

## 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 density<sup>1-3</sup>. The presence of two Li atoms per  $\text{SiO}_4$  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  $334 \text{ mAhg}^{-1}$ . In addition,  $\text{Li}_2\text{FeSiO}_4$  can exhibit remarkable thermal stability<sup>3</sup>, and low cost since resources to prepare the material (*i.e.* Fe, ( $\text{SiO}_4$ )) 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  $\text{Li}^+$  transportation kinetics<sup>3-5</sup>. A clear understanding of the kinetics of the  $\text{Li}^+$  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  $\text{Li}^+$  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  $\text{LiFeSiO}_4$ , concomitant with significant Li/Fe antisite mixing occurring. To elucidate further on the relative stability of these charged  $\text{LiFeSiO}_4$  polymorph phases, DFT calculations were performed using the plane wave code CASTEP<sup>6,7</sup>. On the basis of results from first principle calculations using the lattice parameters obtained from XRD measurements, the configuration of  $\text{LiFeSiO}_4$  with an orthorhombic structure shows a lower total energy relative to its monoclinic counterpart, suggesting that the monoclinic  $\text{LiFeSiO}_4$  is thermodynamically unstable.

**References**

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