

Charge-discharge Mechanism of Lithium-Poor Lithium Iron Silicate

Ryoji Matsui^a, Junya Furutani^a, Keisuke Yamanaka^a, Koji Nakanishi^a, Misaki Katayama^a, Yasuhiro Inada^a, Toshiaki Ohta^a, Yuki Oriksa^a

^a*Ritsumeikan University, Nojihigashi, Kusatsu, Shiga, Japan, 525-0058*

E-mail:sc0045fv@ed.ritsumeai.ac.jp

Li₂FeSiO₄ is one of interesting cathode material for lithium ion batteries. The two lithium composition per one iron atom and one poly-anion unit, in principle, exhibits a multi-electron charge transfer with Fe²⁺/Fe⁴⁺ redox couple, which enables much high theoretical capacity of 331 mAhg⁻¹. However, the accessible charge-discharge capacity of Li₂FeSiO₄ was limited to one-electron reaction with Fe²⁺/Fe³⁺ redox couple in the early research^{1,2}). To maximize this Fe²⁺/Fe³⁺ redox reaction in lithium iron silicate system, we investigate composition dependency of Li_xFe²⁺_{(4-x)/2}SiO₄ on charge-discharge capacity. We synthesized various Li_xFe²⁺_{(4-x)/2}SiO₄ samples and the charge-discharge measurements were performed. Although the nonstoichiometric lithium iron silicate has been reported in the previous conference by the other group³), we cannot access enough data to discuss the possibility of the nonstoichiometric system. We synthesized various Li_xFe²⁺_{(4-x)/2}SiO₄ samples and the charge-discharge measurements were performed. Their reaction mechanisms are discussed by using X-ray absorption spectroscopic data.

Li_xFe²⁺_{(4-x)/2}SiO₄ sample was synthesized by solid phase reaction. The product was characterized by X-ray diffraction and scanning electron microscopy.

Considering the Fe²⁺/Fe³⁺ oxidation-reduction reaction of the Li_xFe²⁺_{(4-x)/2}SiO₄ system, the maximum charge / discharge capacity is 203 mAhg⁻¹ with Li_{1.33}Fe_{1.355}SiO₄. However, from the XRD measurement, in Li_xFe²⁺_{(4-x)/2}SiO₄ that Fe composition is excessive, preparation of Fe₂SiO₄ by phase separation was confirmed. As a result, the discharge capacity of Li_xFe²⁺_{(4-x)/2}SiO₄ that Fe composition is excessive is less than that of stoichiometric system. For a pure Li_xFe²⁺_{(4-x)/2}SiO₄, we attempted to find the composition showing high capacity electrochemical performance and to discuss charge-discharge mechanism using X-ray absorption spectroscopic data.

References:

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