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リチウムイオン電池の正極界面反応の機構解明

Elucidation of chemical reaction at anode/electrolyte interface in lithium ion battery

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In an intensive search for alternative cathode materials for Li-ion batteries, $\text{Li}_2\text{FeSiO}_4$ is reported to be an exciting intercalation host on the basis of its superior theoretical energy density¹⁻³. The presence of two Li atoms per SiO_4 polyanion unit, in principle engenders a multi-electron charge transfer ($\text{M}^{2+}/\text{M}^{4+}$ redox couple), thus providing a high theoretical capacity of 334 mAhg^{-1} . In addition, $\text{Li}_2\text{FeSiO}_4$ can exhibit remarkable thermal stability³, and low cost since resources to prepare the material (*i.e.* Fe, (SiO_4)) are abundant in the Earth's crust. Nonetheless, the major problem is the poor rate performance of this material, which is ascribed to the sluggish Li^+ transportation kinetics³⁻⁵. A clear understanding of the kinetics of the Li^+ extraction and insertion in $\text{Li}_2\text{FeSiO}_4$ is still lacking, and this is pivotal for clarifying the phase transition mechanism in $\text{Li}_2\text{FeSiO}_4$. To examine the rate capability related to its phase transition phenomena, crystal structural changes during charge and discharge processes of $\text{Li}_2\text{FeSiO}_4$ at various rates were investigated by synchrotron X-ray diffraction (XRD) measurements complimented with density functional theory (DFT) calculations.

XRD measurements reveal that slow rates of Li^+ extraction and insertion upon initial cycling lead to a complete reconstructive transformation from a monoclinic $\text{Li}_2\text{FeSiO}_4$ to a thermodynamically stable orthorhombic LiFeSiO_4 , concomitant with significant Li/Fe antisite mixing occurring. To elucidate further on the relative stability of these charged LiFeSiO_4 polymorph phases, DFT calculations were performed using the plane wave code CASTEP^{6,7}. On the basis of results from first principle calculations using the lattice parameters obtained from XRD measurements, the configuration of LiFeSiO_4 with an orthorhombic structure shows a lower total energy relative to its monoclinic counterpart, suggesting that the monoclinic LiFeSiO_4 is thermodynamically unstable.

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