Syntheses of Nanocrystalline Fe_2O_3 and Fe_3O_4 and Lithium Insertion into the Oxides

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Among the transition metals for electrochemistry, iron is most common element in the earth, harmless, inexhaustible, and cheap as an industrial raw material. Iron based oxides of FeOOH, Fe_2O_3, and Fe_3O_4, which are generally known to be contained in rust of corrosion products on metallic iron, also show electroactivity due to Fe(II)/(III) redox couple with lithiation/delithiation compensating for charge balance. Recently, Kim and Manthiram described that the lithium iron oxide of nanocrystalline $Li_xFe_yO_z$ was synthesized by oxidizing Fe(II) in the presence of lithium ion in aqueous solutions followed by heat treatment [1], and the synthetic optimization attained good charge-discharge cycling with a capacity of 140 mAh g^{-1}. One can understand that the nano-structure of crystallites and/or particles of the active material plays an important role, even though the active materials possess the identical atomic ordering; nanosize effects of cobalt- and copper-oxides [2]. Among numerous synthetic routes, a solution technique is essentially suitable for designing nano-structure of the battery materials, such as hydrothermal method [3], emulsion drying method [4], and precipitation [5]. When structural characterization of lithiated α-Fe_2O_3 and Fe_3O_4 was investigated by Thackeray *et al.* [6], their electrochemically reversible performances were not sufficient for the rechargeable battery application. In this paper, we found that nanocrystallite α-Fe_2O_3 and Fe_3O_4 powders, synthesized by precipitation in an aqueous medium at low temperature, demonstrated excellent cyclability which is expected for the application to a 'Li metal' battery cathode required for the IC memory back up.

For synthesis of α-Fe_2O_3, a $Fe(NO_3)_3$ solution was added to a LiOH solution, and then a Li_2O_2 solution was mixed at 0 ˚C [7]. The precipitate was filtered, washed with water, and then dried in air. Heat treatment of the precipitate was carried out. For precipitation of Fe_3O_4, a $FeCl_3/FeCl_2$ (molar ratio of $Fe^{III}/Fe^{II} = 2$) aqueous solution was deoxidized by bubbling with N_2 followed by adding a NaOH solution. The precipitate was filtered, washed with water, and then dried in air. Electrochemical investigation in Li cell was undertaken in 1 mol dm^{-3} $LiClO_4$ propylene carbonate (PC) at 25 ˚C. To investigate the dependence on particle size, commercially available α-Fe_2O_3 and Fe_3O_4 powders were treated by planetary ball milling to reduced their particle size.

After the heat treatment at 200 – 500 ˚C in air, the as-precipitated α-FeOOH was readily converted into α-Fe_2O_3 and γ-Fe_2O_3 which contained small amount of lithium. The sample of α-Fe_2O_3, which was obtained at 200 ˚C, demonstrated the highest discharge capacity *ca.* 200 mAh g^{-1} in the 2 – 3 V range with good cyclability, and the performance was quite different from that of commercially available Fe_2O_3 whose particle size is larger than that of precipitated one. From TEM observation, the as-precipitated α-FeOOH has the needle-like shape with 50 nm in length and 10 nm or less in diameter. As shown in Fig. 1, the sample at 200 ˚C consisted of very fine crystalline particles of α-Fe_2O_3 whose size was less that 10 nm in diameter, which suggested that the electrochemical performance was characterized by the nano-structure. Comparing the *ex situ* XRD patterns after electrochemical reaction, almost all the diffraction peaks would be maintained during the initial discharge/recharge. It is likely that the lithium insertion into nanosized α-Fe_2O_3 is a topochemical reaction, which does not agree with the previous work by Thackeray *et al.* who claimed that the phase transition from α-Fe_2O_3 into cubic spinel phase occurred with lithium insertion [6]. When the commercially available α-Fe_2O_3 powder was tested as a working electrode, the electrochemical activity was also enhanced after reducing particle size by ball milling treatment. Furthermore, we also obtained nanocrystalline Fe_3O_4 powder by the precipitation. From TEM observation, the particle size was 10 – 20 nm in diameter. The Fe_3O_4 electrode exhibited high electroactivity around 2 V. Therefore, we believed that the nanometric structure of the α-Fe_2O_3 and Fe_3O_4 plays an important role in determining and improving electrochemical lithium insertion.

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REFERENCES

[1] J. Kim and A. Manthiram, *J. Electrochem. Soc.*, **146**, 4371 (1999).
[2] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J-M. Tarascon, *Nature*, **407**, 496 (2000).
[3] S. Komaba, N. Kumagai, K. Kato, and H. Yashiro, *Solid State Ionics*, **135**, 193 (2000).
[4] S.-T. Myung, S. Komaba, and N. Kumagai, *J. Electrochem. Soc.*, **148**, A482 (2001).
[5] S. Komaba, N. Kumagai, and N. Kumagai, *Intercalation Compounds for Battery Materials* (Eds.G. A. Nazri, M. Thackeray, T. Ohzuku), The Electrochemical Society Proceeding Series, Pennington, NJ, **PV 99-24**, 68-80 (1999).
[6] M. M. Thackeray, W. I. F. David, and J. B. Goodenough, *Mat. Res. Bull*, **17**, 785 (1982).
[7] S. Komaba, K. Suzuki, and N. Kumagai, *Electrochemistry*, **70**, 506 (2002).

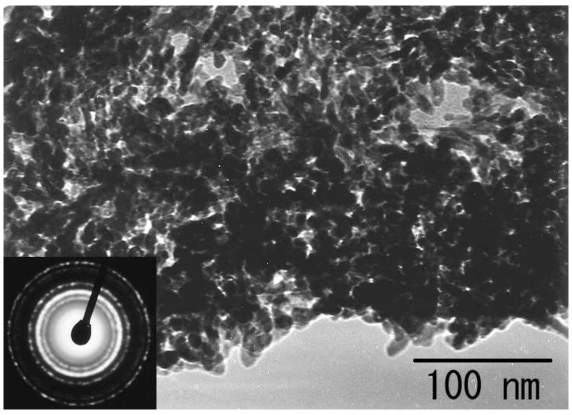

Figure 1 TEM bright field image and selected area diffraction pattern of nanocrystalline α-Fe_2O_3.