

# Lithium battery having a large capacity using Fe<sub>3</sub>O<sub>4</sub> as a cathode material

S. Ito\*, K. Nakaoka, M. Kawamura, K. Ui, K. Fujimoto, N. Koura

*Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda Chiba 278-8510, Japan*

Available online 31 May 2005

## Abstract

The lithium battery using Fe<sub>3</sub>O<sub>4</sub> fine particles has been constructed. The discharge characteristics were improved by the addition of India ink or polyvinyl alcohol (PVA). The discharge potential at 60 °C maintained 2.5 V versus Li/Li<sup>+</sup> up to 500 mAh g<sup>-1</sup> and was 1.8 V at a large capacity of 926 mAh g<sup>-1</sup>. The possibility of secondary battery was discussed from the result of cycling test with 926 mAh g<sup>-1</sup>. Similar potential curve was obtained in the second cycle. Although degradation was observed in the third cycle, cyclability was maintained. However, the test cell stopped in fourth discharge. It is concluded that a large capacity was achieved at 60 °C using fine particles of Fe<sub>3</sub>O<sub>4</sub> with PVA additive. According to the cycling test, it is expected to be a secondary battery by further development in nanostructure of the cathode.  
© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Lithium battery; Fe<sub>3</sub>O<sub>4</sub>; Nanoparticle; High capacity

## 1. Introduction

As a cathode active material for the lithium secondary battery, LiCoO<sub>2</sub> is mainly used [1,2]. However, this material has some problems in resource, in cost and in toxicity [3]. Hence, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiM<sub>y</sub>Mn<sub>2-y</sub>O<sub>4</sub>, etc. have been studied vigorously as alternative materials. On the other hand, the attempts to find out an excellent cathode active material in iron compounds, which have no problem in the points described above, have been performed since 1970s; α-Fe<sub>2</sub>O<sub>3</sub>:1.4 V [4], Fe<sub>3</sub>O<sub>4</sub>:1.5 V [5], LiFe<sub>5</sub>O<sub>8</sub>:1.4 V [6], Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>:3.6 V [7], β-FeOOH:2.0 V [8], LiFePO<sub>4</sub>:3.4 V [9], etc. We have investigated γ-Fe<sub>2</sub>O<sub>3</sub> as a cathode material for lithium battery [10–12]. In this cell, the discharge potential at 60 °C maintained 2.7 V versus Li/Li<sup>+</sup> up to the capacity of 750 mAh g<sup>-1</sup>, and then gradually decreased to 2.0 V at 1007 mAh g<sup>-1</sup>. The capacity 1007 mAh g<sup>-1</sup> is especially large, compared to other lithium batteries, and corresponds to that calculated by assuming the reduction of Fe<sup>3+</sup> to Fe<sup>0</sup>, as shown in Eq. (1).



Larcher et al. indicated that the reduction in α-Fe<sub>2</sub>O<sub>3</sub> occurred to form Fe<sup>0</sup> and Li<sub>2</sub>O [13]. However, the discharge potentials at room temperature were as low as about 1.5 V versus Li/Li<sup>+</sup>. The thermodynamically calculated potential based on Eq. (1) is 1.6 V, which does not largely increase at 60 °C. Therefore, we suggest that the relatively high potential 2.7 V was due to the reaction of lithium and oxygen;



In addition, the cell using γ-Fe<sub>2</sub>O<sub>3</sub> was then charged up to the capacity 1007 mAh g<sup>-1</sup> [10]. However, the discharge characteristics degraded in the second discharge. It is important for the capacity and cyclability to use nanosized fine particles to the cathode material. In this study, Fe<sub>3</sub>O<sub>4</sub> fine particles were prepared and were used as a cathode material for the lithium battery. Improvement of discharge characteristics and cyclability was performed.

## 2. Experimental

Aqueous solutions of FeCl<sub>2</sub> and FeCl<sub>3</sub> (both from Wako Pure Chemical Industries Ltd.) were mixed and NH<sub>4</sub>OH solution was then added to the mixed solution to form Fe<sub>3</sub>O<sub>4</sub> (magnetite) powder, following the process reported

\* Corresponding author. Fax: +81 4 7123 9890.  
E-mail address: [ito@rs.noda.tus.ac.jp](mailto:ito@rs.noda.tus.ac.jp) (S. Ito).

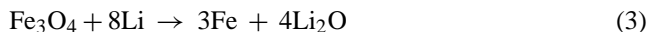
by Massart [14]. The product obtained was confirmed as a magnetite ( $\text{Fe}_3\text{O}_4$ ) by X-ray diffraction method. The  $\text{Fe}_3\text{O}_4$  powder (20 mg) was mixed with acetylene black (20 mg) and PTFE (8 mg). This mixture was pressed against the Ni-mesh (10 mm  $\times$  10 mm) to make a cathode. Counter and reference electrodes were prepared by pressing lithium against Ni-mesh. Using 1 M  $\text{LiClO}_4$  PC, test cell ( $\text{Li} | 1 \text{ M } \text{LiClO}_4 \text{ PC} | \text{Fe}_3\text{O}_4$ ) was constructed. Discharge/charge test was done at room temperature (25 °C) and 60 °C with a current density of  $0.1 \text{ mA cm}^{-2}$ .

After discharge or charge, the cathode was washed by propylenecarbonate and acetonitrile. Lithium content in the cathode was measured by ICP analysis. The cathode materials obtained after discharge and charge were respectively observed by scanning electron microscope (SEM).

### 3. Results and discussion

#### 3.1. Discharge and charge characteristics of the cell using $\text{Fe}_3\text{O}_4$ cathode

Fig. 1 shows the discharge curves of the cell using magnetite powder as a cathode material. The discharge potential at 60 °C was 2.5 V versus  $\text{Li/Li}^+$  at  $100 \text{ mAh g}^{-1}$ , and gradually decreased to 1.5 V at  $400 \text{ mAh g}^{-1}$ . This potential curve was below that in  $\gamma\text{-Fe}_2\text{O}_3$  [10]. At room temperature, the potential revealed about 1.7 V versus  $\text{Li/Li}^+$  at  $100 \text{ mAh g}^{-1}$  and decreased to 1 V versus  $\text{Li/Li}^+$  at  $400 \text{ mAh g}^{-1}$ . The potential curve at room temperature is almost the same as those of the cells using magnetite [5]. However, the potential at 60 °C is higher than 1.6 V, which is calculated from the reduction of  $\text{Fe}_3\text{O}_4$  with Li.



In order to explain this relatively high potential, following discussion will be required. In discharge, the surface of  $\text{Fe}_3\text{O}_4$  grain is covered with  $\text{Li}_2\text{O}$  and Fe. Nanograins of  $\text{Li}_2\text{O}$  and Fe metal separately exist on the surface of  $\text{Fe}_3\text{O}_4$  grain, like a CuO battery reported by Debart et al. [15]. In addition, OCV of this cell was measured as about 3.0 V, which is com-

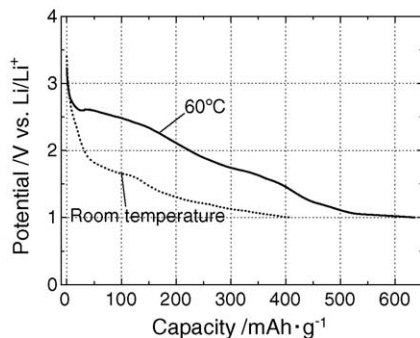


Fig. 1. Discharge curves of the cell using magnetite powder as a cathode material.

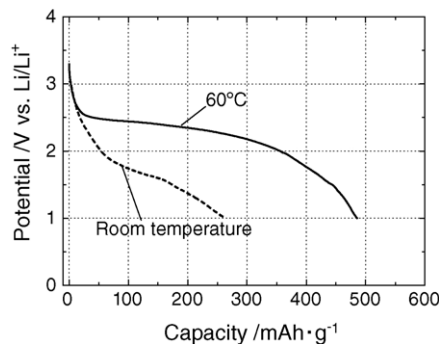


Fig. 2. Discharge curves for magnetite powders prepared with India ink. Magnetite: India ink (dried)=1:0.78 (in weight); current density:  $0.1 \text{ mA cm}^{-2}$ .

parable to the potential calculated from the oxidation of Li (Eq. (2)). Hence, the relatively high potential of this battery is due to the oxidation of lithium to form  $\text{Li}_2\text{O}$ . In order to bring out the high potential, both nanosized particles and nanosized conduction network are important. Hence, acetylene black was added to the solutions in the preparation process of magnetite powder. In this case, although the potential at room temperature was almost the same as that shown in Fig. 1, at 60 °C, the potential was improved to be 2.0 V versus  $\text{Li/Li}^+$  at  $300 \text{ mAh g}^{-1}$ . Fig. 2 shows the discharge curves for magnetite powders prepared with India ink (or Chinese ink), which contains carbon (soot) and gelatin or polyvinyl alcohol (PVA). The discharge potential at 60 °C was improved to be 2.0 V versus  $\text{Li/Li}^+$  at  $350 \text{ mAh g}^{-1}$ . Since India ink was added in the preparation process of magnetite, it seemed that the India ink increased the dispersion of the powder or formed the nanosized conduction network. Fig. 3 shows the discharge curves of the magnetite with India ink and acetylene black. Excellent discharge curve was obtained when the acetylene black was added to the magnetite prepared with the India ink. Discharge potential maintained 2.5 V versus  $\text{Li/Li}^+$  up to  $500 \text{ mAh g}^{-1}$ , 2.0 V at  $800 \text{ mAh g}^{-1}$  and finally decreased to 1.8 V at  $926 \text{ mAh g}^{-1}$ .

Table 1 shows the composition of the cathode active material after discharge and discharge/charge. Amounts of lithium corresponding to the capacity were quantitatively analyzed by

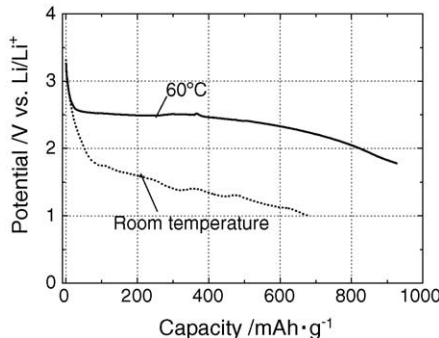


Fig. 3. Discharge curves for the magnetite with India ink and acetylene black. Magnetite: India ink = 1:0.78; current density:  $0.1 \text{ mA cm}^{-2}$ .

Table 1  
Compositions of the cathode active materials after discharge and charge

$x$ in $\text{Li}_x\text{Fe}_3\text{O}_4$	Composition	
	Room temperature (25 °C)	
	Room temperature (25 °C)	60 °C
2	$\text{Li}_{1.8}\text{Fe}_3\text{O}_4$	$\text{Li}_{2.0}\text{Fe}_3\text{O}_4$
2, 2 <sup>a</sup>	$\text{Li}_{0.10}\text{Fe}_3\text{O}_4$	$\text{Li}_{0.25}\text{Fe}_3\text{O}_4$
4	$\text{Li}_{5.3}\text{Fe}_3\text{O}_4$	$\text{Li}_{5.4}\text{Fe}_3\text{O}_4$
4, 4 <sup>a</sup>	$\text{Li}_{0.35}\text{Fe}_3\text{O}_4$	$\text{Li}_{1.3}\text{Fe}_3\text{O}_4$
8	$\text{Li}_{8.1}\text{Fe}_3\text{O}_4$	$\text{Li}_{8.8}\text{Fe}_3\text{O}_4$
8, 8 <sup>a</sup>	$\text{Li}_{1.0}\text{Fe}_3\text{O}_4$	$\text{Li}_{1.4}\text{Fe}_3\text{O}_4$

<sup>a</sup>  $x$  mol discharge/ $x$  mol charge.  $x$  was calculated from the current density and the charge or discharge time.

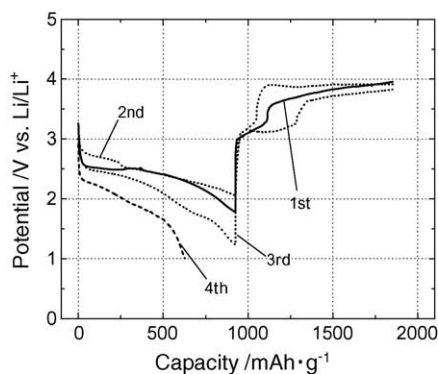


Fig. 4. Cycling test for the cathode material containing India ink and acetylene black.

ICP analysis. The amount of lithium  $x$  in  $\text{Li}_x\text{Fe}_3\text{O}_4$ , which is calculated from the amount of charge in discharge or in discharge/charge, was almost in agreement with the values measured by ICP analysis. Hence, lithiation and delithiation for  $\text{Fe}_3\text{O}_4$  were confirmed. However, a small portion of lithium was still in the cathode, after charge.

Fig. 4 shows the results of cycling test for the cathode material containing India ink and acetylene black. Charge was performed up to  $926 \text{ mAh g}^{-1}$ , in which the potential maintained below 4 V versus  $\text{Li/Li}^+$ . Similar potential curve was obtained in the second cycle. Although degradation was observed in the third cycle, cyclability was maintained. However, the test cell stopped in fourth discharge.

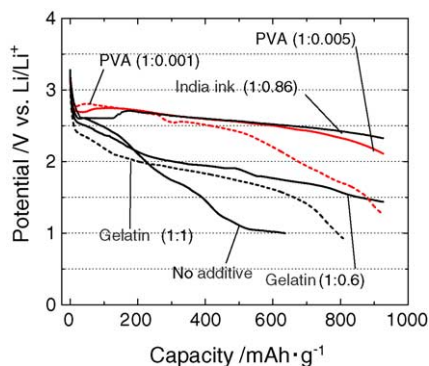


Fig. 5. Discharge curves for the  $\text{Fe}_3\text{O}_4$  cathode containing different additives.

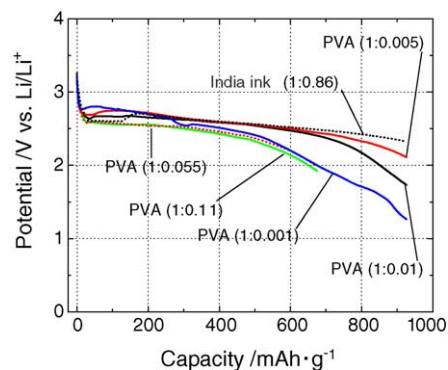
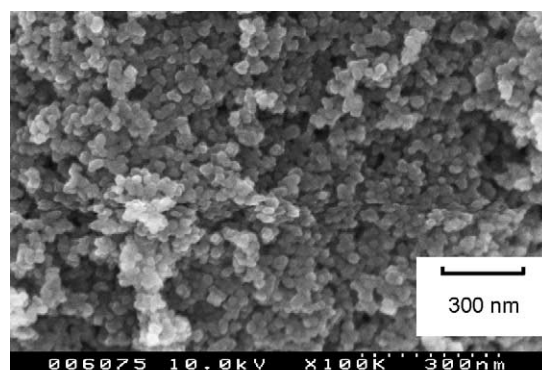
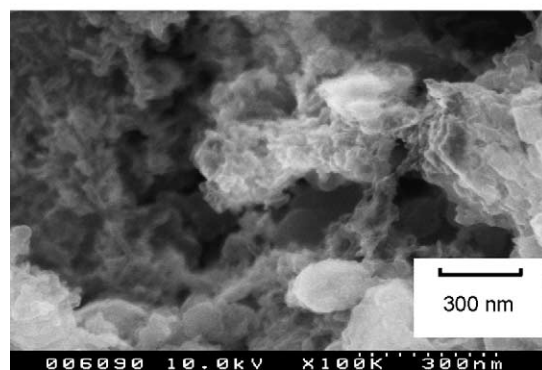


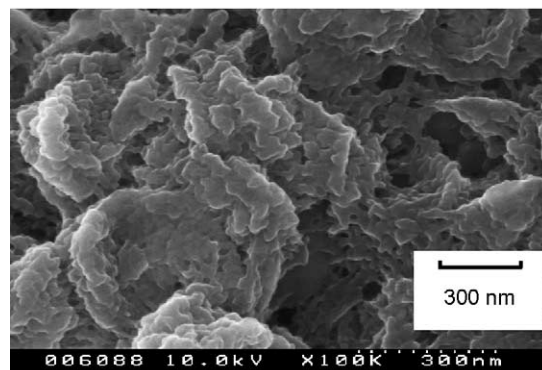
Fig. 6. Discharge curves for the  $\text{Fe}_3\text{O}_4$  cathode containing different amounts of PVA.



(a) Original powder



(b) Discharge(60°C, 8 mol)



(c) Discharge/charge(60°C, 8 mol)

Fig. 7. SEM photographs of cathode materials.

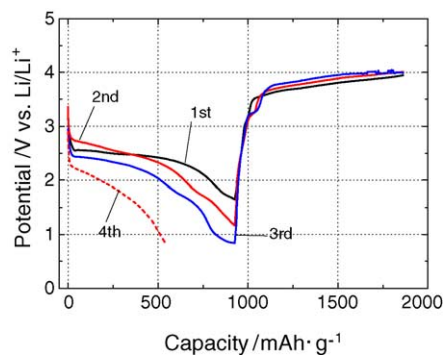


Fig. 8. Cycling test for the cathode material containing PVA and acetylene black.

### 3.2. Role of India ink and effect of PVA

Since the India ink is a commercial product used for the calligraphic works and paintings in Asian countries, its constituents are unclear. In order to study the role of India ink, gelatin and PVA, which are contained in the ink, were added respectively to  $\text{Fe}_3\text{O}_4$  fine powder. Fig. 5 shows the discharge curves of the  $\text{Fe}_3\text{O}_4$  cathode containing these additives. Adding gelatin, the discharge curves were improved, compared to the case of no addition. On the other hand, the discharge curve was largely improved by the addition of PVA. When the 0.005 portion (in weight) of PVA was added to the magnetite powder, the discharge potential was above 2.5 V versus  $\text{Li}/\text{Li}^+$  up to 600  $\text{mAh g}^{-1}$  and was 2.2 V versus  $\text{Li}/\text{Li}^+$  at 820  $\text{mAh g}^{-1}$ . Fig. 6 shows the discharge curves of the  $\text{Fe}_3\text{O}_4$  cathode containing PVA. Discharge curve with 0.005 portion of PVA was almost the same as that of the  $\text{Fe}_3\text{O}_4$  containing India ink. Fig. 7 shows SEM photographs of cathode materials. Original  $\text{Fe}_3\text{O}_4$  consisted of small particles with about 20 nm in size. Massart reported that the average grain size of the powder was 8 nm [14]. After the discharge of 8Li per  $\text{Fe}_3\text{O}_4$ , the particles became obscure. These unclear grains appear to be due to the microstructure containing nanograins of  $\text{Li}_2\text{O}$  and Fe. The shape of particles clearly revealed, after the charge of 8Li. This is due to the recrystallization of iron oxide [16]. Average particle size was slightly larger than that of the original powder. As shown in Fig. 8,

similar cyclability to the case of India ink addition was also confirmed. Hence, the role of India ink appears not to construct the conduction network, but to disperse the fine particles of  $\text{Fe}_3\text{O}_4$ .

## 4. Conclusions

In this study, the lithium batteries using  $\text{Fe}_3\text{O}_4$  fine particles as a cathode material were investigated at 60 °C. It is concluded that a large capacity over 800  $\text{mAh g}^{-1}$  with the discharge potential of 2.0 V versus  $\text{Li}/\text{Li}^+$  was achieved in the lithium battery, using India ink or appropriately PVA additive. According to the results of cycling test, this battery is expected to be a secondary battery by further development in nanostructure of the cathode.

## References

- [1] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [2] K. Ozawa, *Solid State Ionics* 69 (1994) 212.
- [3] M.G.S.R. Thomas, W.I.F. David, J.B. Goodenough, *Mater. Res. Bull.* 20 (1985) 1137.
- [4] M.M. Thackeray, J. Coetzer, *Mater. Res. Bull.* 16 (1981) 581.
- [5] M.M. Thackeray, W.I.F. David, J.B. Goodenough, *Mater. Res. Bull.* 17 (1982) 785.
- [6] L.A. de Picciotto, M.M. Thackeray, *Mater. Res. Bull.* 21 (1986) 583.
- [7] A. Manthiram, J.B. Goodenough, *J. Power Sources* 26 (1989) 403.
- [8] K. Amine, H. Yasuda, M. Yamachi, *J. Power Sources* 81/82 (1999) 221.
- [9] M. Takahashi, S. Tobishima, K. Takei, Y. Sakurai, *Solid State Ionics* 148 (2002) 283.
- [10] S. Ito, Y. Matsuura, T. Fujii, *Proceedings of the Eighth International Conference on Ferrites*, Jpn. Soc. Powder Powder Metall. (2000) 108.
- [11] S. Ito, S. Takahashi, Y. Omomo, Y. Matsuura, T. Fujii, *Trans. Mater. Res. Soc. Jpn.* 25 (2000) 55.
- [12] S. Ito, Y. Omomo, T. Fujii, *Bull. Chem. Soc. Jpn.* 74 (2001) 317.
- [13] D. Larcher, D. Bonnin, R. Cortes, I. Rivals, L. Personnaz, J.M. Tarascon, *J. Electrochem. Soc.* 150 (2003) 1643.
- [14] R. Massart, *IEEE Trans. Magn.* 17 (1981) 1247.
- [15] A. Débart, L. Dupont, P. Poizot, J.-B. Leriche, J.M. Tarascon, *J. Electrochem. Soc.* 148 (2001) 1266.
- [16] M.M. Thackeray, W.I.F. David, J.B. Goodenough, *J. Solid State Chem.* 55 (1984) 280.