Electrode properties of manganese oxide synthesized by sonochemical method in non-aqueous system

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Available online 31 May 2005

Abstract

Manganese oxide was prepared by an irradiation of ultrasound to an acetone solution of potassium permanganate. The chemical analyses of gas, solution and products have shown that the synthetic reaction was not peculiar to sonochemistry but similar to the reaction in the basic aqueous solution. The product contained manganese oxide and by-products such as acetate and oxalate. Those by-products were difficult to be removed thoroughly and a part of them resided even after wash. From XRD, the obtained manganese oxide was likely to be α-MnO$_2$. The product was examined as electrode material of lithium ion battery, and showed $180 \, \text{mAh g}^{-1}$ of specific capacity under $0.5 \, \text{A g}^{-1}$ of current density. Moreover, it could be discharged and charged under a high level of current density (ca. $100 \, \text{mAh g}^{-1}$ at $17C$). The capacity deterioration caused by cycle repetition was also found to be much small.
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Keywords: Manganese oxide; Sonochemistry; Lithium ion battery; Rapid discharge

1. Introduction

Manganese oxide and lithium manganese oxide have attracted much attention as electrode materials of lithium ion battery [1]. It, however, has pointed out that many of them tend to structurally deteriorate during repetition of discharge and charge [2–4]. It is known that the substitution of manganese partly by other species is effective way to improve the cycle performance through the stabilization of structure or reduction in volume change induced by discharge and charge. [5–7]. We have also synthesized manganese oxides by sol–gel or sonochemical method and examined them as cathode materials particularly in terms of rapid discharge and charge [8–10] and demonstrated that those sonochemical prepared could be discharged and charged quickly. Under $10 \, \text{A g}^{-1}$ of current density (corresponding to ca. $55C$), $185 \, \text{mAh g}^{-1}$ of capacity could be drawn. But these manganese oxides also exhibited poor cyclability. The specific capacity of manganese

oxide prepared by sol–gel method reduced to 70% of initial capacity after 100 cycles [9]. The manganese oxide fabricated by sonochemical method suffered 70% loss of initial capacity after 20 cycles [10]. It is known that manganese oxides synthesized in aqueous system often contain structural water [11,12]. If they are applied to electrodes and receive stimulus by repeated discharges and charges, such water would be released into electrolyte or solve the divalent manganese ion and the initial structure would erode, even if the structure including structural water is stable first. Consequently, the synthetic system without water is expected to be effective for low temperature preparation of manganese oxide as electrode material. Kim and Manthiram have reported that manganese oxide as electrode material was synthesized by a reduction of permanganate ion by LiI [13] or methanol [14] in acetonitrile. They found that the products synthesized showed the good cycle performance but included measurable by-products. With a view to fabricating materials in the form of microparticle enabling rapid discharge and charge, we adopt sonochemical method again not in aqueous system as described above but in non-aqueous system in this study.

The distinct chemical reactions are often caused by some radical species that are directly or secondarily induced by

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irradiation of ultrasound to aqueous solutions [15]. It is also known that the sonication is effective method for fabricating particle or composite on a microscale [16–18]. In this study, we expected that permanganate is reduced by some sort of radicals produced by sonication. The permanganate ion is very active oxidizer and many organic solvents can be readily oxidized. For emphasis of an effect of sonication, the solvent used should possess resistance to permanganate. Preliminarily, some organic solvents that were not easily oxidized by permanganate, such as acetonitrile and acetone were tested for potassium permanganate ($KMnO_4$). An irradiation of ultrasound to acetone solution of $KMnO_4$ without any reducing agents precipitated brown particles. Thus, sonication appeared to generate reducing materials or promote reduction of permanganate by acetone. This paper investigates the reaction of acetone with permanganate under sonication and electrode performance of the product.

2. Experimental

Potassium permanganate (1.185 g) was dissolved in acetone (100 ml) to be 75 mmol dm^{-3}. The acetone had been bubbled with Ar for 10 min beforehand. The solution was irradiated by ultrasound (600 W of total power and 28 kHz in frequency) for 3 h 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 min and analyzed with gas chromatograph (GC). After the sonication, a brown precipitate and a colorless and transparent solution were obtained. The precipitate was filtrated, washed by methanol or aqueous solution of methanol. After wash and filtration, it was dried at 120 °C for 12 h in vacuum.

The details of gas analysis are as follows. The amount of CO, CO_2 and CH_4 were determined by GC equipped with a methanation unit and flame ionization detector (FID). Oxygen, nitrogen and acetone were by GC with thermal conductivity detector (TCD). Presence or absence of other organic species was checked by GC-FID. For the solvent before and after the reaction, formaldehyde, acetaldehyde and water were quantitatively analyzed. The former two were converted to pentafluorobenzilhydroxylamine derivatives and subsequently analyzed with GC/MS. The latter was detected with GC-TCD. Presence or absence of other organic species in the solutions was checked by GC-FID.

For the powder obtained, infrared attenuated total reflection spectra and XRD profiles were taken. The chemical composition was determined from the combination of the results of inductively coupled plasma spectrometry (ICPS), CHN analysis and thermal gravimetry and differential thermal analysis (TG–DTA).

The samples were electrochemically measured using a three-electrode beaker cell. For working electrode, the sample was mixed with acetylene black and teflon powders at a weight ratio of 1:1:0.06. 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 assemble were carried out in an argon gas system. The working electrodes were discharged and charged galvanostatically between 1.5 and 4.0 V (versus Li/Li$^+$) under various current densities.

3. Results and discussion

When synthesis was executed at room temperature with sonication or when at 60 °C without sonication, only a small amount of product could be obtained. Thus, the reaction was facilitated by both the temperature and the sonication. Sonochemical reactions are often explained from cavitation collapse or microjet [19]. The former route is related to γ-radiolysis and the latter to shock tube thermolysis [20]. It is known that the γ-radiolysis decomposes acetone to methyl radical and acetyl radical, leading to a generation of methane, carbon monoxide and other organic species [21–23]. The shock tube thermolysis generates methane and other organic species from acetone [24,25]. The analyses of gas picked up in the reaction are summarized in Table 1. Almost no amount of methane was detected. Accordingly, it is deduced that the reaction route was similar to neither γ-radiolysis nor shock tube thermolysis. Here, photolytic route resembling γ-radiolysis [26] is also ruled out. Though the reaction route in which molecular oxygen oxidize acetone is also known [27], it cannot be reasonably assumed, because no oxygen was detected in the gas analysis. While a trace amount of propane was found in gas analysis, no organic product other than acetone, CO, CO_2 and such propane was detected in the reaction gas. The solution after the reaction showed no organic product other than acetone. Water contents of the solution before and after the reaction were determined to be 0.029 ± 0.009 and 0.035 ± 0.004 wt.%, respectively, indicating no increase in water content in the solution. On the other hand, in an aqueous basic solution, acetone is able to be oxidized by permanganate to acetic acid and even to oxalic acid with the formation of H_2O, CO and CO_2 [28]. The gas generation of this route was limited only to CO or CO_2. Assuming that CO and CO_2 generate together, those reactions are summarized as following:
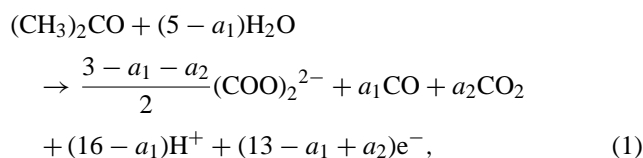
$$(CH_3)_2CO + (5 - a_1)H_2O$$
$$\rightarrow \frac{3 - a_1 - a_2}{2}(COO)_2{}^{2-} + a_1CO + a_2CO_2$$
$$+ (16 - a_1)H^+ + (13 - a_1 + a_2)e^-, \qquad (1)$$

Table 1
The results of the gas analysis in reaction

	Acetone (as purchased)	Sonication period (min)			
		0	30	60	120
CO (vol%)	<0.036	< 0.017	0.236	0.475	0.677
CO_2 (vol%)	0.021		0.139	1.29	1.80	2.16
CH_4 (vol%)	0.007		0.009	0.006	0.007	0.009
C_3H_8 (vol%)	–		–	–	–	0.003
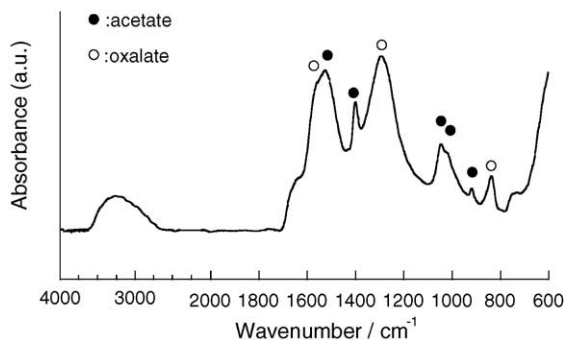
Fig. 1. Infrared spectra (ATR-IR) for the sample before wash.

$$(CH_3)_2CO + (2 + b_2)H_2O$$

$$\rightarrow \frac{3 - b_1 - b_2}{2}(CH_3COO)^- + b_1CO + b_2CO_2$$

$$+ \frac{11 + 3b_1 + 7b_2}{2}H^+ + (4 + 2b_1 + 4b_2)e^-. \qquad (2)$$
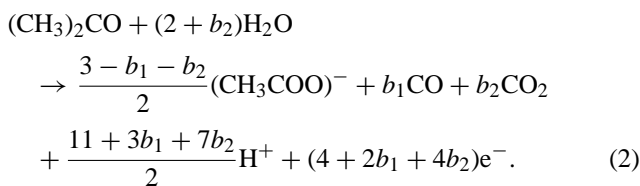
Infrared spectra of the product before washing is shown in Fig. 1. The absorbance bands around 730, 1300 and 1600 cm^{-1} are attributable to oxalate. The bands at 920, 1007, 1045, 1410 and 1560 cm^{-1} are to acetate [29]. The bands due to water can be observed at 3250 and 1620 cm^{-1}. Since no increase in water content in the solution was found as described above, generated water should be captured by the precipitation. These IR results indicate the generation of oxalate, acetate and water and support the above reactions (1) and (2).

Now, we evaluate quantitatively the reactions (1) and (2). As shown in Table 1, while a production of CO and CO$_2$ increases with reaction period, the amounts of them are very small. Let us suppose that they are negligible (corresponding to $a_1 = a_2 = b_1 = b_2 = 0$ in the above reactions (1) and (2)) and that permanganate ion is reduced to manganese dioxide, the calculation of redox equivalence gives the following relation:
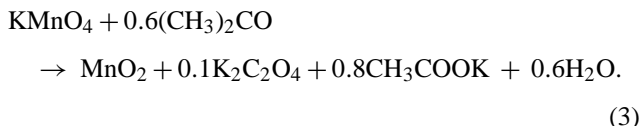
$$KMnO_4 + 0.6(CH_3)_2CO$$

$$\rightarrow MnO_2 + 0.1K_2C_2O_4 + 0.8CH_3COOK + 0.6H_2O. \qquad (3)$$

Assuming that the precipitate contained all the products in the reaction (3), the composition is estimated and compared with experimental result in Table 2. They are found to be consistent well. The compositions for the sample washed with methanol and with water are also tabulated. This calculation of composition is based on the assumption that water can remove both acetate and oxalate and that methanol removes acetate completely but oxalate partly. The experimental and calculated results are in good agreement. This indicates that washing with methanol removed water and that the sample containing no water was synthesized as intended, though oxalate resided. In contrast, washing with water gave rise to incorporation of water in manganese oxide, though no organic remnant resided.

Because of the above quantitative chemical compatibility, it is concluded that ultrasound encourage the reaction similar to that invoked in aqueous basic solution. The manganese oxide earlier precipitated may accelerate this reaction catalytically [30]. The reaction peculiar to the sonochemistry, in terms of the reaction through the cavitations, seemed not to be main route, though the detection of trace amount of methane and propane, as described previously, may indicate generation of some radicals due to irradiation of ultrasound. Some effects such as a vigorous stirring may play an important role [15]. The disappearance of the sonolysis-specific reaction through a collapse of cavitation is probably related closely to the fact that acetone has a poor intensity of sonoluminescence under an irradiation of ultrasound [31].

Fig. 2 shows XRD profiles for the samples before and after methanol wash. They are similar and only a few broad peaks appeared. The peaks of α-MnO$_2$ (JCPDS No. 44-0141) are drawn in the figure, particularly *hk*0 and 00*l* are prominently shown. The observed profiles seemed to correspond to *hk*0 and 00*l* peaks of α-MnO$_2$. Such a selective appearance implies a presence of disorder in the *c* direction or random stacking structure. Cryptomelane, which has the same framework with [2 × 2] tunnels as α-MnO$_2$, contains potassium ions in the tunnels [32]. Since this synthesis employed potassium permanganate as a starting material, there might be potassium ions in the tunnel. The obtained manganese oxide may have to be described as cryptomelane, K$_x$MnO$_2$, though *x* is small.

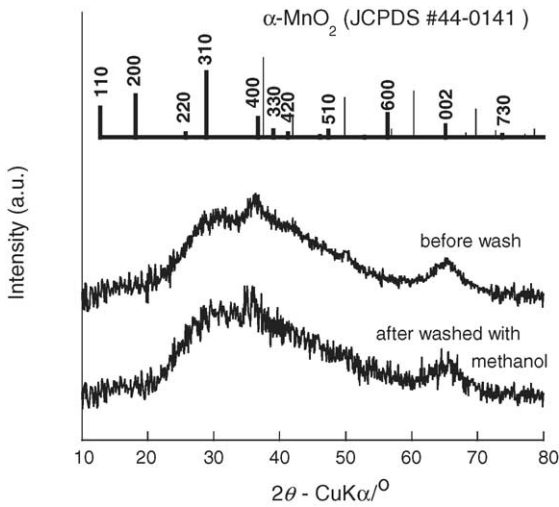Fig. 3 is a scanning electron micrograph of the methanol-washed sample. The particles are found to be small and a

Table 2
The experimental results and calculations of the chemical composition

Sample	K	Mn	C	H	O
Experimental product	0.985(9)	1.00	1.76(2)	3.53(3)	4.54(13)
MnO$_2$·0.1K$_2$C$_2$O$_4$·0.8CH$_3$COOK·0.6H$_2$O (Calc.)	1.00	1.00	1.80	3.60	4.60
After washing with methanol	0.235(2)	1.00	0.27(0)	0.10(1)	2.58(8)
MnO$_2$·0.1K$_2$C$_2$O$_4$ (Calc.)	0.2	1.00	0.2	0	2.4
After washing with water	0.011(1)	1.00	0.05(0)	1.79(2)	2.95(9)
MnO$_2$·0.95H$_2$O (Calc.)	0	1.00	0	1.80	2.95

The molar ratios of each component to manganese are expressed.

Fig. 2. XRD profiles for the sample before and after washing with methanol.

Fig. 3. SEM photograph of the methanol washed sample.

few ten nanometers in size, implying a prompt electrochemical reaction if applied to electrode material. In this figure, the manganese oxide and the organic by-products such as oxalates cannot be distinctively observed. The organic remnants may cover the manganese oxide. In that case, an electrode fabricated by mixing this material and a conducting additive (AB) would have a poor contact condition between manganese oxide and AB. This probably degrades electric
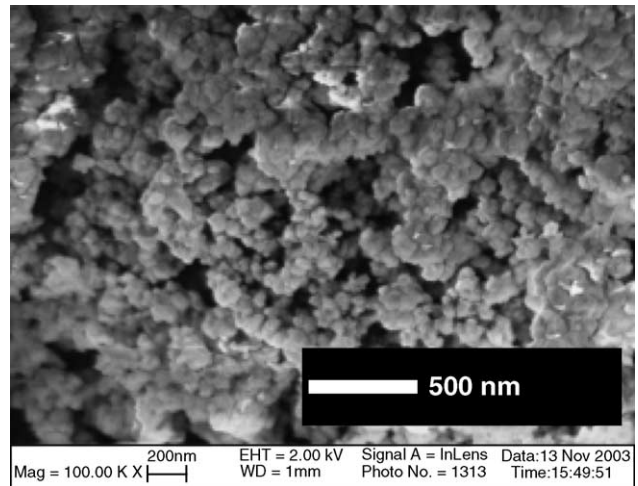
conductance of electrode and rapid discharge–charge performance. Furthermore, the residual by-products were responsible for weight increase and may result in electrochemical side reaction. The former reduces specific capacity and the latter leads to a poor cyclability. Then, such by-products should be eliminated thoroughly or minimized at least. Though the oxalate, which is not removed completely with methanol as stated above, can be extracted with water, washing the
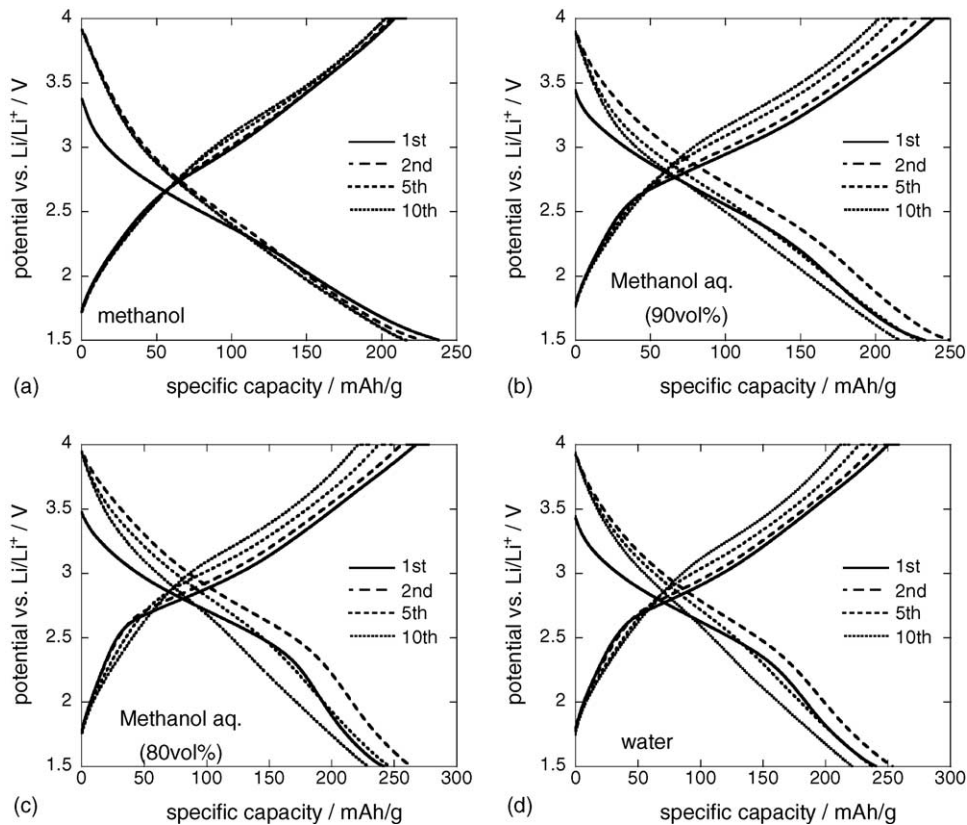

Fig. 4. The discharge and charge profiles for the samples washed with (a) methanol, (b) and (c) methanol–water, and (d) water.

sample with water diminishes the advantage of synthesis in an organic system. Because oxalate is difficult to be eluted by other solvent, methanol–water solutions as well as pure methanol were tested as washing liquid.

The discharge and charge behaviors under $0.5\,A\,g^{-1}$ are depicted in Fig. 4(a–d). The contribution of the KB, which was included in each electrode at ca. 50 wt.%, to the specific capacity was estimated to be ca. $32\,mAh\,g^{-1}$ from another experiment beforehand. The all profile shapes in Fig. 4 are basically similar to that of the samples prepared in an aqueous system [8–10]. The initial value of specific capacity is enlarged with increase in water content in washing liquid. This is explained by the removal of by-products and the increase in the content of active material. However, the specimen washed solely with methanol retains specific capacity after second cycle, whereas the others suffer capacity decline with cycle repetition. Fig. 5 shows the variation in the specific capacity against the cycle number. The sample washed with methanol exhibits a good cycle performance. It was revealed that the wash with the water-added methanol deteriorated cycle performance and that the water addition above 20 vol% reduced cycle performance to the level in the water-washed sample. This is probably because the added water not only dissolved the by-products but also reacted with manganese oxide. Accordingly, the by-products have not yet been eliminated properly at this stage. But, it should be noted that the manganese oxide prepared sonochemically with acetone exhibited a good cycle performance with $180\,mAh\,g^{-1}$ of the specific capacity.

The relationship between the specific capacity for the sample washed with methanol and current density is shown in Fig. 6. C-rates are also denoted. The C-rate is the calculation on the basis of $310\,mAh\,g^{-1}$ of the theoretical specific capacity, in which all manganese ions in MnO_2 are reduced from tetravalent state to trivalent. This material attained a specific capacity of ca. $100\,mAh\,g^{-1}$ on the operating condition of

Fig. 6. Specific capacity for the methanol washed sample as a function of current density.

$17C$ and turned out to be a promising one for rapid discharge and charge.

4. Conclusions

Manganese oxide was synthesized by an irradiation of ultrasound to the acetone solution of $KMnO_4$. From the XRD profile, the manganese oxide thus obtained was likely to be of α-MnO_2 family. Though the detail reaction route has not been clarified yet, it is reasonable to suppose that permanganate ion oxidized acetone to acetate and oxalate. Such reaction is not peculiar to sonochemistry but similar to the reaction in the basic aqueous solution. Whereas the product thus obtained had a similar discharge and charge profile to the specimens fabricated by sol–gel or sonochemical method in aqueous system, it exhibited a good cycle performance. The product, however, included by-products such as oxalate, which could be removed only partly at this stage. If these by-products can be eliminated thoroughly, the specific capacity might be enhanced more than the present result of ca. $180\,mAh\,g^{-1}$. It is also found that the product can be discharged and charged under a high level of current density (ca. $100\,mAh\,g^{-1}$ at $17C$).
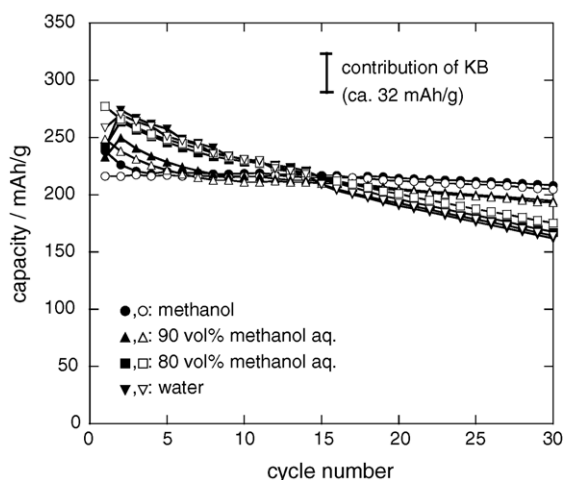

Fig. 5. The specific capacity for the samples washed with various solutions against cycle number. Closed and open symbols are for discharge and charge capacities, respectively.
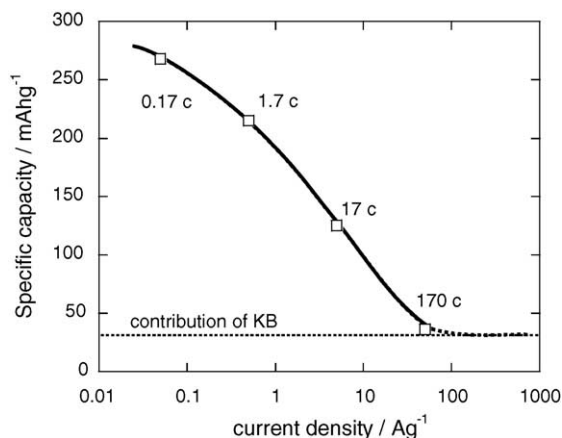
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