

Diffusion of lithium atoms in the lithium manganese spinel with a disordered structure

Nobuo Ishizawa

Ceramics Research Laboratory, Nagoya Institute of Technology

10-6-29, Asahigaoka, Tajimi 507-0071

Crystals of LiMn_2O_4 undergo a first order structural phase transition near the room temperature. The high temperature (HT) form adopts a normal spinel-type structure (cubic, $Fd\bar{3}m$) with the octahedral sites populated statistically with heterovalent Mn^{III} and Mn^{IV} in the equal ratio. The low temperature (LT) form adopts a $3\times 3\times 1$ superstructure (orthorhombic, $Fddd$) with respect to the HT form, containing Mn1^{III} , Mn3^{III} , Mn4^{IV} , Mn5^{IV} and intervalent Mn2 atoms. The synchrotron X-ray electron-density analysis revealed a bond-length fluctuation along the pseudo-tetragonal Jahn-Teller distortion axis parallel to a in the heterocubane Mn_2O_9 cluster which presumably shares three electrons among four e -parentage orbitals of Mn2 and behaves as a core of Zener polaron. The phase transition between the LT and HT forms of LiMn_2O_4 can be regarded as an order-disorder transition of the Zener polarons.

The molecular dynamics (MD) studies revealed that a periodical random switching of Mn valences, reflecting the e -parentage electron hopping model, facilitates the Li-ion self-diffusion. Two distinct but coexistent processes have been proposed for the Li atom diffusion in the HT form of LiMn_2O_4 . One is a conventional thermally-activated diffusion mechanism based on the concentration gradient of Li atoms along the diffusion pathway. The activation energy was estimated from MD to be approximately 0.5 eV when Li hops from $8a$ to $16c$ given that the second neighboring $8a$ site is vacant. The other mechanism is a diffusion which occurs in association with the polaron migration. A Li atom can move from $8a$ to adjacent $16c$ without any activation energy for itself, if the bottle neck in the diffusion be expanded as a result of reduction of a Mn^{IV} in the second coordination shell of the Li.