Electronic Supplementary Information

Solid-state electrochemical reduction process of magnetite in Li batteries: in-situ magnetic measurements toward electrochemical magnets

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1. Calculation of battery capacity
2. In-situ magnetic measurement system
3. Magnetic data

1. Calculation of battery capacity

The theoretical capacity, C^{calc} (Ah/kg), is calculated, using the following equation[S1]:

$$C^{calc} = \frac{F}{3600 \cdot M_W} \quad , \qquad \text{(Eq. S1)}$$

where F is the Faraday constant (96487 C/mol), and M_W (kg/mol) is the molar weight of the Fe_3O_4 to store one electron. The number of reduced electrons during discharge was estimated by dividing the experimental capacity by the value of C^{calc}.

2. In-situ magnetic measurement system

A miniature lithium battery cell with a size of 15 × 7 × 5 mm^3, was prepared, which can be fit to a commercial SQUID susceptometer (Quantum Design MPMS). The anode was made of lithium metal, and the cathode was a mixture of Fe_3O_4 nanoparticle, conductive carbon black, and PVDF. The separator was a glass microfiber filter. The battery cells were charged/discharged with a Hokuto Denko potentiometer (HJ1001-SM8A) in the SQUID.

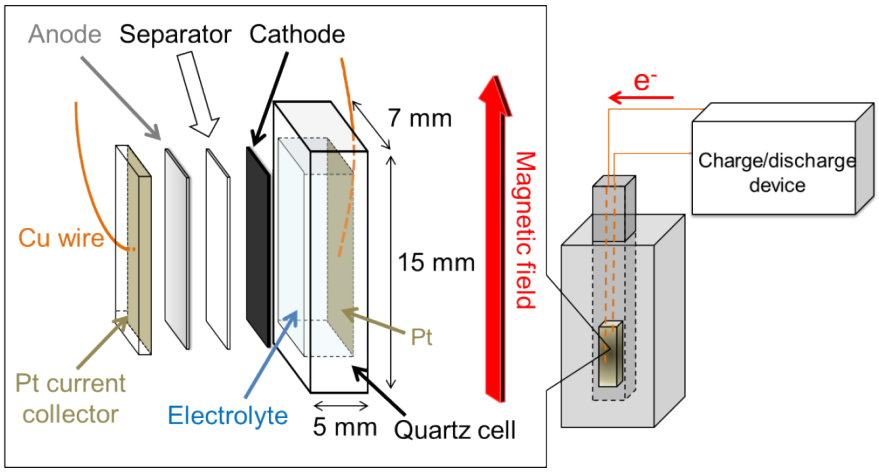

Fig. S1 View of the miniature lithium battery cell for in-situ magnetic measurements

3. Magnetic data

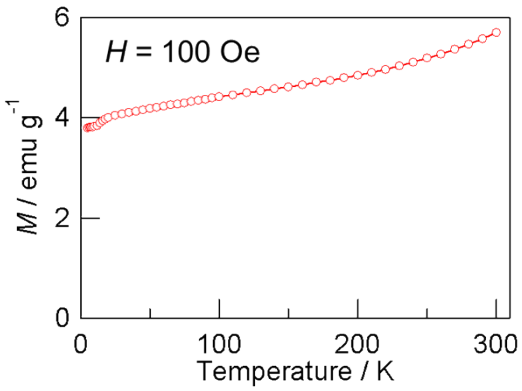

Fig. S2 Temperature dependence of the magnetization of the as-purchased Fe_3O_4 nanoparticles under the field of 100 Oe. The magnetization of the Fe_3O_4 nanoparticles exhibits a gradual decrease with a decrease in temperature due to a ferrimagnetic interaction. The well-known metal-insulator phase transition in Fe_3O_4 (Verwey transition), was not observed due to a nanosize effect.

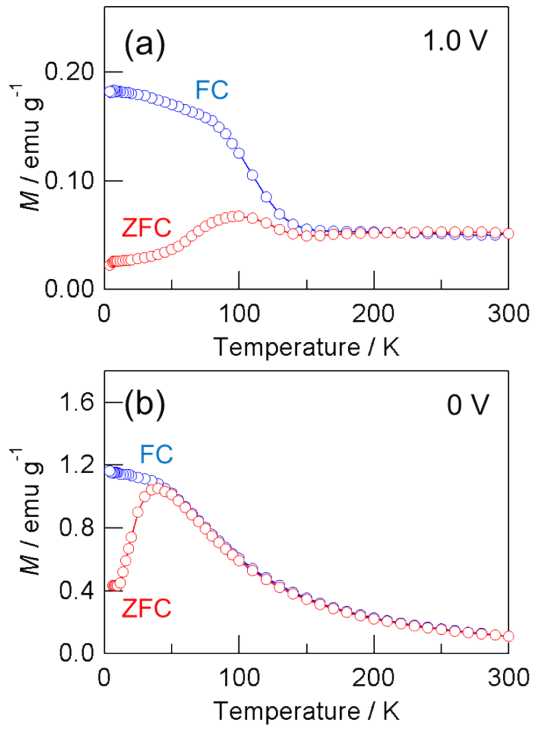

Fig. S3 The field-cooled (FC) and zero-field-cooled (ZFC) curves for the cathode of the Li-Fe_3O_4 battery, at the voltages of 1.0 (a) and 0 V (b), under the field of 100 Oe. This cathode included the Fe_3O_4 particles (10 wt%). The magnetic contributions from the quartz cell, Li metal, etc. were subtracted from the magnetization of the whole battery cell, to extract the magnetic properties of the cathode.

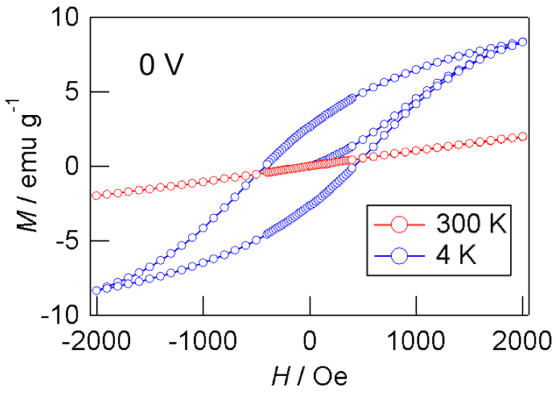

Fig. S4 Magnetic hysteresis loops at measured at 4 and 300 K, for the cathode at 0 V.

Reference

[S1] J. Qu, T. Katsumata, M. Satoh, J. Wada, J. Igarashi, K. Mizoguchi and T.Masuda, *Chem. Eur. J.*, 2007, **13**, 7965-7973.