

## Characterization and Electrochemical Property of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles Prepared by Microwave Heating

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Ultrafine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with an extremely narrow distribution were prepared by microwave heating. The average diameter of the particles was approximately 7 nm. These nanoparticles were extremely stable in the colloidal state, even in the absence of stabilizers. The obtained  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles worked as a rechargeable electrode material. An initial discharge capacity exceeded 400 mA h g<sup>-1</sup> (cut-off voltage: 1.0 V).

Presently, LiCoO<sub>2</sub> is mainly used as a cathode active material for the lithium secondary battery. This material has some problems in resource depletion, in high cost, and in toxicity. Therefore, various kinds of alternative materials have been extensively explored.

Abundant binary iron oxides are one of the most ideal materials because of its low cost and low environmental impact. Recently, some nano-sized iron oxides have been reported to react with lithium in a reversible manner,<sup>1</sup> whereas it was difficult to use conventional large particles as a cathode material for lithium secondary battery.

Microwave heating has been known since the early 1940's, and has been used successfully in the food industry. Microwave heating through dielectric losses is fast and simple, uniform, energy efficient, and has been used in preparative chemistry and materials synthesis only since 1986.<sup>2</sup> Recently, there have been additional reported successes in using microwave irradiation to prepare high-purity nanoparticles with narrow particle size distributions.

The microwave synthetic method can be expected to prepare homogeneous and ultrafine nanoparticles of iron oxides with a high discharge capacity. In this letter, we report the prompt characterization and electrochemical property of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared by microwave heating.

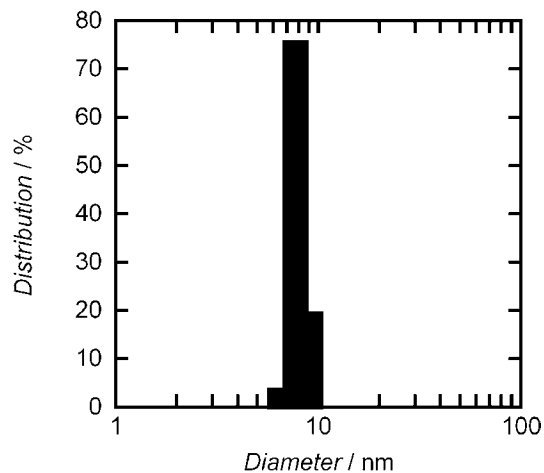
A household microwave oven, modified by Shikoku Keisoku Kogyo Co., was used to prepare the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. This microwave apparatus has a variable power output from 0 to 1200 W, operating at a frequency of 2.45 GHz. A thermo fiber sensor was inserted through a hole made in the ceiling of the oven, and the temperature inside the oven could be monitored and controlled during microwave irradiation. The temperatures were measured using a fiber optic thermometer (Anritsu Meter Co., Ltd., AMOTH FL-2000).

Reagent-grade Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O powder was purchased from Wako Pure Chemical Ind. Ltd. One-hundred cm<sup>3</sup> of 0.1 mol/dm<sup>3</sup> Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O solution was prepared and added to a round-bottomed glass flask in the microwave cavity. This flask was connected to a reflux condenser outside the oven through a port of the oven. The solution was agitated by a magnetic stirrer and irradiated with microwaves continuously for 120 s. The temperature of the solution was increased rapidly to

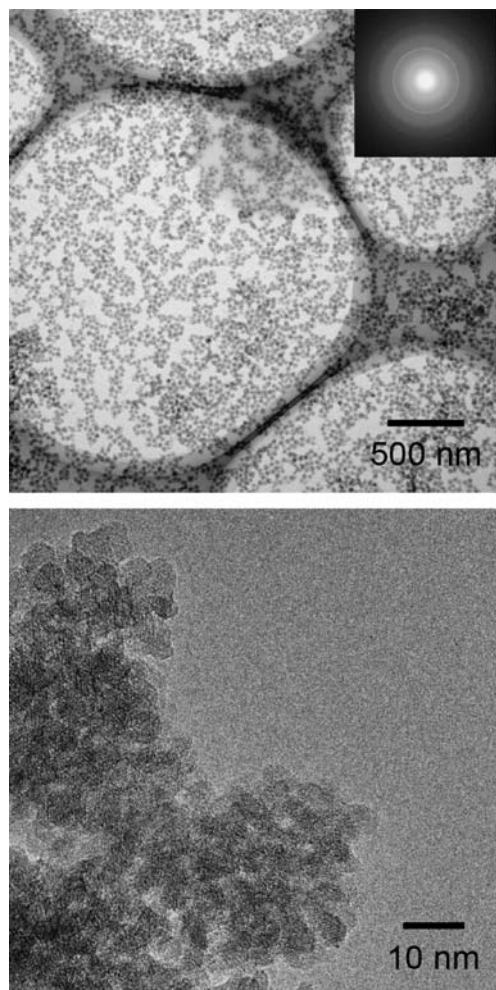
100 °C within 80 s, and the color of the solution was changed from bright yellow to wine red. The product in the solution was washed with deionized water and then freeze-dried. In this condition, the conversion ratio of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was about 47%.

The size distribution of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the microwave-irradiated solutions was obtained by the dynamic light scattering method performed with a Microtrac UPA 150 ultrafine particle analyzer. Transmission electron microscopy (TEM) images of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were taken with a HITACHI H-9000NAR microscope, operated at an acceleration voltage of 300 kV. The TEM images were recorded on the imaging plates at magnifications of 20,000 and 700,000 times. X-ray powder diffraction (XRD) data of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were taken with Cu K $\alpha$  radiation on a Bragg-Brentano-type powder diffractometer (Rigaku RINT-2550V).

An electrochemical test was performed at 25 °C with a stainless steel cell (HS flat test cell, Hohsen Co.) with lithium metal as the anode. The electrolyte was a 1 mol/dm<sup>3</sup> solution of LiPF<sub>6</sub> in blended ethylene carbonate (EC) and dimethyl carbonate (DMC) whose volumetric ratio was EC:DMC = 1:1. The cathode was a mixture of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>:acetylene black:poly(vinylidene fluoride), with the weight ratio of 4:2:1. The mixture was dispersed into the *N*-methyl-2-pyrrolidinone, and the slurry was cast on Al foil to form an electrode, which was dried at 120 °C for 1 day and then pressed under a pressure of 100 MPa. The cell was fabricated in a glove box filled with Ar gas (-88 °C dew point). Galvanostatic charge-discharge cycles were performed with a Solartron 1287 potentiostat/galvanostat.



**Figure 1.** Size distribution histogram of the number of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the microwave-irradiated solution. The data were obtained by the dynamic light scattering method.

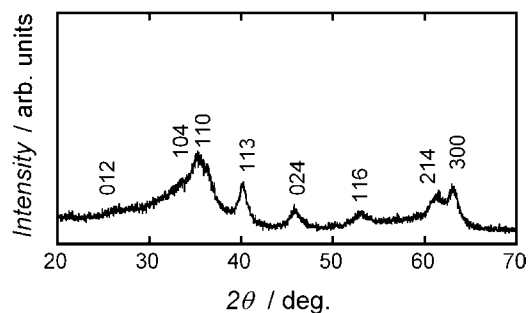


**Figure 2.** TEM images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles generated by microwave irradiation.

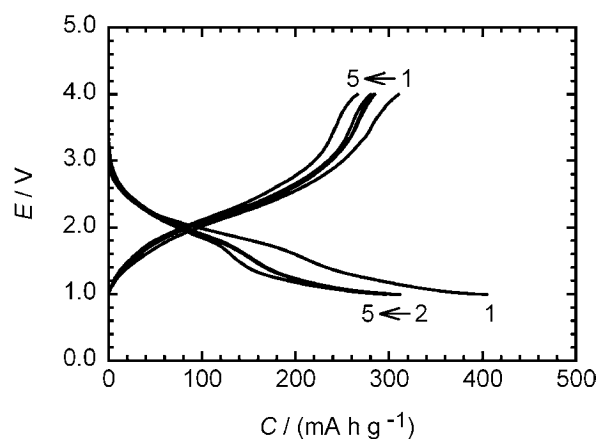
Figure 1 shows the size distribution histogram of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles in the solution microwave-irradiated for 120 s. The average diameter of the particles was approximately 7 nm with a relatively narrow distribution. Although no stabilizer existed in the solution, the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were extremely stable in the colloidal state.

Figure 2 displays TEM images of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Most primary particles had ellipsoid shapes. The average diameter of the primary particles was less than 10 nm at least, which is consistent with that obtained by the dynamic light scattering method. These primary particles connected to each other. This agglomeration would occur when the TEM specimens were prepared. The electron diffraction pattern and fringes in some particles showed that these nanoparticles were single crystals.

Figure 3 shows the XRD pattern of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Although the diffraction peaks were significantly broad because of the effect of particle size, the XRD pattern confirmed that the nanoparticles had a Hematite-type structure. From the Scherrer's equation, the approximative crystallite size of the nanoparticles was calculated at about 10 nm, which is reasonable agreement with the TEM observation.



**Figure 3.** XRD pattern of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles formed by microwave irradiation.



**Figure 4.** Charge–discharge curves for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles over the first 5 cycles; voltage: 1.0–4.0 V, and current rate: 10 mA/g.

Figure 4 presents the charge–discharge curves for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles over the first 5 cycles. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles worked as a rechargeable electrode material. An initial discharge capacity exceeded 400 mA h g<sup>-1</sup> (cut-off voltage: 1.0 V), and the discharge profile was characterized by a sloping voltage plateau. Subsequent rechargeable capacities of about 320 mA h g<sup>-1</sup> could be achieved, which shows that two Li<sup>+</sup> ions per Fe<sub>2</sub>O<sub>3</sub> can be reacted. As compared with other iron oxides reported previously,<sup>1</sup> our ultrafine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles showed the significantly high electrochemical performance because of its uniformity and smallness. This improvement demonstrates the advantage of microwave heating.

## References

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