Cycle Performance of Manganese Oxide / Carbon Composite Synthesized by Sonochemical Method

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Introduction

In resent years, high power battery has been intensively developed for an application to electric vehicles (EVs) or hybrid electric vehicles (HEVs). One approach for a development of such high power battery is an increase in the power density of lithium ion battery. In order to advance the power density, lithium diffusion length in active material should be shortened and electronic conductivity should be increased. We fabricated nanocomposite materials of hydrous sodium manganese oxide (HSMO) coating homogeneously on acetylene black (AB) or ketjen black (KB) as a conducting carbon using sonochemical method [1]. The manganese oxide / KB (S=1270 m^2 g^{-1}) composite exhibited enough high discharge capacity under large current densities (about 155 mAh g^{-1} under 10 A g^{-1}, based on the weight of composite, corresponding to about 65 C). These composites exhibited poor cyclability mainly due to dissolution of manganese into electrolyte. In this study, an effect of heat-treatment on the cycle performance of the manganese oxide / KB composite was investigated.

Experimental

Manganese oxide / KB (S=1270 m^2 g^{-1}) composite was fabricated from an aqueous solution of 1 M sodium permanganate ($NaMnO_4$) with carbon powder by sonication (100 kHz, 600 W, 25 °C, 3 hours). A pH of the solution was adjusted to 12 by 1M NaOH solution. Ketjen black (KB, S=1270 m^2 g^{-1}) was used as conducting additive. A bath-type ultrasound generator was used for the sonochemical reaction. After sonication, the suspension was filtered and washed several times using deionized water, and then dried at 120 °C in air for 12 hours. The obtained samples were heat-treated at 160 ~ 200 °C for 12 ~ 48 hours under dry air flow or in vacuum. The crystalline phase of the sample was identified from X-ray diffraction pattern using CuKα. A valence of manganese in the composite was determined by X-ray photoelectron spectroscopy (XPS).

For electrochemical measurements, a three-electrode cell was assembled in argon gas. For working electrode, the composite powder was mixed with 5 wt% of binder Teflon, ground, and pressed on a nickel mesh (100 mesh). Li metals on nickel mesh were used as counter and reference electrodes. An electrolyte was a 1 M $LiClO_4$ solution in equal volumes of ethylene carbonate (EC) and dimethyl carbonate (DMC).

Result and Discussion

An as-prepared sample contained 64 wt% manganese oxide. XRD indicated a presence of birnessite in the sample as shown in Fig. 1(a). After heat-treatment at 200 °C for 48 hours under dry air flow, the carbon content in the composite decreased to 17 wt%, and the change in the average valence of manganese was small. The obvious change in the crystal structure of manganese oxide was not observed in the XRD (Fig. 1(b)). After treatment at 200 °C for 24 hours in vacuum, Mn_3O_4 was appeared as shown in Fig. 1(c). This was supported by the fact that the increase of Mn(III) and the presence of Mn(II) were confirmed by XPS.

Figure 2 shows the variation in the discharge capacity of as-prepared and heat-treated samples between 1.5 and 4.0 V under 1.0 A g^{-1}. The current density and specific capacity were based on the weight of composite. The discharge capacity of the as-prepared sample decreased from 163 to 98 mAh g^{-1} during 20 cycles as shown in Fig. 2. The samples heat-treated in vacuum exhibited an obvious improvement of their cyclability. However, it was revealed that an excessive heat-treatment in vacuum caused a degradation of the initial capacity of composite due to the generation of the inactive Mn_3O_4.

References

[1] H. Kawaoka, M. Hibino and I. Honma, *Proceedings of 204th Meeting of the Electrochem. Soc.*, (2004) 350

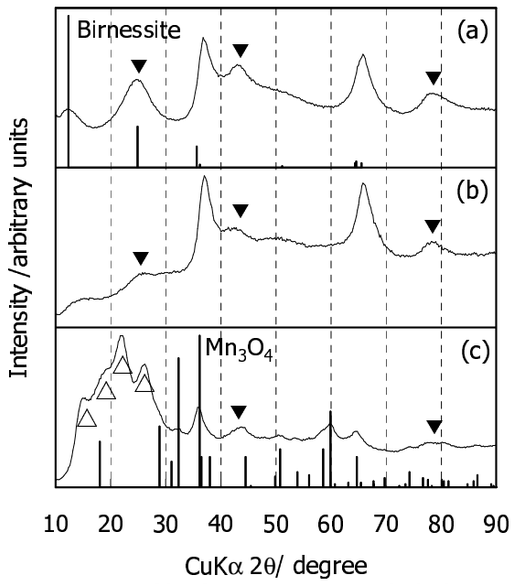

Fig. 1 XRD profiles for (a) as-prepared, (b) heat-treated (200 °C, 48 hours, in Air) and (c) (200 °C, 24 hours, in Vacuum). The closed and opened triangles indicate the peaks attributed to Ketjen black and Kapton® film, respectively.

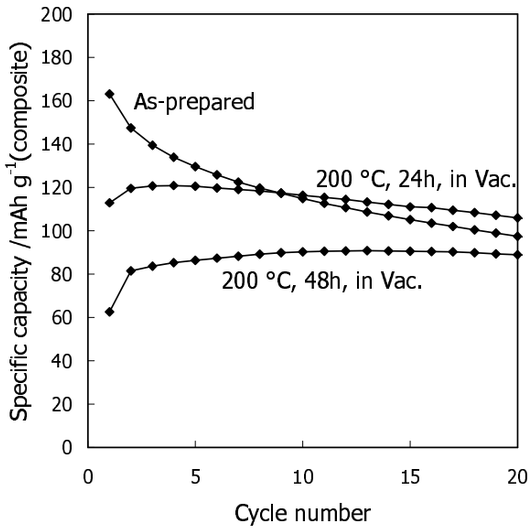

Fig. 2 Variation in discharge capacities of as-prepared and heat-treated samples.