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Effects of manganese acetate on the anodic performance of carbon nanotubes for Li ion rechargeable batteries

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Abstract

Effects of the addition of various manganese compounds on anodic performance of carbon nanotube were investigated. It was seen that the Li intercalation capacity decreased drastically by the addition of most manganese compounds. However, addition of $Mn(CH_3COO)_2$ greatly improved the capacity for Li intercalation. Li intercalation capacity increased with increasing $Mn(CH_3COO)_2$ concentration and the largest capacity of 360 and 330 mAh/g for the insertion and reversible Li intercalation was achieved when 1 wt.% $Mn(CH_3COO)_2$ was added. The increased capacity was sustained after 50 times of charge and discharge cycles. X-ray absorption near edge spectra (XANES) suggests that the state of added Mn ion is close to MnO_2 and so the added $Mn(CH_3COO)_2$ decomposed during preparation. The surface organic layer formed by the acetic acid appears to give a superior solid electrolyte interface (SEI). The positive effects of $Mn(CH_3COO)_2$ are obtained only when manganese ion and acetic acid coexist. Therefore, it is believed that the coexisting Mn ion works as a catalyst for the decomposition of acetic acid.
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1. Introduction

Li ion rechargeable batteries are now used widely as an electric source for mobile equipment such as mobile phone or laptop computer. At present, $LiCoO_2$ and graphitic carbon are generally used for the cathode and anode of commercial batteries, respectively [1]. In order to improve the capacity and to decrease the cost, alternative cathode materials containing Mn such as $LiMn_2O_4$ or $LiMnO_2$ are investigated extensively [2–4]. In particular, from the viewpoint of potential and capacity, $LiMn_2O_4$ doped with Ni is strongly expected as an alternative cathode material of Li ion rechargeable battery [5]. However, small amount of Mn is eluted into electrolyte, in particular, at high temperature resulting in the significant capacity fading [6–8]. Since it is reported that the capacity of not only the cathode but also the anode decrease by the elution of Mn ion from Mn-based oxide cathode [9], the influences of eluted Mn on the anodic performance of carbon are an important subject. However, effects of coexisting Mn acid have not been studied thoroughly. In our previous study, we investigated the Li inter-

calation into graphitic carbon nanotube and it was found that carbon nanotubes obtained by the decomposition of CH_4 exhibit good anodic properties and are usable as anodes for Li ion rechargeable batteries [10,11]. In this study, effects of various Mn compound on the anodic performance of graphitic carbon nanotube were investigated. Since positive effects on anodic performance were observed by the addition of $Mn(CH_3COO)_2$, effect of $Mn(CH_3COO)_2$ was investigated in detail in this study.

2. Experimental

Graphitic carbon nanotube material was obtained by the decomposition of CH_4 with Ni/SiO_2 catalysts at 973 K for 6 h. Ni/SiO_2 catalyst was obtained by the impregnation of $Ni(NO_3)_2$ in aqueous solution and SiO_2 with BET surface area 380 m^2/g (Aerosil Co. Ltd.) was used for the support. The obtained catalyst was calcined at 723 K for 3 h in air and then reduced in H_2 flow (40 ml/min) at 773 K for 3 h. Decomposition of CH_4 into carbon was performed with the conventional fixed-bed reactor at 973 K. One gram of Ni/SiO_2 catalyst was used and the commercial CH_4 without any purification was fed to the catalyst bed at feed rate of

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50 ml/min. Deposited carbon was separated from the catalyst by dissolving the catalyst in 1 M HF at room temperature. After removal of the Ni/SiO$_2$ catalyst, the obtained carbon nanotube was filtered and dried at 343 K for 6 h. Addition of Mn was carried out by impregnation of thus obtained carbon tube with various manganese compounds in aqueous solution. One weight percent Mn compound based on carbon nanotube was added unless otherwise specified. Aqueous solution of Mn compound was dissolved into water and added to the carbon nanotube suspended water. After mixing, water was evaporated and the sample was finally dried at 343 K for 6 h.

The anodic performance of carbon nanotube was measured by applying the constant current (0.4 mA/cm^2) in the potential window of 0.0–1.5 V. For the counter electrode, Li metal was always used and the details of the used cell was described in our previous paper [10]. Each carbon sample was mixed with ethylene-propylene-dimethyl monomer (EPDM) in cyclohexane and then pressed into a stainless-steel grid on the stainless-steel plate as an anode. Polypropylene (PP) was used as separator and EC-DMC (1:2) dissolved with 1 M LiPF$_6$ (Ube Co. Ltd.) was used for the electrolyte. In this study, Li intercalation capacity and de-intercalation on the first cycle are defined as the insertion capacity and reversible capacity, respectively.

3. Results and discussion

Table 1 summarizes the effects of the manganese compound (1 wt.% based on carbon material) on the Li intercalation capacity of carbon nanotube at the first cycle. The used carbon nanotube is a multiwalled one and exhibits 352 and 268 mAh/g for the insertion and reversible capacity respectively. As summarized in Table 1, it is seen that addition of MnCl$_2$ and Mn(NO$_3$)$_2$ decreased the reversible capacity for Li intercalation. In particular, Li intercalation capacity decreased dramatically by addition of Mn acethylacetone (Mn–C$_{10}$H$_{14}$O$_4$). In addition, the cycle stability also decreased by addition of small amount of these compounds. Consequently, when a Mn-based oxide such as LiMn$_2$O$_4$ is used for cathode of Li ion battery, elution of a small amount of manganese ion from the Mn-based cathode causes the serious negative effects on the anodic performance of carbon
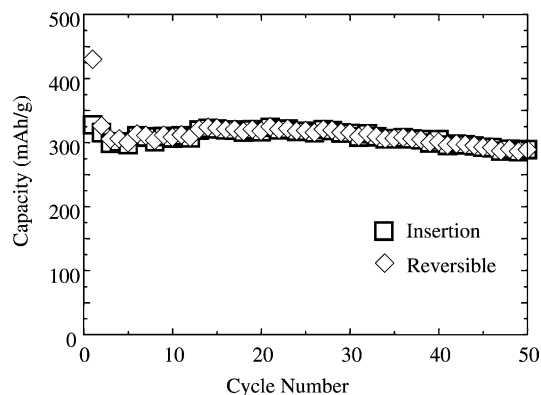

Fig. 1. Cycle stability of Mn(CH$_3$COO)$_2$ added carbon nanotube.

anode. On the other hand, it is highly interesting that the Li intercalation capacity for insertion as well as the reversible capacity increased by addition of Mn(CH$_3$COO)$_2$. Therefore, coexisting Mn(CH$_3$COO)$_2$ seems to give the positive effects on the Li intercalation capacity.

The cycle stability of Mn(CH$_3$COO)$_2$ added carbon nanotube was shown in Fig. 1. It was seen that the improved capacity was sustained over 40 cycles of charge and discharge. Therefore, the positive effects of Mn(CH$_3$COO)$_2$ addition are stably sustained during charge and discharge cycles. After 50 charge and discharge cycles, the reversible capacity was 320 mAh/g which is 1.4 times larger capacity than that of carbon naotube without modification, and also the coulombic efficiency was as high as 100% after second cycle. Therefore, it can be said that Mn(CH$_3$COO)$_2$-containing carbon naotube exhibits superior anodic performance. The positive effects of Mn(CH$_3$COO)$_2$ addition were studied in further detail in this study.

Fig. 2 shows the Li intercalation and reversible capacity as a function of the amount of Mn(CH$_3$COO)$_2$ addition. It is seen that the capacity for Li intercalation increased with increasing the amount of Mn(CH$_3$COO)$_2$ and attained the maximum at 1.0 wt.%. Further increase in the amount of

Table 1
Effects of Mn compound added to carbon nanotube on the electrochemical intercalation of Li at first cycle

Added Mn acid	Insertion capacity (mAh/g)	Reversible capacity (mAh/g)	Coulomb efficiency (%)
Non-addition	352.3	268.1	76.1
MnCl$_2$	402.2	264.9	65.9
Mn(NO$_3$)$_2$	379.8	253.0	66.6
Mn–C$_{10}$H$_{14}$O$_4$	190.1	128.3	67.5
Mn(CH$_3$COO)$_2$	429.9	327.7	76.2

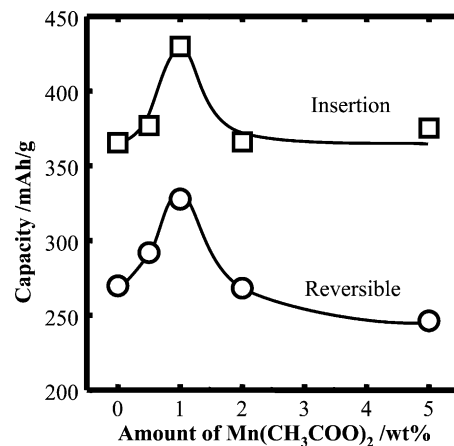Amount of additives; 1 wt.% based on carbon.

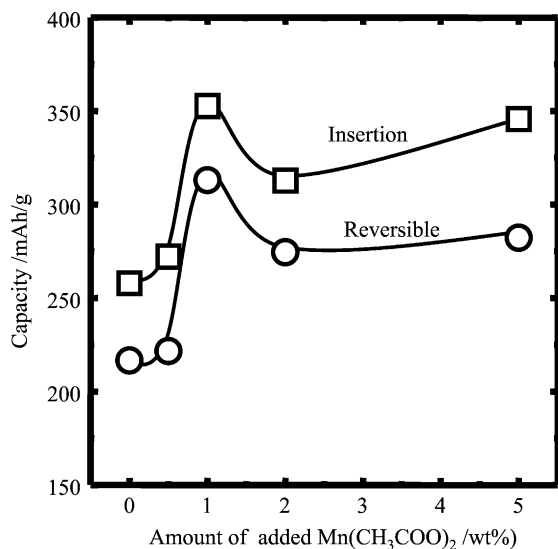Fig. 2. Li intercalation and reversible capacity as a function of the amount of Mn(CH$_3$COO)$_2$ addition.

Fig. 3. Insertion and reversible capacity of the filament-type graphitic carbon, FM14 as a function of the amount of added $Mn(CH_3COO)_2$.

Fig. 4. Charge–discharge curve of CH_3COOH, CH_3COOLi and $Mn(CH_3COO)_2$ added carbon nanotubes.

$Mn(CH_3COO)_2$ addition decreased the Li intercalation capacity. Therefore, the optimum amount of $Mn(CH_3COO)_2$ addition seems to be 1.0 wt.%. An increase in the Li intercalation capacity by addition of $Mn(CH_3COO)_2$ may be brought about by the formation of organic film-like solid electrolyte interface (SEI) of which the structure in the organic part is close to those of carbonate, carboxylic acids or ketones [12]. On the other hand, a decrease in Li intercalation capacity for an excess amount of $Mn(CH_3COO)_2$ addition seems likely to be caused by the excess thickness of the organic layer. In any case, it was found that the most positive effect of $Mn(CH_3COO)_2$ was obtained at 1 wt.% addition.

In order to confirm the positive effects of $Mn(CH_3COO)_2$ addition, effects of $Mn(CH_3COO)_2$ on another type carbon was investigated in this study. Fig. 3 shows the insertion and reversible capacity of the filament-type graphitic carbon, FM14 (Petoka Materials. Ltd.) [13] as a function of the amount of $Mn(CH_3COO)_2$ added. In similar manner to the homemade carbon nanotube, Li intercalation capacity increased with increasing amount of $Mn(CH_3COO)_2$ and attained a maximum value at 1 wt.%. Therefore, it is obvious that the addition of $Mn(CH_3COO)_2$ shows positive effects on the Li intercalation capacity on the graphitic carbon anode. It is reported that the SEI layer consists of the organic and inorganic layers and the organic layer is believed to contain the carbonate, carboxylic acid and/or ketone like compounds which form from the organic liquid electrolyte [14]. Because of the similar molecular structure of CH_3COOH, the positive effects of $Mn(CH_3COO)_2$ addition may be brought about by coating of the SEI-like organic film from CH_3COO^-.

Fig. 4 shows the charge–discharge curve of CH_3COOH, CH_3COOLi and $Mn(CH_3COO)_2$ added carbon nanotubes. Although the same carbon nanotube is used, Li intercalation
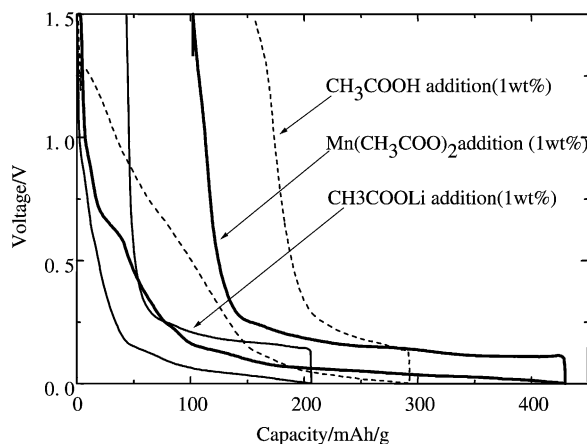
capacity was greatly affected by the added compounds. As discussed earlier, Li intercalation capacity increased by addition of $Mn(CH_3COO)_2$, however, it greatly decreased by the addition of CH_3COOH only or CH_3COOLi. Therefore, not only CH_3COO^- but also Mn ions are essential for the positive effects on Li intercalation capacity. This may suggest that the coexisting Mn works as a catalysts for the decomposition of CH_3COO^- into a SEI-like organic layer.

In order to estimate the oxidation condition of Mn cation after addition to carbon nanotube, X-ray absorption near edge spectra (XANES) was measured in this study. Fig. 5 shows the Mn XANES spectra of Mn on carbon nanotube added with $Mn(CH_3COO)_2$, MnO_2, and $Mn(CH_3COO)_2$ as references. It is clear that the energy of absorption edge of Mn^{4+} is higher than that of Mn^{2+} and the pre-edge peak of X-ray absorption more clearly appeared on Mn^{4+} compared with that of Mn^{2+}. Comparing the XANES spectra of Mn^{2+} in $Mn(CH_3COO)_2$, it is seen that the Mn-XANES of Mn on
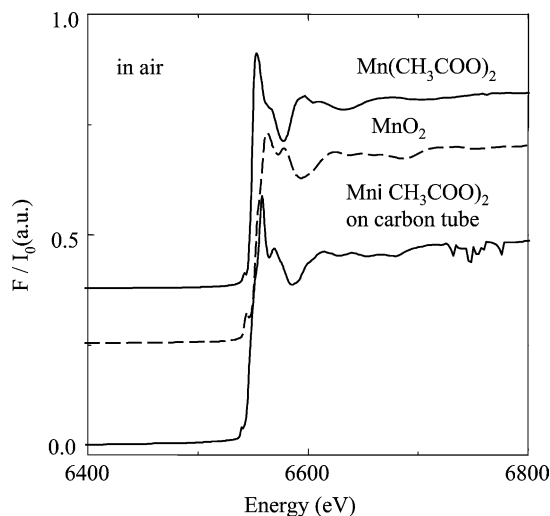

Fig. 5. Mn XANES spectra on carbon nanotube added with $Mn(CH_3COO)_2$, MnO_2, and $Mn(CH_3COO)_2$.

carbon nanotube is close to that of MnO_2. This suggests that the added $Mn(CH_3COO)_2$ decomposed during preparation and the state of Mn cation on the carbon nanotube is close to MnO_2. These data also support the prediction that Mn works as the catalyst for the decomposition of CH_3COO^- to form the SEI-like organic layer on the surface of carbon nanotubes. It is noted that ESR is highly sensitive to Mn^{3+}. However, in agreement with the XANES data, no ESR signal assigning to Mn^{3+} species were observed. Consequently, this study revealed that the addition of $Mn(CH_3COO)_2$ is effective for improving the capacity for Li intercalation into graphitic carbon.

4. Conclusion

Although Mn compounds generally decrease the Li intercalation capacity, it was found that addition of $Mn(CH_3COO)_2$ improved the Li intercalation capacity of carbon nanotubes. The Li intercalation capacity increased with an increasing amount of $Mn(CH_3COO)_2$ and attained a maximum at 1 wt.% addition. These positive effects of $Mn(CH_3COO)_2$ were also observed on the graphitic carbon filament, FM14 (Petoca Materials Ltd.). Therefore, it is believed that similar positive effects of $Mn(CH_3COO)_2$ are exhibited on the graphitic carbon anode in general. The insertion and reversible Li intercalation capacity of the 1 wt.% $Mn(CH_3COO)_2^-$ added carbon nanotube were 430 and 328 mAh/g respectively. XANES spectra suggest that the added $Mn(CH_3COO)_2$ decomposed during preparation and the resulting organic film obtained by decomposition of $Mn(CH_3COO)_2$ may have similar structure of SEI film. Therefore, Li intercalation is considered to occur smoothly on $Mn(CH_3COO)_2$ added carbon nanotube.

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