MLF Experimental Report		提出日 Date of Report
		2012.03.25
課題番号 Project No.	装置責任者 Name of responsible person	
2012A0001	Toru Ishigaki	
実験課題名 Title of experiment	装置名 Name of Instrument/（BL No.）	
Occupation Site Analysis of Electrochemically Inserted Lithium in γ-Fe$_2$O$_3$	BL-20	
実験責任者名 Name of principal investigator	実施日 Date of Experiment	
Takeshi Yao	2012.04.18 17:00 ~ 2012.04.19 17:00	
所属 Affiliation		
Kyoto University		

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions.　Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

- Name of sample : Lithium inserted iron oxide

- Chemical formula : Li$_x$Fe$_2$O$_3$ (x=0.0 and 1.1)

2. 実験方法及び結果 （実験がうまくいかなかった場合、その理由を記述してください。）
　Experimental method and results.　If you failed to conduct experiment as planned, please describe reasons.

γ-Fe$_2$O$_3$ with particle size of 8-10 nm (Alfa Aesar Co., Ltd) was used for this experiment. Lithium was electrochemically inserted into the γ-Fe$_2$O$_3$ using an Ar-sealed three-electrode glass beaker cell. For working electrode, the γ-Fe$_2$O$_3$ was mixed with AB (Acetylene Black, Surface area: 133m^{2}g^{-1}, Denkikagaku Kogyo Corp., Ltd) as a supplemental conductor and PTFE powder as an adhesive agent in a weight ratio of 0.7:0.3:0.05. The mixture was ground, spread and pressed onto a nickel mesh as a current collector. Lithium metal was used for the counter and reference electrode. 1M ethylene carbonate and a 1,2-dimethoxyethane solution (1:1, v/v) of lithium perchlorate (LiClO$_4$ EC/DME, Kishida chemical Corp., Ltd) was used for the electrolyte. The electrode fabrication and the cell assembly were carried out under argon gas system. The samples are discharged from the natural potential of approximately 3 V (vs. Li/Li+) at a current density of 0.01 Ag^{-1}. The amount of Li estimated by integrating the current is x= 1.1 in terms of Li$_x$Fe$_2$O$_3$. After the required electrochemical conditions are attained, the circuits are opened immediately. And the working electrode is detached from the glass beaker cell and set in a vanadium cell in an argon gas system and this is used for neutron diffraction.

Due to limitation of measuring time, we made samples with various relaxation time after the lithium insertion. Neutron powder diffraction is measured at room temperature for all specimens.

We investigated the iron occupancy changes after lithium insertion as a function of relaxation times. We focused on the two peaks of 220 and 222. 220 peak appeared when iron or lithium ions are occupied at tetrahedron sites of 8*a* or 8*b*, while 222 peak appeared when iron or lithium ions are occupied at octahedron sites of 16*c* or 16*d*. In this case, iron ions are more effective to make difference of the intensity because the bound coherent scattering length (*bc*) for iron, is far bigger than lithium. We investigated the integrated intensity changes with relaxation times after lithium insertion by peak fitting using Lorentz function. Compared to sample before lithium insertion, just after lithium insertion sample with a relaxation time of 25 hours, the integrated intensity of 220 peak decreased and that of 222 peak increased which means that iron ions were migrated from 8*a* site to 16*c* site. And as the increase of relaxation time, the integrated intensity of 220 peak gradually increased and that of 222 peak decreased which means that iron ions were diffused from 16*c* site to 8*a* site in the process of relaxation.

Previously, we analyzed the relaxation structure of lithium inserted γ-Fe_2O_3 by means of X-ray diffraction and the Rietveld method using RIEVEC program coded by T. Yao [1-3]. *Fd-3m* are employed as the space group of the samples. For each of the 8*a*, 8*b*, 16*c*, and 16*d* cation sites, the amount of iron are optimized with the relaxation time. Peaks derived from the nickel collector and AB observed in the patterns are also evaluated as background at the same time. In this case, contribution of lithium was ignored. The X-ray Rietveld analysis revealed that the iron occupancy of 8*a* site decreased and that of 16*c* site increased during lithium insertion process and after lithium insertion, the iron occupancy of 8*a* site increased and that of 16*c* site decreased gradually with time. The iron occupancy of 8*b* site was almost zero and that of 16*d* site was almost unchanged all over the process. At lithium insertion process, it was considered that lithium was inserted at 8*a* site and iron migrated from 8*a* site 16*c* site. After the lithium insertion, it was considered that lithium migrated from 8*a* site to 16*c* site and iron moved from 16*c* site to 8*a* site. Based on these results, we concluded that lithium prefers 8*a* site to occupy kinetically and prefers 16*c* site thermodynamically.

Cation distribution results from neutron diffraction and X-ray diffraction were very consistent. By the precise analysis the neutron diffraction measurement, the detail behaviors of lithium ions will be clear.

Reference

[1] Seungwon Park, Masaya Oda, and Takeshi Yao, *Solid State Ionics*, 203 (2011), pp. 29-32.

[2] Seungwon Park, Shota Iot, Kaoru Takasu, Takeshi Yao, *Electrochemistry*, 80(10), (2012), pp. 804-807.

[3] Seungwon Park, Kaoru Takasu, and Takeshi Yao, T. Yao (ed.), *Zero-Carbon Energy Kyoto 2012*, Green Energy Kyoto 2012, Green Energy and Technology, Springer, (2013), pp. 161-166.