

## PHASE TRANSITION IN $\text{LiMn}_2\text{O}_4$ DESCRIBED IN TERMS OF BIPOLARONS

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ascribed to the complicated, mixed-valency  
manganospinel structure.

Stoichiometric  $\text{Li}_1\text{Mn}_2\text{O}_4$  spinel exhibits a structural transition at 290 K due to Jahn-Teller distortion of the  $\text{Mn}^{+3}$  ions. The orthorhombic distortion of initial Fd-3m cubic structure is accompanied by simultaneous charge ordering within the manganese sublattice. The phase transition is expected to worsen the properties of the cathode material, but there is no data on the dependence of the phase transition on deintercalation degree  $x$  in the  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ .

Investigations on electrical properties of the  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  ( $0.4 \leq 1-x \leq 1$ ) system together with structural and thermal characterisation at subsequent stages of deintercalation process were undertaken.

Samples were deintercalated in  $\text{Li}/\text{Li}^+/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  cells. Electrical conductivity, thermoelectric power and DSC measurements of deintercalated samples reveal sharp maxima in Seebeck coefficient  $\alpha$ , stepwise changes in the electrical conductivity and corresponding thermal effects on DSC curves. The obtained DSC results indicate also presence of an order-disorder transition.

All observed phenomena can be ascribed to localised polaron condensation: an appearance of a short and a long distance orders of "molecular polarons". A dynamical Jahn-Teller active cluster composed of four  $16d$  manganese positions and four neighbouring oxygens plays role of a self-trapped small polaron. Below the "phase transition temperature" the interaction between such bipolarons becomes dominant resulting in observed long distance charge ordering accompanied by small lattice distortions. Within the cluster charge density fluctuations related with lattice distortion are present as a vibronic state of the bipolaron, in which the motion of the electron and atomic displacements are dynamically coupled.

A sophisticated nature of the observed phase transition as well as the appearance of a possible new conduction mechanism during deintercalation may be