Electrode properties of manganese oxide prepared sonochemically from acetone solution of KMnO₄

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INTRODUCTION

For the system in which not only high-energy but also high-power operation is required, such as pure and hybrid electric vehicles, it is crucial to develop auxiliary power sources for rapid discharge and charge. If lithium ion battery is applied to this use, its electrode materials should possess low-price, low-toxicity in terms of widespread diffusion as well as high electrode performance. Many manganese oxides have attracted the attentions as electrode materials of lithium ion battery because they can intercalate lithium and have above nature. With a view to rapid discharge and charge, an active material should be prepared in the form of microparticle and contact preferably with conducting additives. The microparticle of many materials has been prepared conveniently by sonochemical method, in which ultrasound is irradiated to a synthetic solution. It was previously found that the synthesis in an aqueous system lead inevitably to the presence of structural water in product. Without careful removal, residual water degrades cyclability of discharge and charge [1]. In this study, manganese oxides are synthesized sonochemically in non-aqueous system and examined as electrode materials.

EXPERIMENTAL

An acetone solution of potassium permanganate was irradiated by ultrasound (600 W of total power and 28 kHz in frequency) for 3 hours using bath-type ultrasound washer (Honda electronics, W-118T). The bath temperature was kept at 60°C. A small amount of gas was taken every 30 minutes and analyzed on GCMS. After sonication, a brown precipitate was filtrated, washed by methanol and dried at 120°C for 12 hour in vacuum.

Electrochemical measurements were performed using a three-electrode beaker cell. For working electrode, the sample was mixed with acetylene black and Teflon powders at a weight ratio of 1:1.0:0.06. The mixture was ground, spread and pressed on a nickel mesh. The reference and counter electrodes were lithium and an electrolyte was 1 M of EC and DMC solution (1:1, v/v) of lithium perchlorate. The electrode fabrication and the cell assembly were carried out in an argon gas system. The working electrodes were discharged and charged galvanostatically between 1.5 and 4.0 V (vs. Li/Li²⁺) under various current densities.

RESULTS AND DISCUSSION

The product contained manganese oxide and some by-products. The gas analysis in the reaction process and infrared spectra of the product revealed that permanganate ion oxidized acetone to acetate and oxalate ions, though the reaction detail has not been clarified yet. Some by-products such as potassium acetate could be removed by methanol, but other by-products, including unidentified ones, resided to some extent. The complete removal of such by-product remains a critical issue.

Figure 1 shows XRD profile of the sample after washed with methanol. The positions and intensities of peaks were similar to that of α-MnO₂. As indicated distinctly in Fig. 1, only k0 and 00l peaks appeared, implying that there existed a disorder in the direction of c-axis of α-MnO₂.

Figure 2 shows discharge and charge behaviors under 0.5 A g⁻¹ of current density. The shape of profile was similar to that for the manganese oxide synthesized from aqueous solution. [1, 2]. After the 2nd cycle, the discharge and charge profiles stayed unchanged against cycle repetitions. The relationship between specific capacity and current density are shown in Fig. 3. C-rates are also given in the figure. These C-rates are calculated on the basis of the assumption of 310 mAh/g as a theoretical specific capacity, which corresponds to the specific capacity in the case that all tetravalent manganese ion in MnO₄ are reduced to trivalent one. About 100 mAh/g of the specific capacity can be discharged even under high power operation of 17 C. These results show that the manganese oxide obtained sonochemically from potassium permanganate in acetone is expected to have a potential as a cathode material for rapid operation of lithium ion battery.

REFERENCES