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ELECTRICAL CONDUCTIVITY AND PHASE DIAGRAM STUDIES OF
SOME SOLID ELECTROLYTES BASED ON Li_2SO_4 AND Na_2SO_4

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ELECTRICAL CONDUCTIVITY AND PHASE DIAGRAM STUDIES OF SOME

SOLID ELECTROLYTES BASED ON Li_2SO_4 AND Na_2SO_4

by

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ABSTRACT

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Electrical conductivity of the $\text{Li}_2\text{SO}_4 - \text{CaSO}_4$, $\text{Li}_2\text{SO}_4 - \text{CaSO}_4$ eutectic + Al_2O_3 , $\text{Li}_2\text{SO}_4 - \text{Li}_2\text{WO}_4$, $\text{Na}_2\text{SO}_4 - \text{CaSO}_4$, $\text{Na}_2\text{SO}_4 - \text{MgSO}_4$, $\text{Na}_2\text{SO}_4 - \text{Na}_2\text{SeO}_4$ and the $\text{Na}_2\text{SO}_4 - \text{Li}_2\text{SO}_4 - \text{CaSO}_4$ systems have been measured using ac impedance technique. Phase diagrams of the $\text{Na}_2\text{SO}_4 - \text{CaSO}_4$ and the $\text{Na}_2\text{SO}_4 - \text{MgSO}_4$ systems have been determined in detail using the differential scanning calorimetry and the high temperature powder X-ray diffraction.

In the $\text{Li}_2\text{SO}_4 - \text{CaSO}_4$ system, the eutectic composition which is at 17.5 mol% CaSO_4 shows the maximum conductivity, e.g. $2.1 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 500°C . When Al_2O_3 was added to the eutectic mixture of $\text{Li}_2\text{SO}_4 - \text{CaSO}_4$, a further enhancement of conductivity could be seen and the maximum was observed for 40 mol% Al_2O_3 . The conductivity enhancement of the eutectic mixture is attributed to the composite effect due to the maximum grain boundary area in the eutectic mixture and the additional conductivity enhancement is attributed to the increased interfacial area due to the presence of Al_2O_3 grains.

In the $\text{Li}_2\text{SO}_4 - \text{Li}_2\text{WO}_4$ system, two conductivity maxima have been observed below 500°C . They were at about 34 and 70 mol% Li_2WO_4 . The first maximum is due to the composite effect, and the second one is due to the partial replacement of WO_4^{2-} with SO_4^{2-} creating more interstitial sites. The high ionic conductivity of $\alpha\text{-Li}_2\text{SO}_4$ has been

explained by the paddle-wheel mechanism in which the cationic mobility is enhanced by the coupled rotation of translationally static SO_4^{2-} ions. Replacement of SO_4^{2-} by larger WO_4^{2-} ions has shown a conductivity drop within the solid solubility region of α -phase. This is a strong experimental evidence for the proposed paddle-wheel mechanism of ion transport in $\alpha\text{-Li}_2\text{SO}_4$.

In the $\text{Na}_2\text{SO}_4\text{-CaSO}_4$ system, two intermediate compounds have been observed at 7.7 and 33 mol% CaSO_4 . The solid solubility of the $\text{Na}_2\text{SO}_4(\text{I})$ phase extends up to 40 mol% CaSO_4 at 915°C . The electrical conductivity of this solid solution increases rapidly with increasing CaSO_4 content and reaches a maximum at about 5 mol% CaSO_4 and the maximum conductivity at 300°C is $3.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$. In the $\text{Na}_2\text{SO}_4\text{-MgSO}_4$ system, $\text{Na}_2\text{Mg}(\text{SO}_4)_2$ and $\text{Na}_2\text{Mg}_3(\text{SO}_4)_4$ have been identified as intermediate compounds. The solid solution of the $\text{Na}_2\text{SO}_4(\text{I})$ phase is stable up to 35 mol% MgSO_4 at 680°C . The electrical conductivity of this solid solution increases rapidly with increasing MgSO_4 content and reaches the maximum at 20 mol% MgSO_4 . The maximum conductivity is about $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 520°C . In both these systems, the conductivity maxima can be explained by the formation of clusters and defect interactions at high vacancy concentration.

In the $\text{Na}_2\text{SO}_4\text{-Na}_2\text{SeO}_4$ system, the conductivity up to 30 mol% Na_2SeO_4 has been studied and the conductivity enhancement observed is very small compared to the enhancement due to the cation substitution in Na_2SO_4 . The conductivity enhancement can be attributed to the lattice expansion due to the replacement of smaller SO_4^{2-} by larger SeO_4^{2-} in the solid solubility region.

In the $\text{Na}_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-CaSO}_4$ ternary system, the highest conductivity is observed for the composition $\text{Na}_{1.6}\text{Li}_{0.2}\text{Ca}_{0.1}\text{SO}_4$ which has the Na_2SO_4

(I) structure, and the conductivity of this composition is $1.0 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 350°C . The conductivity enhancement observed in this system is possibly caused by the creation of more vacancies due to Ca^{2+} substitution combined with high Li^+ ion mobility.

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