

E1-04: New Li⁺ ion conductors of LISICON type, Li_{4-2x}Co_xGeO₄, solid solutions

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There is a considerable interest in finding new Li⁺ ion conducting solid electrolytes with potential applications in solid state batteries and other devices. Several studies have been made on Li⁺ ion conductivity in solid solutions based on low conductivity parent phases such as γ -Li₃PO₄ and γ -Li₂ZnGeO₄. These solid solutions contain extra mobile Li⁺ ions in interstitial sites which give rise to high Li⁺ ion conductivity. The first to be discovered in this family, was LISICON or Li₁₄Zn(GeO₄)₄ which is a solid solution in the binary system Li₄GeO₄-Li₂ZnGeO₄. It had high conductivity at high temperatures, e.g. 0.13 Scm⁻¹ at 300°C.

In the present work the structure, phase equilibria and conductivity of the Li₄GeO₄-Li₂CoGeO₄ system are reported. X-ray powder diffraction was used

to establish the solid solution range and complex impedance measurement in the 100 Hz to 10 MHz range to study the conductivity variation with composition and temperature.

A new range of γ -solid solutions with formula $\text{Li}_{4-2x}\text{Co}_x\text{GeO}_4$: $0.2 < x < 0.6$ was found; for $x > 0.6$ a two-phase mixture of γ_{ss} and $\beta\text{-Li}_2\text{CoGeO}_4$ forms, whereas for $x < 0.2$, a range of two phase mixture of Li_4GeO_4 and γ_{ss} forms. The highest conductivity of $1.3 \times 10^{-3} \text{ Scm}^{-1}$ at 300°C was observed for the $x=0.3$ composition, and it was found that the conductivity was very high compared to that of Li_4GeO_4 but still lower than the conductivity of LISICON, $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$.