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Modulating the Structure and Magnetic Properties of ϵ -Fe₂O₃ Nanoparticles via Electrochemical Li⁺ Insertion

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Abstract

ε -Fe₂O₃, a metastable phase of iron oxide, is widely known as a room temperature multiferroic material or as a super-hard magnet. Element substitution into ε -Fe₂O₃ has been reported in the literature; however, the substituted ions have a strong site preference depending on their ionic radii and valence. In this study, in order to characterize the crystal structure and magnetic properties of ε -Fe₂O₃ in the Fe²⁺/Fe³⁺ coexisting states, Li⁺ was electrochemically inserted into ε -Fe₂O₃ to reduce Fe³⁺. The discharge and charge of Li⁺ into/from ε -Fe₂O₃ revealed that Li⁺ insertion was successful. X-ray magnetic circular dichroism results indicated that the reduced Fe did not exhibit site preference. Increasing the Li⁺ content in ε -Fe₂O₃ resulted in decreased saturation magnetization and irregular variation of the coercive field. We present a comprehensive discussion of how magnetic properties are modified with increasing Li⁺ content using transmission electron microscopy images and considering the Li⁺ diffusion coefficient. The results suggest that inserting Li⁺ into crystalline ε -Fe₂O₃ is a useful tool for characterizing crystal structure, lithiation limit, and magnetic properties in the coexistence of Fe²⁺/Fe³⁺.

1. Introduction

Fe is an abundant transition metal usually found in the 2+, 3+ or 4+ oxidation states. Iron oxide, which is made up entirely of Fe³⁺, is known to exhibit multiple structures, such as α -Fe₂O₃, γ -Fe₂O₃ and ε -Fe₂O₃.⁽¹⁾ Among these, α -Fe₂O₃ (hematite) is the most stable phase, with a corundum structure⁽²⁾ showing Morin transition at 260 K.⁽³⁾ This transition is known not to exist in the nanoparticle state.⁽⁴⁾ γ -Fe₂O₃ is one of the metastable phases stabilized in the nanoparticle state⁽⁵⁾; its defective spinel structure give

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6 rise to a spin glass state.^(6,7) Recently, ϵ -Fe₂O₃ has gained attention because of its room
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8 temperature multiferroic properties.^(8,9) The structure of ϵ -Fe₂O₃ is shown in Figure 1(a).
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10 Here, four Fe sites are defined: Fe1d, Fe2d, Fe3r, and Fe4t, where d, r, and t indicate
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12 distorted octahedron, regular octahedron, and tetrahedron, respectively. This structure can
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14 be understood as a combination of the α -Fe₂O₃ and γ -Fe₂O₃ structures stacked along the
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16 *c*-axis. Recently, our group has been investigating the multiferroic properties of ϵ -Fe₂O₃
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18 using epitaxial thin films.^(10–14)
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22 ϵ -Fe₂O₃ nanoparticles are known for exhibiting hard magnetism with a coercive
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24 field of 20 kOe.⁽¹⁵⁾ Such a large coercive field makes them suitable for applications in
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26 magnetic recording media and as millimeter wave absorbers in the GHz range.⁽¹⁶⁾ ϵ -Fe₂O₃
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28 has two Néel temperatures T_N of 480 K and 850 K.⁽¹⁷⁾ Tuning of its magnetic properties
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30 by substituting Al,⁽¹⁸⁾ Ga,⁽¹⁹⁾ In,⁽²⁰⁾ and Rh⁽²¹⁾ has also been reported. However, the site of
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32 the ion substitution can differ depending on the element, since ion substitution is strongly
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34 governed by the ionic radii. Moreover, the valence of the ions should be 3+ because
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36 substitution is otherwise difficult in ϵ -Fe₂O₃. To evaluate the effects of ions with a
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38 different valence on ϵ -Fe₂O₃, we first shed light on the reduction of Fe³⁺. We then carried
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40 out the reduction in ϵ -Fe₂O₃ by introducing Li⁺ into the crystal using electrochemical
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42 methods. We were able to tune the crystal structure and magnetic properties by changing
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44 the oxidation state from Fe³⁺ to Fe²⁺. Therefore, the electrochemical insertion of Li⁺
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46 proves significant in understanding the magnetic properties of ϵ -Fe₂O₃.
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51 Reversible Li⁺ insertion/removal into/from α -Fe₂O₃ has already been
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53 reported.⁽²²⁾ In that study, the corundum structure of α -Fe₂O₃ was maintained during Li⁺
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55 insertion up to a critical quantity. The results suggested that α -Fe₂O₃ is a potential anode
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57 material because its capacity is over 600 mAh g⁻¹.⁽²²⁾ In addition, it was reported that the
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spinel structures of LiMn_2O_4 ⁽²³⁾ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ⁽²⁴⁾ are suitable electrode materials for Li ion batteries. In consideration of these reports, Li^+ insertion into $\epsilon\text{-Fe}_2\text{O}_3$ should be possible because its structure is a compromise between a corundum and a spinel one. To the best of our knowledge, there have been no reports on the magnetic properties of such a system. Therefore, we considered that it would be of great interest to investigate the changes in the electrochemical and magnetic properties of $\epsilon\text{-Fe}_2\text{O}_3$ due to Li^+ insertion.

In this study, we prepared $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles by the sol-gel method. After assembling coin cells, we electrochemically introduced Li^+ into the $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles. We then disassembled the coin cells and characterized the Li^+ -inserted $\epsilon\text{-Fe}_2\text{O}_3$ samples by X-ray diffraction (XRD), X-ray magnetic circular dichroism (XMCD), X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), Mössbauer spectroscopy, and magnetic hysteresis (M - H loop) measurements.

2. Experimental Section

Preparation of $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles: Tetraethyl orthosilicate (TEOS) was added dropwise into iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), dissolved in an ethanol/water solution, and mixed. The molar ratio of TEOS/ethanol/water was 1:5:6. The solution was heated to 60 °C and then to 100 °C. A powder was obtained after evaporation. The powder was sintered at 1100 °C for 3 h, and then soaked in a 12 M NaOH solution at 110 °C for four days to remove the outer silica shell. Finally, $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles were obtained.

Preparation of coin-cell for electrochemical treatments: The electrode was prepared with $\epsilon\text{-Fe}_2\text{O}_3$, carbon, and polyvinylidene difluoride (PVDF) in a weight ratio of 10:1:1.

Here, carbon and PVDF were used as conductive material and linker, respectively. The mixture was grounded well with an agate mortar and pestle, and the paste was then cast onto Cu foil. The foil was patterned to an electrode after drying in a vacuum chamber for one night. We assembled 2032-type coin cells in an Ar-filled glove box using the prepared electrode as the cathode, Li metal as the anode, and LiPF₆ solution (ethylene carbonate (EC): diethyl carbonate (DEC)) as the electrolyte.

Electrochemical treatments: The electrochemical tests were carried out in a Solartron 1287 (Hokuto Denko) and a B580 Battery Test System (Toyo Corp.). The cyclic voltammetry measurements were performed under the following conditions: sweep voltage – 0.1 mV s⁻¹; voltage window – 0.4–3.0 V vs. Li⁺/Li. In the discharge-charge measurements, we applied a current of 8.0 mA g⁻¹ and followed this sequence three times: discharging (Li⁺ insertion, cutoff voltage: 0.4 V), resting (1 h), charging (Li⁺ removal, cutoff voltage: 2.0 V), and resting (1 h). The Li⁺ content in the nanoparticles was calculated from the capacity using the equivalence 1.0 Li⁺ = 167.8 mAh g⁻¹. The Li_xFe₂O₃ ($x = 0.33, 0.67, 0.95, 1.91$) samples were prepared by charging the cells for each calculated time followed by a 24 h rest, then disassembling the coin cells in an Ar-filled glove box. The disassembled samples were washed with DEC solution.

Characterization of Li_xFe₂O₃: After disassembling the coin cells, we measured the XRD patterns of Li_xFe₂O₃ samples by CuK α X-ray and RINT (Rigaku). (S)TEM characterization was carried out using a JEM-ARM200F (JEOL) and Titan G2 60-300 cubed (FEI) system at acceleration voltages of 200 kV and 300 kV, respectively. The samples were dispersed in hexane and cast onto a carbon mesh. ⁵⁷Fe Mössbauer

spectroscopy was carried out at 300 K. The magnetic properties were measured using PPMS (Quantum Design). For the M - H measurements, magnetic fields ranging from -50 kOe to 50 kOe were applied at 300 K.

3. Results

3.1. XRD and SEM measurements of as-prepared ϵ -Fe₂O₃ nanoparticles

Figure 1(b) shows the XRD pattern of the as-prepared ϵ -Fe₂O₃ nanoparticles. This diffraction pattern corresponds to ϵ -Fe₂O₃ (space group: $Pna2_1$ ICDD 00-058-0266). This indicates that Fe₂O₃ particles with a single ϵ -phase were obtained.

Figure 1 (a) Structure of ϵ -Fe₂O₃. (b) XRD pattern of as-prepared ϵ -Fe₂O₃ nanoparticles.

3.2. Li⁺ insertion into ϵ -Fe₂O₃ nanoparticles

To insert Li⁺ into the ϵ -Fe₂O₃ nanoparticles, we first prepared an electrode (detailed provided in the experimental section). After the coin cells were assembled, cyclic voltammetry measurements were performed. Figure 2(a) presents the results. A

single cathodic peak and single anodic peak were observed, with voltages of 0.654 V and 1.61 V, respectively, manifesting a large polarization. This indicates that the reaction voltage of this electrode is 1.13 V vs. Li^+/Li . In addition, there was no contribution from electrolyte decomposition.⁽²⁵⁾ These results suggest that Li^+ can be inserted into/removed from $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles.

Figure 2 (a) Results of cyclic voltammetry on a $\epsilon\text{-Fe}_2\text{O}_3$ electrode. (b) discharge-charge curves of the $\epsilon\text{-Fe}_2\text{O}_3$ electrode for three cycles.

We then performed the discharge and charge measurements. The resulting curves for three cycles are shown in Figure 2(b). During the first discharge cycle, two voltage plateaus were observed at 1.10 V and 0.96 V. The latter was only observed during this cycle. The same results were obtained for previously reported Li^+ insertion into $\alpha\text{-Fe}_2\text{O}_3$.⁽²²⁾ The capacity of the first discharge (expressed by the Li^+ amount) in $\epsilon\text{-Fe}_2\text{O}_3$ was 4.0 Li^+ per Fe_2O_3 ; however, the capacity of the first charge was only 2.3 Li^+ . Moreover, the discharge/charge capacities decreased as the cycling number increased.

This suggests that the cycling ability of this electrode was below that of a α -Fe₂O₃ anode.⁽²²⁾ Additionally, the voltage plateau was observed only during the charging process.

We then evaluated the Li⁺ diffusion coefficient (D_{Li}) of the ε -Fe₂O₃ nanoparticles via galvanostatic intermittent titration technique (GITT).^(26,27) We used the following conditions to perform GITT measurements during the first discharge: titration current amplitude of 16 mA g⁻¹, current application time of 30 min, and resting time of 2 hours. The results of D_{Li} are shown in Figure 3. As the cell voltage decreased, the D_{Li} value increased by one order of magnitude at around 2.0 V vs. Li⁺/Li. At around 1.10 V and 0.96 V, where the voltage plateaus were observed, the D_{Li} value increased by two orders of magnitude. These results are discussed further in below.

Figure 3 Diffusion coefficient of the ε -Fe₂O₃ electrode measured by GITT.

3.3. Preparation of Li⁺-inserted ε -Fe₂O₃

Cyclic voltammetry and discharge-charge measurements revealed that Li⁺ could be inserted into/removed from ε -Fe₂O₃ nanoparticles. Moreover, the inner diffusion

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6 coefficient of Li^+ varied depending on its content. To further investigate the Li^+ -inserted
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8 $\varepsilon\text{-Fe}_2\text{O}_3$ nanoparticles, we prepared four samples of $\text{Li}_x\text{Fe}_2\text{O}_3$ with Li^+ content (x) – 0.33,
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10 0.67, 0.95, and 1.91 by controlling the current application time. First, we measured XRD
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12 patterns for the four samples. The samples collected after disassembling the coin cells
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14 weighed less than 3 mg. Since that volume was insufficient for XRD analysis, the entire
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16 cathode was used on Cu foil for the measurement. Thus, the XRD results shown in Figure
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18 4(a) include diffraction patterns from the Cu foil. We note that it has already been reported
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20 that carbon and polyvinylidene fluoride (PVDF) diffraction peaks are not observed when
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22 the range of the angle 2θ is over 20° .⁽²⁸⁾ Hence, we collected XRD data under the
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24 following conditions: $\text{CuK}\alpha$ 2θ scan from 20° – 90° , measurement step: 0.02° ,
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26 integration time: 5 s. The results indicated that the peak intensities attributed to $\varepsilon\text{-Fe}_2\text{O}_3$
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28 diffraction decreased with an increase in the Li^+ content.
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33 Figure 4(b) shows an expansion of the XRD data from Figure 4(a) in the 38 – 44°
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35 range. Although the position of the peak observed at 43.2° , corresponding to Cu 111 , did
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37 not change when the amount of inserted Li^+ was increased, the peak attributed to $\varepsilon\text{-Fe}_2\text{O}_3$
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39 at 40.5° moved to lower angles. We evaluated the lattice constant and lattice volume by
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41 the Rietveld analysis with RIETAN-FP⁽²⁹⁾, as a function of Li^+ content (x) in $\varepsilon\text{-Fe}_2\text{O}_3$, as
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43 shown in Figure 4(c, d). The results for $x = 0.33$ showed a moderate increase in lattice
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45 volume. However, the lattice constant of c increased and that of b decreased with Li^+
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47 content in the range $0.67 < x \leq 0.95$, while a was nearly stable. The inserted Li^+ resides
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49 in the cavities formed between closed packed layers of oxygen in the $\varepsilon\text{-Fe}_2\text{O}_3$ structure,
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51 and the lattice expansion originating from the Fe^{3+} reduction is reflected by the c -axis
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53 elongation. The b -axis contraction may reflect the weaker chemical bonds perpendicular
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to the one-dimensional octahedral and tetrahedral chains. For $x > 0.95$, the lattice constant of c and the volume slightly increased.

Figure 4 (a) XRD patterns of $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x = 0$ (black), 0.33 (blue), 0.67 (green), 0.95 (yellow) and 1.91 (red)). (b) Expanded XRD results of (a) at $38\text{--}44^\circ$. (c) Lattice constants of the a (red inverted-triangle), b (blue triangle), c (green square) axes, and (d) lattice volume plotted as a function of Li^+ content in Fe_2O_3 .

We also carried out XAS and XMCD measurements on the $\varepsilon\text{-Fe}_2\text{O}_3$ ($x = 0.67$) sample to evaluate the oxidation state of Fe and to identify the reduced Fe sites. In Figure 5(a), the XAS spectrum of the $\varepsilon\text{-Fe}_2\text{O}_3$ ($x = 0.67$) sample is shown with the spectra of Fe^{3+} oxide ($\alpha\text{-Fe}_2\text{O}_3$ and $\varepsilon\text{-Fe}_2\text{O}_3$) with Fe^{2+} oxide (FeO) as reference. The L_3 absorption edge

of Fe^{3+} is known to split in two peaks, and the intensity ratio of the lower (709 eV) and higher (711 eV) energy peaks is about 1:2.^(30,31) In the case of Fe^{2+} , the L_3 absorption edge is a single peak and is observed at around 709 eV. As a result, the intensity ratio of the two L_3 peaks depends on the ratio of Fe^{2+} and Fe^{3+} . Therefore, we can estimate the average oxidation state of Fe in $\varepsilon\text{-Fe}_2\text{O}_3$ from its value.⁽³²⁾

Figure 5(b) shows the result of fitting the XAS spectra of $\varepsilon\text{-Fe}_2\text{O}_3$ ($x = 0.67$) with the reference data of FeO and $\varepsilon\text{-Fe}_2\text{O}_3$. From the fitting, we found that the average oxidation state of Fe was +2.8. This value does not correspond to the Li^+ amount estimated from integrating the electric current over time. For a given amount of Li^+ in Fe_2O_3 of 0.67, the expected average oxidation state of Fe is +2.67. However, the average valence evaluated from the XAS spectra was slightly higher than this value. This difference is addressed below.

The XMCD spectra are shown in Figure 5(c). Though a Fe^{2+} (O_h) signal was observed, we could not determine whether the Fe^{2+} ions occupied tetrahedral sites because, to the best of our knowledge, XMCD measurements for Fe^{2+} (T_d) have never been reported. On the other hand, the intensity ratio of Fe^{3+} (T_d) and Fe^{3+} (O_h) remained unchanged. Hence, these results suggest that Fe^{2+} does not have a preferential site and Fe is equally reduced in the four sites as a result of Li^+ insertion.

Figure 5 (a) XAS spectrum of $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x = 0.67$) and reference spectra. (b) The curve resulting from fitting the XAS spectrum of $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x = 0.67$) using the FeO (Fe^{2+} oxide) and $\epsilon\text{-Fe}_2\text{O}_3$ (Fe^{3+} oxide) spectra. (c) XMCD spectra of $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x = 0.67$) and $\epsilon\text{-Fe}_2\text{O}_3$.

The XAS results revealed that the average Fe oxidation state was +2.8 in $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x = 0.67$). Nevertheless, the Li^+ amount calculated from the discharge curve differed from the XAS results. It is well known that XAS is a surface-sensitive technique⁽³³⁾ and the Fe oxidation state can vary between the surface and the bulk of nanoparticles. Therefore, we decided to inspect the $\text{Li}_x\text{Fe}_2\text{O}_3$ particles by TEM. Although the sample was a mixture of Li^+ -inserted $\epsilon\text{-Fe}_2\text{O}_3$, carbon, and PVDF, we could use the energy-dispersive X-ray spectroscopy (EDX) mappings of Fe and O (shown in Figure S1) to identify the $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles. The high-resolution TEM (HRTEM) image of the as-prepared $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles is shown in Figure 6(a). The stripes corresponding to the lattice fringes can be clearly observed for each nanoparticle, reflecting their single-crystal nature.

Figure 6 (a) HRTEM image of the as-prepared ϵ -Fe₂O₃ nanoparticles. The inset shows the particles with additional magnification. (b-e) HRTEM images of Li_xFe₂O₃ particles and corresponding FFT patterns (inset) for $x = 0.33, 0.67, 0.95$ and 1.91 , respectively.

HRTEM images of ϵ -Fe₂O₃ nanoparticles with Li⁺ inserted are shown in Figure 6(b–e). These HRTEM images revealed a core-shell structure for all Li⁺-inserted samples. No lattice fringes were observed in the shell layer, indicating that this layer turned into an amorphous-like structure. Its thickness was around 2–3 nm for all samples. On the other hand, in the core, the lattice fringes darkened with the increase of x . Moreover, they appeared randomly orientated for $x = 1.91$. The fast Fourier transform (FFT) patterns of the core layer of each sample are shown as inset in Figure 6 (b–e). Halo patterns were clearly observed for increasing amounts of Li⁺ in ϵ -Fe₂O₃. From these results, we conclude that the shell layer was first formed during the insertion of Li⁺ into the ϵ -Fe₂O₃ nanoparticles. Then, the core partly turned into an amorphous-like structure and the remnant micronized crystalline parts showed a tendency to tilt slightly. Particle size

expansion was also observed. The average nanoparticle diameters measured from HRTEM images are plotted in Figure 7. The expansion ratio of 18% (21.9 nm in the $x = 0$ sample and 25.9 nm in the $x = 1.91$ sample) could not be explained simply by the lattice expansion of 4.9% (calculated from the lattice volumes of the $x = 0$ sample and the $x = 1.91$ sample shown in Figure 4(d)), indicating that the main contribution to the particle expansion is from the amorphous-like parts.

Figure 7 Average particle diameter of $\text{Li}_x\text{Fe}_2\text{O}_3$.

3.4. Magnetic properties of Li^+ -inserted $\epsilon\text{-Fe}_2\text{O}_3$

The magnetization of the Li^+ -inserted $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles was measured at room temperature. The M - H curves of the as-prepared samples are shown in Figure 8. The $x = 0$ sample showed the same hysteresis curve as the reported one.⁽¹⁵⁾ The coercive field H_c and the saturation magnetization M_s of the $x = 0$ sample were 17.7 kOe and 13.9 emu g^{-1} , respectively. The $x = 0.33$ sample displayed a sharp decrease in M_s to 8.7 emu g^{-1} . The H_c value also decreased, to a value of 8.8 kOe. Moreover, the shape of the hysteresis loop was distorted, appearing as a combination of soft and hard magnetism.

For the $x = 0.67$ sample, both the M_s and H_c values decreased and the hysteresis curve became simple. The $x = 0.95$ sample showed a hysteresis curve nearly equal to the $x = 0.33$ sample, despite a decrease in M_s decrease. Lastly, the curve of $x = 1.91$ turned into a single hysteresis curve, with $M_s = 2.7 \text{ emu g}^{-1}$ and $H_c = 8.6 \text{ kOe}$. The M_s and H_c values are plotted in Figure 9(a) and (b) as a function of Li^+ content in $\epsilon\text{-Fe}_2\text{O}_3$.

Figure 8 M - H curves at 300 K of $\text{Li}_x\text{Fe}_2\text{O}_3$ for $x = 0$ (black), 0.33 (blue), 0.67 (green), 0.95 (yellow) and 1.91 (red).

Figure 9 (a) M_s and (b) H_c values as a function of Li^+ content in $\epsilon\text{-Fe}_2\text{O}_3$.

4. Discussion

Our results demonstrate the effect of Li^+ insertion into and removal from $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles by assembling coin cells. The discharge and charge measurements revealed that two voltage plateaus appear at 1.10 and 0.96 V during the first cycle only. Generally, a voltage plateau is observed when two phases coexist, *e.g.* in LiCoO_2 , the most widespread cathode material,⁽³⁴⁾ which exhibits a first-order phase transition at 3.93 V vs. Li^+/Li due to a hexagonal (1) to hexagonal (2) transition.⁽³⁵⁾ The coexistence of hexagonal (1) and (2) can be recognized by in-situ XRD patterns.⁽³⁶⁾ In our study, however, no additional peaks were observed in XRD measurements as the amount of Li^+ increased. On the other hand, the plateaus corresponded in voltage to the diffusion coefficient peaks measured by GITT, revealing that a high diffusion coefficient is achieved at these voltages. In other words, Li^+ diffusion is enhanced above a critical Li^+ content in $\epsilon\text{-Fe}_2\text{O}_3$. Therefore, an inhomogeneous distribution of Li^+ in each nanoparticle is expected.

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As seen from the measurements, the two voltage plateaus appearing in the first discharge curve were substituted by a single voltage plateau at 1.10 V after the second discharge. This is in agreement with the reported results.⁽²²⁾ The Li⁺ insertion first caused formation of a shell layer and the crystalline ϵ -Fe₂O₃ structure then turned into an amorphous-like one in the core. We will begin by discussing the core-shell structure formation. The core-shell structure was observed in all Li⁺-inserted samples, and the thickness of the shell layer was nearly constant (2–3 nm). This suggests that suggest that the shell layer was primarily formed during the first discharge process. The average diameter of the $x = 0.33$ sample shown in Figure 7 was almost the same as that of the as-prepared nanoparticles. This indicates that the shell layer originates not from deposition of the electrolyte decomposition product,⁽³⁷⁾ but from the Li⁺-inserted Fe₂O₃.

The diffusion coefficient measured by GITT was low, on the order of 10⁻¹⁵ cm² s⁻¹ at around 2.0 V. A low diffusion coefficient may imply the appearance of a Li⁺ gradient from the surface to the center in each particle. Thus, there would be a high Li⁺ concentration layer (shell layer) and a low Li⁺ concentration layer (core part) at voltages above 1.2 V. In addition, the core gradually gained an amorphous-like structure as Li⁺ insertion proceeded. This suggests that over-insertion of Li⁺ into ϵ -Fe₂O₃ would break the crystal structure and amorphize it. The amorphous-like core part was especially observed in the $x = 1.91$ samples, signifying that the crystal structure breaking would occur in the second voltage plateau.

We will now discuss the discharge and charge capacities. The first discharge and charge capacities were 714 mAh g⁻¹ and 391 mAh g⁻¹, respectively. In this study, we used carbon as a conductive supporting material mixed with PVDF and ϵ -Fe₂O₃, in the weight ratio of 1:1:10. The discharge capacity of Li⁺ in carbon has been reported as about 180

mAh g⁻¹ at the cutoff voltage of 0.4 V,⁽³⁸⁾ and the corresponding capacity from the carbon contribution is estimated to be less than 15 mAh g⁻¹. In the absence of the carbon contribution, the first discharge capacity was about 700 mAh g⁻¹. The discharge and charge capacities and Coulomb efficiency are presented in Table S1. The discharge and charge capacities decreased as the cycle number increased, indicating that an irreversible capacity loss originated from poor contact between the electrode and current collector due to particle expansion. The first discharge capacity was found to be 4.0 Li⁺ per Fe₂O₃. This value is sufficient to reduce all Fe³⁺ ions to Fe²⁺.

Previous results in the literature reported a repetition discharge capacity of over 600 mAh g⁻¹ and an estimated reduction to Fe⁰⁺.⁽²²⁾ In contrast, the capacities in this study were below 600 mAh g⁻¹, except for the first discharge. The ⁵⁷Fe Mössbauer spectra of Li_xFe₂O₃ were measured at 300 K to consider the existence of Fe⁰⁺. The results are shown in Figure S3. The results of Mössbauer spectroscopy results indicated that Fe⁰⁺ did not exist in the Li⁺-inserted ε-Fe₂O₃. Hence, the redox reaction of Fe³⁺/Fe²⁺ is repeated in ε-Fe₂O₃ nanoparticles in the voltage window of 0.4–2.0 V vs. Li⁺/Li.

The results of fitting the XMCD spectra revealed that the average valence of Fe was +2.8 in Li_{0.67}Fe₂O₃ nanoparticles, whereas the valence estimated from the discharge capacity was +2.67. The HRTEM image showed a core-shell structure in Li_{0.67}Fe₂O₃ nanoparticles with an amorphous-like structure for the shell layer. We speculate that the difference in Fe valence would originate from the shell structure formation. To ensure consistency in the Li⁺ amount in ε-Fe₂O₃ nanoparticles, we used the value derived from the discharge capacity to express its content. To investigate the local Fe oxidation state, we carried out electron energy-loss spectroscopy (EELS) measurements at the Fe L_{2,3}-edge in the scanning TEM (STEM) mode as shown in Figure S2. However, the measured

particles were damaged by the e-beam radiation even though the spectrum imaging was performed with low probe current of 40 pA and short acquisition time of 0.2 s/pixel (pixel size: 0.015 nm²). Also, the intensity was below that needed to determine the Fe oxidation state.

The M - H curve of the $x = 0.33$ sample showed decreases in M_s and H_c , and a distortion of the hysteresis curves. In addition, the lattice constant of the $x = 0.33$ sample showed only a small change compared to that of $x = 0$. Based on the above discussion, the amount of Li⁺ inserted into the ϵ -Fe₂O₃ lattice was estimated to be smaller than that calculated from the amount of Li⁺ passing through the cell. Assuming a particle diameter of 20 nm and a shell layer thickness of 2 nm, the volume ratio of the shell to the whole particle would be 49%, which was attributed to the 63% decrease in M_s (8.7 emu g⁻¹ ($x = 0.33$) /13.9 emu g⁻¹ ($x = 0$)). Moreover, since amorphous Fe₂O₃ was reported to be paramagnetic at room temperature,⁽³⁹⁾ the amorphous-like shell layer is estimated to be paramagnetic at 300 K. The volume of the crystalline ϵ -Fe₂O₃ shrunk in the particles due to the shell formation; thus, the diameter can be estimated as 15 nm. It was reported that the H_c of ϵ -Fe₂O₃ nanoparticles decreased with a decreasing diameter.⁽⁴⁰⁾ Therefore, the decrease of H_c at $x = 0.33$ might be attributable to the reduced core diameter. In addition, the hard ferrimagnetic hysteresis of ϵ -Fe₂O₃ would have turned into a soft ferrimagnetic one because of the inserted Li⁺ breaking the O-Fe bonds, resulting in weaker superexchange interactions. The low diffusion coefficient helped to maintain the separation of the Li⁺-rich and the Li⁺-poor parts. Consequently, the hysteresis curve was distorted.

We now consider the results of the second ($x = 0.67$) sample are discussed. The M_s and H_c values continuously decreased for $x = 0$ and $x = 0.33$. The GITT results revealed

that at a composition of $x = 0.67$ the value of the diffusion coefficient increased by two orders of magnitude. Therefore, the Li^+ amount became uniform in each particle and all particles displayed a soft magnetic hysteresis curve. In terms of the result of the $x = 0.95$ sample, the hysteresis curve shape was quite similar to that of $x = 0.33$. Since the $x = 0.95$ sample corresponded to the Li^+ content immediately below the second voltage plateau, the diffusion coefficient was on the order of $10^{-14} \text{ cm}^2 \text{ s}^{-1}$. Thus, a non-uniform Li^+ concentration was found in each particle, resulting in a distorted hysteresis curve with soft and hard magnetism contributions, as in the $x = 0.33$ sample case.

Moreover, the core structure partially turned into an amorphous-like one, and the amorphous-like structure could be a pinning center for magnetic domain motion.⁽⁴¹⁾ The hard magnetism in the Li^+ -inserted $\epsilon\text{-Fe}_2\text{O}_3$ for Li^+ content over $x = 0.67$ may have been caused by this pinning. The XMCD results suggested that there was no site preference for reducing Fe. The net magnetization known to appear in the a -axis of $\epsilon\text{-Fe}_2\text{O}_3$ originates in the two sets of antiferromagnetic couplings—the coupling of Fe1d and Fe4t in the spinel layer, and the coupling of Fe2d and Fe3r in the corundum layer—which do not cancel each other.⁽⁴²⁾ If the reduced Fe were distributed randomly over the four Fe sites, the decrease in magnetic moment originating from the Fe reduction would be the same in each site. Consequently, the magnetization should not change if changes in the Fe-O chemical bond are neglected. For this reason, the M_s value of the $x = 0.95$ sample was almost same as that of the $x = 0.67$ sample.

Finally, the results of the $x = 1.91$ sample showed the second plateau, the core layer turned amorphous resulting in a decreased M_s . Additionally, it is estimated that the amount of Li^+ inserted into the $\epsilon\text{-Fe}_2\text{O}_3$ crystal lattice exceeded the maximum ($x \sim 0.9$) and broke the crystal structure. Therefore, there were two contributions, one from the

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hard magnetism of $\text{Li}_x\text{Fe}_2\text{O}_3$ ($x \sim 0.9$) and one from the paramagnetic amorphous-like phase.

We summarize the magnetic behavior of $\text{Li}_x\text{Fe}_2\text{O}_3$ in Figure 10. The magnetic behavior changed continuously with the increasing amount inserted of Li^+ . The shell structure formed at $x < 0.3$ (Figure 10(ii)), where only a small volume expansion was observed as shown in Figure 7. At the same time, the structure of the shell layer became amorphous. After the shell layer formation, Li^+ insertion into the crystal occurred at the first voltage plateau in the range $0.3 < x < 1.0$ (Figure 10(iii – v)). Due to the substantial change in the diffusion coefficient, which strongly depends on the amount of Li^+ in $\epsilon\text{-Fe}_2\text{O}_3$, Li^+ -rich and Li^+ -poor regions coexisted in the nanoparticles (Figure 10(iii)). At the limits of the first plateau ($x = \sim 0.7$), the uneven distribution of Li^+ in each particle might have vanished (Figure 10(iv)). Further Li^+ insertion resulted again in a two-phase state due to the decreased diffusion coefficient (Figure 10(v)). In the second plateau ($1.0 < x$), although the Li^+ insertion persisted, Li^+ -saturated nanoparticles could not maintain their crystal structure, resulting in a mosaic of a mesh-patterned amorphous-like structure and a micronized crystal (Figure 10(vi)). At the same time, the diameter of the particles grew. Considering all of the above, we estimated a Li^+ insertion limit of around 0.9 Li^+ per $\epsilon\text{-Fe}_2\text{O}_3$. The second plateau corresponded to the voltage of the irreversible transformation from crystalline to amorphous-like structure, and it was therefore not observed after the second cycle.

Figure 10 Li^+ insertion curve for $\epsilon\text{-Fe}_2\text{O}_3$ nanoparticles and schematic illustration of prepared samples.

The Li^+ insertion technique is usually employed for the charge-discharge process of electrode materials in Li-ion batteries. However, the phenomena observed in this experiment are much more complicated than those observed for conventional electrode materials such as LiCoO_2 . We revealed the core-shell formation in the initial step of Li^+ insertion into crystalline $\epsilon\text{-Fe}_2\text{O}_3$ and the fragmentation of that core in particles into a coexistence of crystals of single-nanometer size and an amorphous phase with increasing Li^+ amount in $\epsilon\text{-Fe}_2\text{O}_3$, accompanied by unique M - H hysteresis curves.

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6 **5. Conclusion**
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8 In this study, we investigated the changes induced in the structural and magnetic
9 properties of ϵ -Fe₂O₃ nanoparticles by Li⁺ insertion by combining electrochemical,
10 magnetic, and structural observations. The Li_xFe₂O₃ ($x = 0.33, 0.67, 0.95, 1.91$) samples
11 were prepared by controlling the charging time. Samples were then characterized by XRD,
12 XMCD, M - H measurement, Mössbauer spectroscopy, and TEM. The first charging curve
13 showed two voltage plateaus, corresponding to the Li⁺ composition at which the diffusion
14 coefficient increased by two orders of magnitude. The XMCD results suggest that there
15 was no site preference for the reduced Fe. The HRTEM images revealed that all Li⁺-
16 inserted samples had a core-shell structure. However, the thickness of the shell layer was
17 around 2–3 nm for all samples, indicating that it must have formed at the initial stage of
18 Li⁺ insertion.
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33 M - H measurements showed that the increase in Li⁺ content in ϵ -Fe₂O₃ caused
34 the saturation magnetization to decrease and the coercive field to change irregularly. The
35 distortion in the M - H hysteresis curves at $x = 0.33$ originated from a non-uniform
36 distribution of Li⁺ in the nanoparticles at low diffusion coefficient in ϵ -Fe₂O₃. The hard
37 ferrimagnetic behavior of ϵ -Fe₂O₃ was first softened for $x < 0.67$ and then hardened again
38 for $x > 0.67$ because of a pinning effect. Moreover, at the second plateau, the crystal
39 structure of the core gradually turned to an amorphous-like structure due to Li⁺ over-
40 insertion. These results suggest that Li⁺ insertion into crystalline ϵ -Fe₂O₃ is a useful
41 method to characterize its changes in crystal structure, lithiation limit, and magnetic
42 properties in the coexistence of Fe²⁺/Fe³⁺.
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Supporting Information

High-angle annular dark-field (HAADF)-STEM and EDX mappings of $x = 0.67$ sample, electron energy loss spectroscopy, Coulomb efficiency of prepared ε -Fe₂O₃ electrode and Mössbauer spectroscopy.

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SYNOPSIS TOC:

The electrochemically Li^+ -inserted $\varepsilon\text{-Fe}_2\text{O}_3$ nanoparticles exhibit interesting magnetic properties, alternating hard and soft magnetism to paramagnetic behaviour depending on the Li^+ concentration. A core-shell structure first forms during the lithiation process, followed by Li^+ inserted in the core structure of the $\varepsilon\text{-Fe}_2\text{O}_3$ nanoparticles. Upon over-lithiation, the $\varepsilon\text{-Fe}_2\text{O}_3$ crystal structure turns into an amorphous-like structure.

Electrochemical Li^+ insertion into $\varepsilon\text{-Fe}_2\text{O}_3$ nanoparticles

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