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 MLF Experimental Report	提出日 Date of Report 2011.06. 25
課題番号 Project No. 2010B0007 実験課題名 Title of experiment Occupancy Site Analysis of Electrochemically Inserted Lithium in γ -Fe ₂ O ₃ 実験責任者名 Name of principal investigator Takeshi Yao 所属 Affiliation Kyoto University	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/(BL No.) BL-08 実施日 Date of Experiment 2010. 11. 12 13:00 ~ 2010. 11. 13 13:00 2011. 03. 08 13:00 ~ 2011. 03. 09 13:00

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 and 1.5)

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.
<p>FeCl₂·4H₂O is dissolved in a buffer solution of pH 6.2. The solution is stirred for 30 min at room temperature under oxygen atmosphere. γ-FeOOH is obtained by collecting the precipitate using a vacuum filter and drying at 70 °C. This precipitate is vacuum-dried for 72 h at 200 °C to obtain γ-Fe₂O₃.</p> <p>Lithium are inserted electrochemically into synthesized nano γ-Fe₂O₃. Electrochemical measurement is performed using an Ar-sealed three-electrode glass beaker cell. The working electrode is formed by mixing γ-Fe₂O₃ as the active material, AB as a supplemental conductor, and PTFE (polytetrafluoroethylene) as an adhesive agent at a ratio of 70:30:5 by weight. The working electrode samples are crimped to a nickel mesh as the current collector. Li metal is used for the counter electrode and reference electrode. 1 mol dm⁻³ LiClO₄/(EC+DME) (1:1 v/v) is used for the electrolyte solution. 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= 1.5 in terms of Li_xFe₂O₃. 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.</p>

2. 実験方法及び結果(つづき) Experimental method and results (continued)

Due to limitation of measuring time, we made several samples with elapsed time after lithium insertion. (Sample with elapsed time of 8, 30, 64, 100, and 300 hour after lithium insertion) Neutron powder diffraction is measured at room temperature for all specimens. The obtained neutron diffraction patterns are analyzed by the Rietveld method.

Previously, we measured XRD and analyzed the structure of $\gamma\text{-Fe}_2\text{O}_3$ by the Rietveld method by using RIEVEC program coded by T. Yao [1-3]. $Fd3m$ are employed as the space group of the samples. For each of the 8a, 8b, 16c, and 16d cation sites, the amount of iron are optimized. 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 8a site decreased and that of 16c site increased with lithium insertion process and after lithium insertion, the iron occupancy of 8a site increased and that of 16c site decreased gradually with time. It was considered that lithium was inserted at 8a site in the process of lithium insertion and after lithium insertion, lithium migrated from 8a site to 16c site. [3-10]

In this study, neutron diffraction pattern was analyzed similar to XRD analysis but including lithium for analysis. For the sample before lithium insertion, obtained structure was very consistent with that of XRD analysis. This is the first time for us to measure the sample by neutron diffraction. It is considered that the neutron diffraction measurement was well conducted for our sample. After lithium insertion, iron occupancy at 8a site decreased and that of 16c site increased, these are very similar to the result of XRD analysis, however different from XRD analysis, iron occupancy at 16d site decreased. From XRD analysis, we estimated that inserted lithium occupied 8a site and this was well shown by neutron diffraction analysis. On the contrary to XRD analysis, lithium occupancy at 8b site was indicated. This is a new information for the structure for lithium inserted $\gamma\text{-Fe}_2\text{O}_3$, and we think it is necessary to make a more detail measurement and precise analysis.

Reference

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