Beyond One-Lithium Reaction Mechanism in Li_2FeSiO_4

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1. Introduction

Li_2FeSiO_4 has received prime attention as an alternative cathode material for Li-ion batteries on the basis of its superiour electrochemical properties, environmental benignity and low cost [1]. In particular, the presence of two Li atoms per polyanion unit engenders a multi-electron charge transfer (M^{2+}/M^{4+} redox couple), which is suitable for large-scale applications. Recently, Rangappa and co-workers [2] reported the feasibility of a reversible extraction and insertion of a close-to-two lithium ions from / in Li_2FeSiO_4. Although most of the recent works are focusing only on the optimisation of the electrochemical performance (capacity) of this material, little has been done to clarify the mechanism (particularly the crystal structural changes and the participating redox species) during the close-to-two lithium extraction / insertion in Li_2FeSiO_4. Hard and soft X-ray measurements have herein been employed to better clarify the mechanism underlying the lithium extraction in Li_2FeSiO_4 nanoparticles that exhibit a capacity nearing two lithium ions.

2. Experimental

Li_2FeSiO_4 nanoparticles were prepared via the conventional solid state reaction method at 800°C under argon atmosphere. The crystal structure and morphology of the pristine Li_2FeSiO_4 powders were characterised by XRD, SEM, TEM and elemental carbon analysis. Charge and discharge tests were performed by using coin cell-type batteries that were cycled at different rates within the capacity ranges of two Li^+ per Fe at 55℃. Working electrodes comprised a composite mixture of the active materials, carbon black and PTFE binder (4:5:1) coated on Al current collectors. Reference and counter electrodes were Li foils. 1M $LiClO_4$ in PC solution was used as the electrolyte. XRD measurements were performed at BL02B2 (SPring-8, Japan), while XAS measurements were conducted at BL01B2 (SPring-8) and at SR Center (Ritsumeikan University).

3. Results and Discussion

Electrochemical cycling tests showed that a capacity close to a two Li^+ extraction and insertion could be obtained at elevated temperature and at low current drains. The theoretical capacity for a complete two lithium ion extraction / insertion in Li_2FeSiO_4 is *ca.* 340 $mAhg^{-1}$. Structural evolution of $Li_{2-x}FeSiO_4$ electrodes in a Li cell were investigated using *ex situ* XRD and XAS measurements. We will discuss in detail the mechanism underlying a close-to-two lithium extraction and insertion from / in Li_2FeSiO_4.

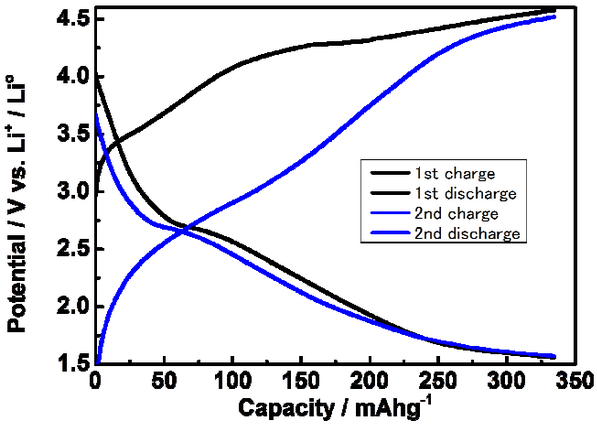

Fig. 1 Galvanostatic charge / discharge curves of $Li_{2-x}FeSiO_4$ electrode during initial and subsequent charging and discharging at C/50 rate (55°C)

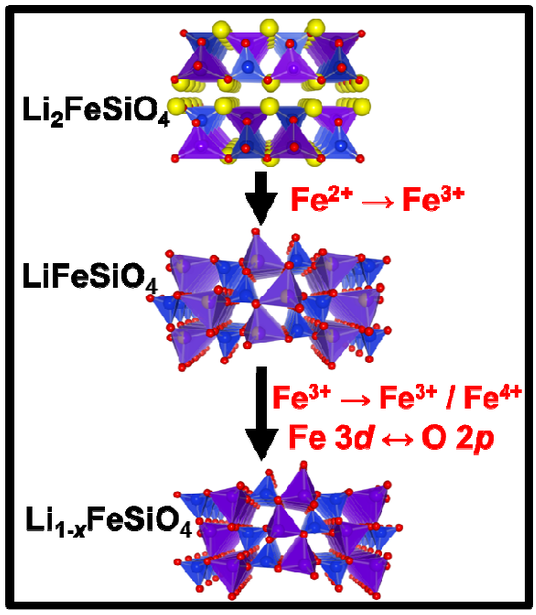

Fig. 2 Schematic of the reaction mechanism of $Li_{2-x}FeSiO_4$ upon extraction of a capacity exceeding one lithium ion

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References

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