

# Charge-discharge Mechanism of Lithium-Poor Lithium Iron Silicate

Ryoji Matsui<sup>a</sup>, Junya Furutani<sup>a</sup>, Keisuke Yamanaka<sup>a</sup>, Koji Nakanishi<sup>a</sup>, Misaki Katayama<sup>a</sup>, Yasuhiro Inada<sup>a</sup>, Toshiaki Ohta<sup>a</sup>, Yuki Oriksa<sup>a</sup>

<sup>a</sup>*Ritsumeikan University, Nojihigashi, Kusatsu, Shiga, Japan, 525-0058*

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

$\text{Li}_2\text{FeSiO}_4$  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  $\text{Fe}^{2+}/\text{Fe}^{4+}$  redox couple, which enables much high theoretical capacity of  $331 \text{ mAhg}^{-1}$ . However, the accessible charge-discharge capacity of  $\text{Li}_2\text{FeSiO}_4$  was limited to one-electron reaction with  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple in the early research<sup>1,2)</sup>. To maximize this  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox reaction in lithium iron silicate system, we investigate composition dependency of  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  on charge-discharge capacity. We synthesized various  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  samples and the charge-discharge measurements were performed. Although the nonstoichiometric lithium iron silicate has been reported in the previous conference by the other group<sup>3)</sup>, we cannot access enough data to discuss the possibility of the nonstoichiometric system. We synthesized various  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  samples and the charge-discharge measurements were performed. Their reaction mechanisms are discussed by using X-ray absorption spectroscopic data.

$\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  sample was synthesized by solid phase reaction. The product was characterized by X-ray diffraction and scanning electron microscopy.

Considering the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  oxidation-reduction reaction of the  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  system, the maximum charge / discharge capacity is  $203 \text{ mAhg}^{-1}$  with  $\text{Li}_{1.33}\text{Fe}_{1.355}\text{SiO}_4$ . However, from the XRD measurement, in  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  that Fe composition is excessive, preparation of  $\text{Fe}_2\text{SiO}_4$  by phase separation was confirmed. As a result, the discharge capacity of  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$  that Fe composition is excessive is less than that of stoichiometric system. For a pure  $\text{Li}_x\text{Fe}^{2+}_{(4-x)/2}\text{SiO}_4$ , 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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