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Effects of synthesis condition of graphitic nanocarbon tube on anodic property of Li-ion rechargeable battery

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Abstract

Effects preparation condition of multiwall carbon nanotube on Li intercalation were investigated in this study. Both Li intercalation and reversible capacities increased with increasing contact time of CH₄ on Ni catalyst when the multiwall carbon nanotube was prepared. Raman spectroscopy suggested that the content of graphitic carbon tube increased with increasing the contact time of CH₄ upon synthesis. Therefore, in case of tubular carbon, graphitic carbon also exhibited a larger capacity for Li intercalation comparing with that of amorphous one. Intercalation and reversible capacity for Li insertion at first cycle were attained to a value of 430 and 320 mAh/g, respectively, on the carbon nanotube obtained at the contact time higher than 100 g-cat h/mol. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbon nanotube; Anode; CH₄ decomposition; Propylene carbonate electrolyte

1. Introduction

Lithium-ion rechargeable battery is a highly attractive power source for a mobile electronic equipment, because of its high current density, high specific energy, superior cycle characteristics. This battery incorporates a lithiated metal oxide (typically LiCoO₂) as the positive electrode and carbonous materials as the negative electrode [1]. Various type of carbon has been investigated extensively as the anode for lithium-ion rechargeable batteries. Among them, carbon nanotube is attracting a much attention because of its unique shape and a high capacity, if Li can intercalate into a inner tube. It was reported at first time that the carbon nanotube prepared by a template method exhibits a large Li-ion intercalation capacity of 490 mAh/g [2]. Recently, the Li intercalation property into another type carbon nanotube is also reported by another group [3,4]. However, there are some types of carbon tube with the different structure [2,3] and the property of carbon nanotube for Li intercalation have not been studied thoroughly. In the previous study, the authors investigated the Li intercalation capacity of carbon tubes obtained by CH₄ decomposition with Ni catalyst [5,6]. It was found that multiwall carbon tube obtained by CH₄

decomposition exhibited a Li intercalation capacity higher than 200 mAh/g. Therefore, graphitic carbon nanotube is attracting much interest as the anode of Li-ion battery. However, the relationship between Li intercalation capacity and the synthesis condition is not thoroughly understood. In the present study, effects of decomposition condition of CH₄ with Ni catalyst on the Li intercalation capacity were investigated in detail.

2. Experimental

Multiwall carbon nanotube was synthesized by decomposition of CH₄ with Ni catalyst (1.0 g) by using a conventional fixed bed reactor. Ni catalyst obtained by reduction of commercial NiO (Wako, 95% in pure) was always used as a catalyst for CH₄ decomposition. CH₄ decomposition was generally performed at 973 K for 20 h under CH₄ stream (20 cc/min). After reaction, Ni was removed from carbon tube by dissolving into HF acid solution. Li intercalation capacity was measured with applying a constant current of 0.4 mA/cm². Li metal was always used as a counter electrode. Organic electrolyte of ethylene carbonate (EC)-dimethyl carbonate (DMC) (1:2) solution dissolved with LiPF₆ (1 wt.%) was generally used as an electrolyte. Organic electrolyte containing propylene carbonate (PC)

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was obtained by mixing PC with either of EC, DMC, diethyl carbonate (DEC), or methyl ethyl carbonate (MEC) followed by addition of LiPF_6 (1 mol%). Carbon sample was mixed with ethylene-propylene-dimethyl-monomer (EPDM) cyclohexane solution and then pressed to the stainless steel grid on the stainless steel plate. The cycle property was measured over the potential from 0 to 1.5 V. TEM observation was performed by JEOL JEM2010 with an acceleration voltage of 200 kV. Raman spectroscopy was measured with an initial 50 mW Ar laser of 532 nm (Kizer Optical systems, Holoprobe 532) in air.

3. Results and discussion

XRD pattern of the obtained carbon tube was always assigned to the typical diffraction pattern for 2H-type graphitic carbon. Therefore, the large part of the obtained carbon was graphitic carbon, although the decomposition temperature of CH_4 was as low as 973 K. Fig. 1 shows the TEM observation results at low and high magnification. Observation at low magnification in Fig. 1(a) confirmed that large part of the obtained graphite was a tubular filament of which average diameter was 20 nm and the thickness of wall was around 5 nm. On the other hand, observation at high magnification in Fig. 1(b) suggested that the wall of tubular graphite was consisted of multiwall carbon sheets which was oriented at ca. 87° in average to growth direction. Therefore, the obtained carbon nanotube was very close to a carbon tube reported as a “herringbone”-type carbon tube [7].

On the other hand, it was found that the size and crystallinity of tubular carbon was strongly dependent on the synthesis condition, in particular, reaction temperature and contact time of CH_4 . The capacity for Li intercalation

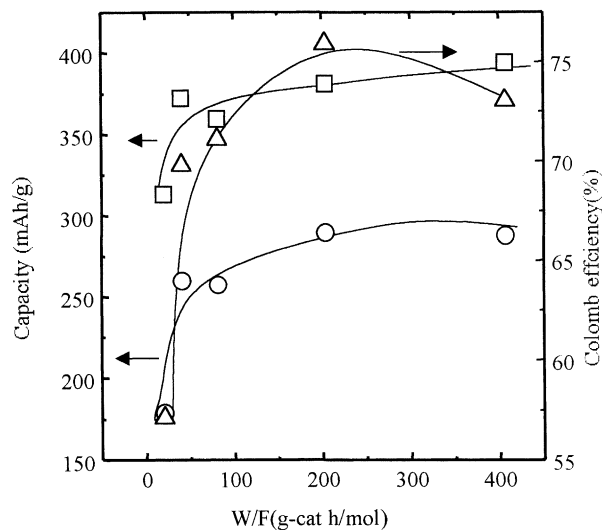


Fig. 2. Li intercalation and reversible capacity of carbon nanotube as a function of contact time of CH_4 upon synthesis: □, intercalation capacity; ○, reversible capacity; △, coulomb capacity.

increased with increasing the decomposition temperature and it attained to the maximum value at 973 K. On the carbon obtained at this condition, intercalation and reversible capacity was attained to values of 380 and 260 mAh/g, respectively. Therefore, the optimum reaction temperature for CH_4 decomposition seems to exist at 973 K. In the following study, reaction temperature was fixed at 973 K. It is also expected that the crystallinity is also strongly affected by the contact time of CH_4 on Ni catalyst. Therefore, effects of contact time on intercalation and reversible capacity for Li insertion were studied in detail.

Fig. 2 shows the intercalation and reversible capacity for Li insertion at first cycle as a function of contact time of CH_4

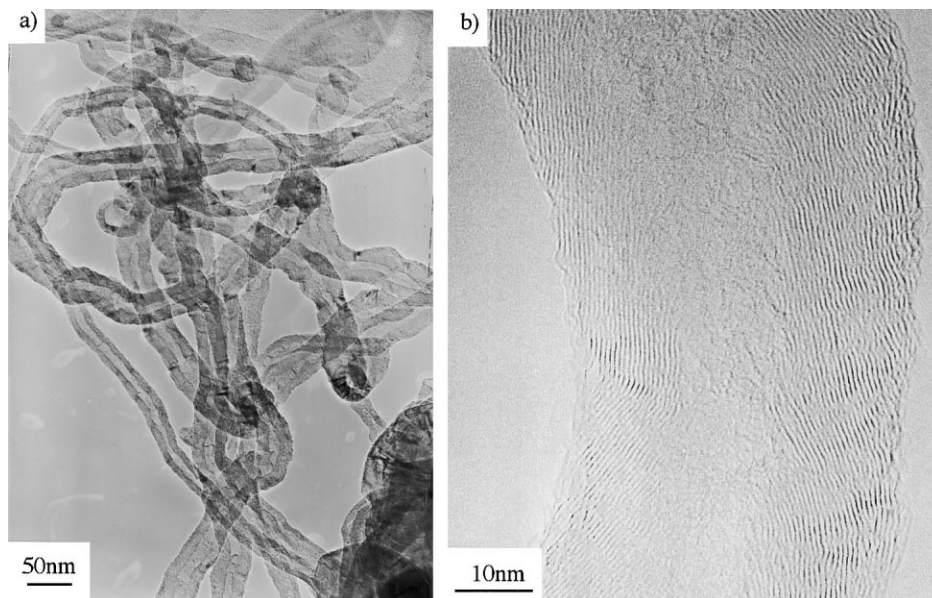


Fig. 1. TEM photographs of the carbon nanotube obtained by decomposition of CH_4 : (a) low magnification; (b) high magnification.

upon synthesis of carbon nanotube. It is clear that both intercalation and reversible capacity increased with increasing contact time and it attained to a constant value at W/F larger than 100 g-cat h/mol. At this condition, intercalation and reversible capacity were attained to values of 370 and 280 mAh/g, respectively. Therefore, slower rate for deposition of carbon seems to be effective for obtaining a large capacity for Li intercalation, because the deposition rate of carbon became smaller with increasing contact time. Since it is reported that trapping lithium in lattice deficiency was one explanation for the irreversible capacity [8], the improved capacity by increasing contact time seems to be attributed to an increase in crystallinity of graphitic nanotube.

X-ray diffraction analysis was performed on the deposited graphitic carbon nanotube at various contact time in order to measure the difference in crystal structure. However, all specimens exhibited a typical diffraction pattern of graphitic carbon and no significant difference was observed. It is also noted that the estimated length of (0 0 2) direction was 0.338 nm, which is almost the same as that of 2H-type graphite carbon [9]. Therefore, XRD measurement suggested that the structure of the obtained carbon nanotube in long range order was almost independent of the contact time of CH_4 upon synthesis. It is well-known that Raman spectroscopy is effective tool for analyzing crystallinity of carbon. In Raman spectroscopy, two absorption peaks at around 1350 and 1580 cm^{-1} , which could be assigned to amorphous and graphitic carbon, respectively, was observed. Fig. 3 shows the Raman spectroscopy of the carbon nanotube obtained at various contact time. It is obvious that three absorption peaks were observed at 1350, 1556, and 1580 cm^{-1} . Considering the reported absorption frequency on bulk carbon, absorption peaks at 1350 and 1580 cm^{-1} could be assigned to the peaks from

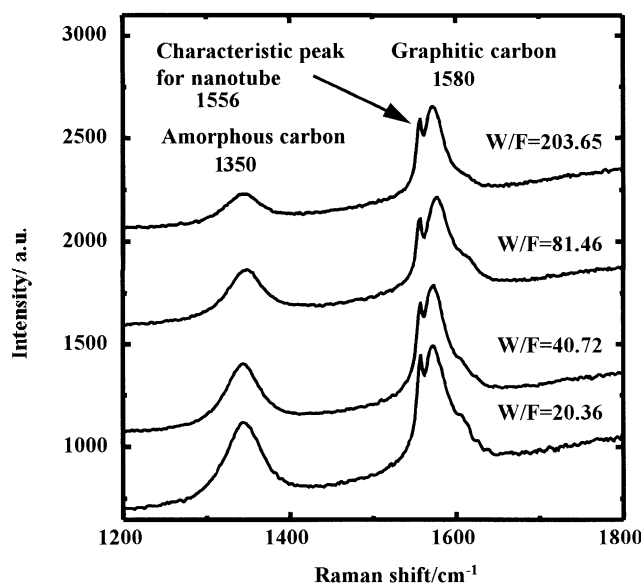


Fig. 3. Raman spectra of carbon nanotube obtained at various contact time of CH_4 upon synthesis. Unit of W/F in figure is g-cat h/mol.

amorphous and graphitic carbon, respectively. At present, it was not clear where amorphous carbon exist in specimens, since SEM and TEM observation suggests that the obtained carbon was consisted of the tubular and negligible amount of bulk carbon. In any way, Raman spectroscopy suggests that some part of the obtained carbon nanotube was amorphous carbon. On the other hand, sharp absorption peak at 1556 cm^{-1} was not observed on a bulk graphitic carbon. Therefore, this peak seem to be a typical Raman peak for tubular shape carbon, although further detail analysis was required. The intensity of the peak at 1350 cm^{-1} , which reflects the content of amorphous carbon, became weaker with increasing the contact time. Since the intensity ratio of these two peaks, I_{1350}/I_{1580} , decreased with increasing contact time, the content of graphitic carbon seems to be improved by increasing contact time. Therefore, it seems likely that formation rate of graphitic carbon nanotube was rather slow and it is expected that the formation of amorphous carbon can be suppressed at slow fed rate of CH_4 decomposition. It is also noted that both intercalation and reversible capacity increased with decreasing I_{1350}/I_{1580} ratio. Since content of graphitic carbon increased with decreasing I_{1350}/I_{1580} ratio, Li intercalation capacity increased with increasing the crystallinity of carbon nanotube. This suggested that the lattice vacancy have some relationship with the irreversible Li intercalation. The intercalation and reversible capacity for Li insertion were attained to a value of 430 and 320 mAh/g, respectively, at the contact time higher than 100 g-cat h/mol. Although the some irreversible capacity was observed at first cycle, coulomb efficiency was always almost 100% after second cycles. Both intercalation and reversible capacity decreased gradually with increasing the cycle number. However, after 50 cycles, the reversible capacity of 270 mAh/g was still sustained.

Application of propylene carbonate-based system for electrolyte has an advantage in improving the performance of the Li-ion battery at low temperature. Therefore, usage of organic electrolyte based on propylene carbonate is desired from a view point of wider operating temperature and cost. In this study, the anodic performance of graphitic multiwall carbon nanotube in propylene carbonate-containing electrolyte was further investigated. Table 1 summarized a intercalate and reversible capacity of carbon nanotube in various

Table 1
Charge and discharge capacity of carbon nanotube in various organic electrolyte

Electrolyte	Capacity (mAh/g)		Coulomb efficiency (%)
	Li intercalation	Reversible	
EC-DMC (1:2)	352.3	268.1	80.7
PC-MEC (1:4)	420.3	262.3	62.6
PC-DMC (1:4)	393.3	264.4	67.6
PC-DEC (1:4)	359.6	257.1	71.5

organic electrolyte containing 20–25 vol.% PC. Large irreversible capacity was observed in all examined electrolytes containing PC. This is because a large peak assigned to a decomposition of electrolyte was observed at 0.5 V in all examined electrolyte. In particular, extremely large peak was observed on PC–MEC system resulting in a much lower coulomb efficiency. Apart from the large irreversibility in first cycle, capacity larger than 250 mAh/g was attained in all examined electrolyte. Therefore, it can be said that surface activity of carbon nanotube prepared in this study is not so high that decomposition of organic electrolyte was suppressed without any additives. Consequently, Li intercalation can be observed even in the electrolyte containing unstable PC. Considering large BET surface area of carbon nanotube, so-called solid electrolyte interface (SEI) layer would be easily formed and Li^+ ion was smoothly intercalated into carbon nanotube. However, further increase in PC content significantly enlarged a peak at 0.5 V and irreversible capacity also became significantly large. Furthermore, reversible capacity became negligibly small. Consequently, PC-rich composition cannot be used as electrolyte in all system when carbon nanotube is used as anode. Among the examined PC contained electrolyte system, the highest coulomb efficiency was obtained in PC–DMC system electrolyte. Fairly large capacity for Li intercalation was stably exhibited in PC–DMC (1:4) electrolyte after 40 charge and discharge cycles. Although a large irreversible capacity was observed at the first cycle, almost 100% coulomb efficiency was always exhibited in the following cycles. Therefore, after SEI formation at the initial few cycles, intercalation of Li into graphitic carbon nanotube was highly reversible even in PC-based electrolyte.

4. Conclusion

Although the detail study on anodic property of carbon nanotube for Li-ion rechargeable battery is not enough, the

multiwall carbon nanotube obtained by decomposition of CH_4 is highly interesting, since fairly large capacity for Li intercalation was exhibited. Both Li intercalation and reversible capacity were strongly dependent on the synthesis condition and this study revealed that the optimized synthesis condition for carbon tube by decomposition of CH_4 was the reaction temperature of 973 K and contact time of CH_4 longer than 100 g-cat h/mol. At present, capacity for Li intercalation is comparable with those of bulk hard carbon. However, if lithium can be inserted into an inner tube of carbon nanotube, the extremely large capacity which should be larger than 370 mAh/g is expected. From a view point of possible larger capacity, carbon nanotube is highly interesting as an anode of Li-ion rechargeable battery.

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