ELECTRICAL CONDUCTIVITY OF THE $Li_{0.22}Na_{1.33}Zn_{0.22}SO_4$ SOLID ELECTRLYTE

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Pure Li_2SO_4 and certain compositions of the binary systems of Li_2SO_4 such as $LiNaSO_4$, $LiAgSO_4$ and $Li_{1.33}Zn_{0.33}SO_4$ are very good solid electrolytes with ionic conductivities of the order of 1 $ohm^{-1}cm^{-1}$ above their solid-solid phase transition temperatures (1). In an attempt to discover further high conducting phase, Bjorn Heed investigated the ternary system of li_2SO_4, Na_2SO_4 and $ZnSO_4$, using a quick conductivity scanning method, and found that the eutectoid composition corresponding to $Li_{0.22}Na_{1.33}Zn_{0.22}SO_4$ to have a stable conducting phase above 325^oC (2). Accurate conductivity values for this phase were not reported by Heed.

Proper conductivity measurements on this $Li_{0.22}Na_{1.33}Zn_{0.22}$ composition over a wide temperature range revealed that the solid-solid electrolyte phase transition occurs between 330^oC and 335^oC and the high conducting solid electrolyte phase extends upto 560^oC. In the sold electrolyte phase the conductivity ranges from 0.01 to 0.25 $ohm^{-1}cm^{-1}$ with an activation energy of 0.54 eV.

An X-ray diffraction study has shown that this solid electrolyte phase is identical to that of the high temperature hexagonal phase of Na_2SO_4. This is reasonable because the composition contains 67 mole percent of Na_2SO_4 and the solubility of mono and divalent cations is large in the high temperature phase of Na_2SO_4 (1). However, the electrical conductivity of this solid electrolyte is much higher than that of pure Na_2SO_4. For example at 400^oC ultra pure Na_2SO_4 has a conductivity of $3.2 \times 10^{-5} ohm^{-1}cm^{-1}$ (3), where as the conductivity of $Li_{0.22}Na_{1.33}Zn_{0.22}SO_4$ is $6.2 \times 10^{-2} ohm^{-1}cm^{-1}$ which corresponds to an enhancement of three orders of magnitude. The observed high conductivity of this solid electrolyte can be attributed to the increased movement of ions due to to the presence of additional vacancies in the structure.

References: 1. Lunden A., Materials for Solid State Batteries, Eds. B.V.R.Chowdri and Radhakrishna S.,World Scientific, Singapore (1986), p149.
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