

## Electrochemical Interaction of Nano-sized $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with lithium.

Sho Kanzaki<sup>1</sup>, Taro Inada<sup>1</sup>, Tadaaki Matsumura<sup>2</sup>,  
Noriyuki Sonoyama<sup>1</sup>, Atsuo Yamada<sup>1</sup>, Mikio Takano<sup>3</sup>  
and Ryoji Kanno<sup>1</sup>

<sup>1</sup>Department of Electronic Chemistry,  
Interdisciplinary Graduate School of Science and Engineering,  
Tokyo Institute of Technology  
4259 Nagatsuta, Midori, Yokohama, 226-8502 Japan

<sup>2</sup>Department of Chemistry for Materials,  
Factory of Engineering, Mie University,  
1515 Kamihama-cho, Tsu, 514-8507 Japan

<sup>3</sup>Institute for Chemical Research, Kyoto University,  
Gokasho, Uji, 611-0011 Japan

Iron oxides are one of the most ideal materials for lithium battery cathode because of its low cost and nontoxicity for environment, and have been a continuous research subject. Recently, it is reported nano-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> react with lithium reversibly without phase transformation<sup>1</sup>. The structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is categorized into the defect spinel in which a part of the octahedral sites is vacant, and provides larger path for lithium movement. With respect to this advantageous inherent crystallographic aspect, we have decided to explore the electrochemical properties of nano-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> as a lithium battery cathode. Technical interests of nano-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are (i) suppression of spinel-rocksalt transformation which have hindered the reversible redox reaction, (ii) maximizing the lithium reactivity by huge surface area, and (iii) kinetic improvement by the minimum distance for lithium to pass across the particle.

Iron oxide with nanosize morphology was synthesized by mild oxidation process of Fe(CO)<sub>5</sub> method by Hyeon et al<sup>2</sup>. Organic impurity phase of ca. 40% was included in the as-obtained sample and was carefully removed by the heat treatment at 400°C in vacuum for 6 hours. The x-ray diffraction profile was analyzed using the space group P4<sub>3</sub>32 and was identified to that of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. TEM observation indicates the particle diameter was typically 7 nm.

All electrochemical tests were performed at 25°C with a stainless steel cell (HS test cell, Hosen Co) with lithium metal anode and 1M LiPF<sub>6</sub> / EC:DEC = 3:7 as electrolyte. The cathode mixture was set to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> : acetylene black : PVDF = 4:2:1. The discharge capacity of nano-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> measured at 56.5  $\mu$ A/cm<sup>3</sup> was ca. 230 mAh/g. Corresponding to *ex-situ* XRD patterns measured during the discharge process (Fig. 3) showed significant suppression of the spinel-rocksalt transformation as compared with the conventional large particle  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and the Mössbauer spectroscopy revealed that the valence state of Fe remained to be Fe(III)/Fe(II) = 45/55 after discharge (Fig. 2), it means 193 mAh/g as a capacity. This result indicates some residual current is consumed to form decomposed composite as SEI layer or lithium cluster on the particle surface. Details of the surface reaction will be discussed in the poster.

## REFERENCES

- [1] D. Larcher, C. Masqyelier, D. Bonnin, V. Masson, J.-B. Leriche, and J.-M. Tarascon, *J Electrochem. Soc.*, **150** A133 (2003)  
[2] T. Hyeon, S. S. Lee, J. Park, Y. Chung, and H. B. Ma, *J. Am. Chem. Soc.*, **123**, 12798 (2001)

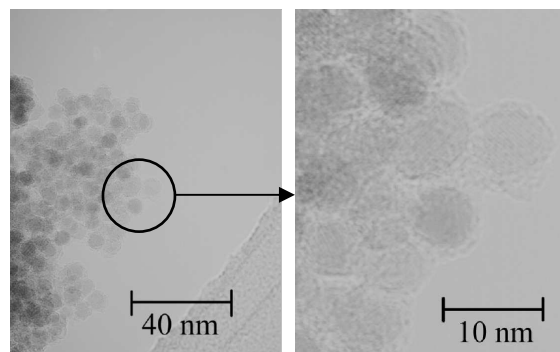


Fig. 1 TEM image of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle after heat treatment at 400°C in vacuum.

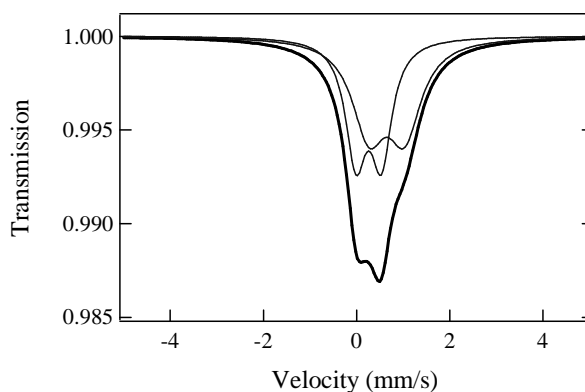


Fig. 2 Mössbauer spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, underwent Li intercalation by the discharge process at 100 $\mu$ A with the cut-off voltage of 1.0 V

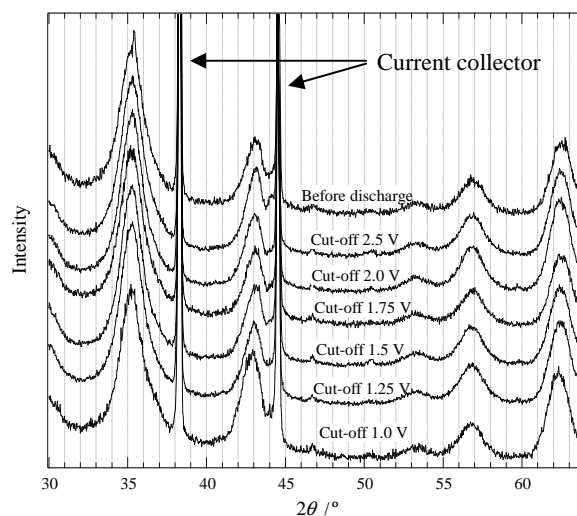


Fig. 3 X-ray diffraction patterns of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with the different discharge stage.