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

Electrical conductivity of the Li_2SO_4 - $CaSO_4$, Li_2SO_4 - $CaSO_4$ eutectic + Al_2O_3, Li_2SO_4 - Li_2WO_4, Na_2SO_4 - $CaSO_4$, Na_2SO_4 - $MgSO_4$, Na_2SO_4 - Na_2SeO_4 and the Na_2SO_4 - Li_2SO_4 - $CaSO_4$ systems have been measured using ac impedance technique. Phase diagrams of the Na_2SO_4-$CaSO_4$ and the Na_2SO_4-$MgSO_4$ systems have been determined in detail using the differential scanning calorimetry and the high temperature powder X-ray diffraction.

In the Li_2SO_4-$CaSO_4$ system, the eutectic composition which is at 17.5 mol% $CaSO_4$ shows the maximum conductivity, e.g. $2.1x10^{-3}$ $\Omega^{-1}cm^{-1}$ at 500°C. When Al_2O_3 was added to the eutectic mixture of Li_2SO_4-$CaSO_4$, 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 Li_2SO_4-Li_2WO_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 α-Li_2SO_4 has been

explained by the paddle-wheel mechanism in which the cationic mobility is enhanced by the coupled rotation of translationaly 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 evidance for the proposed paddel-wheel mechanism of ion transport in α-Li_2SO_4.

In the Na_2SO_4-$CaSO_4$ system, two intermediate compounds have been observed at 7.7 and 33 mol% $CaSO_4$. The solid solubility of the Na_2SO_4(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 $3.5 \times 10^{-3}\ \Omega^{-1}cm^{-1}$. In the Na_2SO_4-$MgSO_4$ system, $Na_2Mg(SO_4)_2$ and $Na_2Mg_3(SO_4)_4$ have been identified as intermediate compounds. The solid solution of the Na_2SO_4(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 $2 \times 10^{-2}\ \Omega^{-1}cm^{-1}$ 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 Na_2SO_4-Na_2SeO_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 Na_2SO_4-Li_2SO_4-$CaSO_4$ ternary system, the highest conductivity is observed for the composition $Na_{1.6}Li_{0.2}Ca_{0.1}SO_4$ which has the Na_2SO_4

(I) structure, and the conductivity of this composition is 1.0×10^{-2} $\Omega^{-1}cm^{-1}$ 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.