Modulating the Structure and Magnetic Properties of $\varepsilon$-Fe$_2$O$_3$ Nanoparticles via Electrochemical Li$^+$ Insertion

Sou Yasuhara$^1$, Yosuke Hamasaki$^2$, Tsukasa Katayama$^3$, Takahiro Ao$^4$, Yoshiyuki Inaguma$^4$, Hajime Hojo$^5$, Maarit Karppinen$^6$, Anish Philip$^6$, Shintaro Yasui$^1$, and Mitsuru Itoh$^1$.

1. Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.
2. Department of Applied Physics, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, 239-8686, Japan.
3. Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.
4. Department of Chemistry, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan.
5. Department of Advanced Materials Science and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580, Japan.
6. Department of Chemistry and Materials Science, Aalto University, FI-00076 Espoo Finland.
Figure S1 (a) High-angle annular dark-field (HAADF) STEM image of the $x = 0.67$ sample and EDX mappings of (b) Fe $K$-edge and (c) O $K$-edge.

Figure S2 HAADF STEM images (a) before and (b) after EELS measurements. The red and blue rectangles in (a) correspond to the position of the EELS measurements shown in (c).
Table S1 Discharge/charge capacities and Coulomb efficiency.

<table>
<thead>
<tr>
<th></th>
<th>First cycle</th>
<th>Second cycle</th>
<th>Third cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge capacity</td>
<td>713.6</td>
<td>412.8</td>
<td>328.4</td>
</tr>
<tr>
<td>(mAh g⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge capacity</td>
<td>390.8</td>
<td>315.2</td>
<td>268.1</td>
</tr>
<tr>
<td>(mAh g⁻¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coulomb efficiency</td>
<td>54.8</td>
<td>76.3</td>
<td>81.6</td>
</tr>
<tr>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure S3 Mössbauer spectra measured at 300K and fitting results of LiₓFe₂O₃ (x = 0, 0.67, 0.95, 1.91).
The $^{57}\text{Fe}$ Mössbauer spectra of Li$_x$Fe$_2$O$_3$ were measured at 300K to evaluate the valence state of Fe. The experimental data and fitting results are shown in Figure S2. The fitting data is shown in Table S2. The Mössbauer spectrum of $\varepsilon$-Fe$_2$O$_3$ has been reported as consisting of two regions, the core and shell layers; each layer shows four pairs of sextets. (S1) The large part of the spectrum for $x = 0$ showed the similar one in the previous report. (S1) In addition, we can see the spectrum of $\alpha$-Fe$_2$O$_3$ at ±8 mm s$^{-1}$. The experimental result was well reproduced fitting by nine sextets (eight for $\varepsilon$-Fe$_2$O$_3$ and one for $\alpha$-Fe$_2$O$_3$). The Mössbauer spectrum of $x = 0.67$ also showed multiple splitting, however, these peaks were found broadened. Moreover, non-magnetic Fe ions was found to exist, being reflected in the change of intensity ratio. Then, we carried out the fitting of experimental data adding two sub-spectra. Indeed, the fittings of experimental results of Li$^+$-inserted Fe$_2$O$_3$ was quite difficult to discuss the average valence state of Fe because the emerged sub-spectra originated from unknown product. This result indicated that the magnetic order was kept in $x = 0.67$ sample, however, that would be locally broken by the Li$^+$ insertion. Additionally, the two sub-spectra were estimated as composed of Fe$^{3+}$ and Fe$^{2+}$ based on the isomer shifts. (S2) The result of $x = 0.95$ sample showed one broad magnetic peak and two pair of quadrupoles. Furthermore, the broad magnetic peak disappeared and only two pair of quadrupoles were observed in $x = 0.95$. The result of $x = 1.91$ sample showed two pair of quadrupoles without the broad magnetic peak that was observed in $x = 0.95$. These results suggest that the Fe$^{3+}$ was reduced to Fe$^{2+}$ without Fe$^{0+}$ formation.
Table S2 Hyperfine parameters of Li$_x$Fe$_2$O$_3$ ($x = 0, 0.67, 0.95, 1.91$) obtained from room temperature Mössbauer spectra. The symbol † attached to fixed parameters.

The result of the $x = 0$ in Li$_x$Fe$_2$O$_3$. The Fe(1–4) and Fe(5–8) correspond to the core and shell of $\varepsilon$-Fe$_2$O$_3$, respectively. The Fe(9) corresponds to $\alpha$-Fe$_2$O$_3$.

$$\begin{array}{cccc}
\hline
x = 0 & IS & QS & HF \\
\text{(mm/s)} & \text{(mm/s)} & \text{(T)} \\
\hline
\text{Fe}(1) & 0.40 & -0.13 & 45.3 \\
\text{Fe}(2) & 0.35 & -0.35 & 45.1 \\
\text{Fe}(3) & 0.38 & -0.04 & 39.8 \\
\text{Fe}(4) & 0.21 & -0.15 & 26.6 \\
\text{Fe}(5) & 0.40 & 0.00 & 41.3 \\
\text{Fe}(6) & 0.35 & 0.00 & 37.8 \\
\text{Fe}(7) & 0.38 & 0.00 & 34.3 \\
\text{Fe}(8) & 0.21 & 0.00 & 22.9 \\
\text{Fe}(9) & 0.38 & -0.19 & 51.6 \\
\hline
\end{array}$$

($\chi^2 = 4.25$)

The result of the $x = 0.67$ in Li$_x$Fe$_2$O$_3$. The Fe(1–4) corresponds to $\varepsilon$-Fe$_2$O$_3$. The Fe(5) and Fe(6) correspond to non-magnetic phases.

$$\begin{array}{cccc}
\hline
x = 0.67 & IS & QS & HF \\
\text{(mm/s)} & \text{(mm/s)} & \text{(T)} \\
\hline
\text{Fe}(1) & 0.36 & -0.21 & 44.8 \\
\text{Fe}(2) & 0.39 & -0.08 & 39.7 \\
\text{Fe}(3) & 0.35 & -0.09 & 35.1 \\
\text{Fe}(4) & 0.21 & -0.1 & 26.1 \\
\text{Fe}(5) & 0.38 & 0.66 & - \\
\text{Fe}(6) & 0.63 & 1.65 & - \\
\hline
\end{array}$$

($\chi^2 = 2.08$)
The result of the $x = 0.95$ in Li$_x$Fe$_2$O$_3$. The Fe(1) corresponds to the broaden magnetic phase of Fe$^{3+}$. The Fe(2) and Fe(3) correspond to non-magnetic phases.

<table>
<thead>
<tr>
<th></th>
<th>IS</th>
<th>QS</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.95$</td>
<td>$\delta_1$</td>
<td>$2\varepsilon_1$ or $\Delta$</td>
<td>$B_{hf}$</td>
</tr>
<tr>
<td></td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(T)</td>
</tr>
<tr>
<td>Fe(1)</td>
<td>0.29</td>
<td>-0.21</td>
<td>30.3</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>0.35</td>
<td>0.67</td>
<td>-</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>0.67</td>
<td>1.68</td>
<td>-</td>
</tr>
</tbody>
</table>

($\chi^2 = 1.76$)

The result of the $x = 1.91$ in Li$_x$Fe$_2$O$_3$. The Fe(1) and Fe(2) correspond to non-magnetic phases.

<table>
<thead>
<tr>
<th></th>
<th>IS</th>
<th>QS</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 1.91$</td>
<td>$\delta_1$</td>
<td>$\Delta$</td>
<td>$B_{hf}$</td>
</tr>
<tr>
<td></td>
<td>(mm/s)</td>
<td>(mm/s)</td>
<td>(T)</td>
</tr>
<tr>
<td>Fe(1)</td>
<td>0.38</td>
<td>0.63</td>
<td>-</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>0.67</td>
<td>1.68</td>
<td>-</td>
</tr>
</tbody>
</table>

($\chi^2 = 1.86$)
