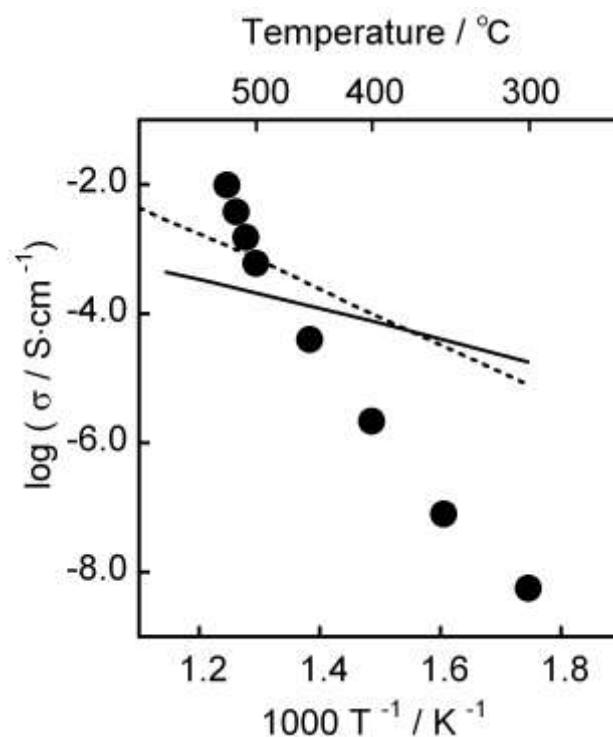


Figure 1. Temperature dependence of the electrical conductivity for the α - Te_2MoO_7 solid (●) on heating with the corresponding data for typical solid electrolytes of divalent O^{2-} ion conducting yttria stabilized zirconia (---) and tetravalent Zr^{4+} ion conducting $Zr_{39/40}TaP_{2.9}W_{0.1}O_{12}$ (-).

Table 1. Mass changes measured for three α - Te_2MoO_7 pellets after modified Tubandt electrolysis performed by applying a DC voltage of 4 V at 400 °C for 7 days.

Sample	Observed weight change (mg)	Calculated weight change (mg)		
		Charge carrier		
		Te^{4+}	Mo^{6+}	O^{2-}
Anodic pellet (A)	-0.0925	-0.0946	-0.0569	0
Middle pellet (B)	-0.0008	0	0	0
Cathodic pellet (C)	+0.0929	+0.0946	+0.0569	0

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