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Graphitic Carbon Tube Obtained by Catalytic Decomposition of CH₄ for Anode of Li Ion Rechargeable Battery

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Graphitic carbon nanotubes were prepared by the decomposition of CH₄ over the Ni catalysts and the anodic properties of the obtained tubular graphite for Li-ion rechargeable battery were investigated. The Li intercalation capacity increased, however, the reversible intercalation capacity was decreased with increasing graphitic nanotube surface area. Graphitic tubes prepared at 973 K exhibited almost the theoretical Li intercalation capacity. In addition, it was found that a post annealing treatment of the graphite tube was effective for improving the coulomb efficiency.

Key Words : Graphitic Nanotube, Li Ion Rechargeable Battery, Anode, CH₄ Decomposition

1 Introduction

The lithium-ion rechargeable battery is a highly attractive power source for mobile electronic equipment, because of its high current density, high specific energy, and superior cycle characteristics.¹⁾ This battery incorporates a lithiated metal oxide (typically LiCoO₂) as the positive electrode, carbonaceous materials as the negative electrode, and an organic lithium-ion conducting electrolyte. Various type of carbon have been investigated extensively as the anode for lithium-ion rechargeable batteries. It was reported that certain types of carbon, in particular, non-graphitic carbon, exhibit a larger Li intercalation capacity than the theoretical capacity of 372 mAh/g corresponding to the formation of LiC₆.^{2,3)} However, the plateau potentials in the charge and the discharge curves of these non-graphitic carbons are not close to 0 V and these potentials gradually decrease with increasing Li intercalation.³⁾ In contrast, graphitic carbon has the advantages of a flat plateau potential close to 0 V and exhibits a sharp decrease in potential when the intercalation attends to its final stage. Consequently, graphitic carbon is now used as the anode in the commercial Li-ion rechargeable batteries. Improving the capacity of the carbon anode is an important goal for increasing the battery capacity, because the capacity per unit volume of anode is smaller than that of the cathode. In addition, an extremely large energy is required to obtain a graphitic carbon due to the high synthesis temperature of 3000 K.

On the other hand, various shaped carbons such as fiber⁴⁾ were also investigated for the anode of Li ion secondary battery. Among them, carbon nanotubes are attracting an interest, because it was reported

that the carbon nanotube prepared by a templating method exhibits a large Li ion intercalation capacity of 490 mAh/g.⁵⁾ Recently, the Li intercalation property into carbon nanotubes is also reported.⁶⁾ However, there are some types of carbon tube with the different structure^{5,6)} and the property of carbon nanotubes for Li intercalation have not been studied thoroughly. In our previous study, the decomposition of CH₄ into C and H₂ was investigated for the production of hydrogen. Hydrogen can be obtained under a mild condition by the decomposition of CH₄ with the membrane reactor in which a hydrogen-permeable Pd-Ag tube was used.⁷⁾ On the other hand, it was found that the formed carbon in this reaction is a nano-sized tubular carbon. Therefore, it is expected that this tubular carbon may exhibit unique properties for the Li intercalation. The anodic property of Li ion rechargeable battery was investigated with the tubular carbon obtained by the decomposition of CH₄ in this study. In addition, post annealing treatment on the anodic property of tubular carbon was also studied.

2 Experimental

Tubular carbon was synthesized by the catalytic decomposition of CH₄ with a conventional fixed bed reactor. Nickel metal or 10 wt % nickel supported on SiO₂ were used as catalyst. Catalyst was pressed into disk and then screened to 16-32 mesh. Before reaction, catalyst was reduced in hydrogen stream at 673 K for 1 h. Commercial CH₄ (99.5 %) was fed to the catalyst bed at temperature from 673 to 873 K with W/F=50 g-cat.h/mol. Ni and Ni/SiO₂ catalyst was removed from carbon by dissolving into HNO₃ and HF solution, respectively. X-ray fluorescence analysis sug-

gested that the impurity in the obtained carbon was not observed. Thus obtained carbon tube was dried at 343 K for 12 h. The anodic property of carbon tube was measured by using Li metal as a counter electrode in a setup which is the same as that in the previous report.⁹⁾ Carbon sample mixed with ethylene-propylene-dimethyl-monomer (EPDM) cyclohexane solution was pressed to the stainless steel grid on the stainless steel plate. Ethylene carbonate (EC)-Dimethyl carbonate (DMC) (1:2) solution dissolved with LiPF_6 was used as the electrolyte. The cycle property was measured over the potential from 0 to 1.5 V under the application of constant current. The current density of 0.5 mA/cm^2 was always used for the measurements in this study. TEM observation was performed by JEOL JEM2010 with an accelerated voltage of 200 kV.

3 Results and Discussion

Figure 1 shows the TEM photograph of the obtained carbon filament at 973 K. It is evident that the obtained carbon has the tubular structure. Diameter of the obtained tube was *ca.* 20 nm and the thickness of wall was about 5 nm. Further detail observation at a high magnification suggests that the wall of carbon tube consisted of the layered carbon. The main plane of $\langle 002 \rangle$ was oriented at about 85-75 degree to the growth direction as shown in Fig. 1 (b). Similar tubular carbon was also reported by several groups.^{9,10)} It is also noted that the structure of carbon tubes obtained in this study was different from that studied by Che *et al.*⁵⁾ or Wu *et al.*⁶⁾

XRD pattern of the obtained carbon tube was the typical diffraction pattern for graphitic carbon as shown in Fig. 2. Considering the *d* value of the strongest diffraction peak from $\langle 002 \rangle$ plane, it can be said that the obtained carbon tube has the graphitic structure of which the interplanar distance was 0.338 nm. In addition, considering that the high temperature is essential for synthesis of graphitic carbon, it is interesting that the graphitic carbon can be obtained at temperature as low as 673 K in this study. Any way, the obtained carbon nanotube was graphitic carbon from X-ray diffraction point of view. However, the crystallinity of the carbon tube became lower with

Fig. 2 X-ray diffraction patterns of the carbon tube obtained by decomposition of CH_4 at various temperatures. (○) graphite, (□) Ni, (△) unknown.

decreasing reaction temperature, since the main X-ray diffraction peak was weakened and broaden. SEM observation shows that the carbon obtained at 673 K still mainly consisted of the tubular carbon. Therefore, the diameter of carbon tube seem to decrease with decreasing reaction temperature. On the other hand, the crystallinity of the carbon tube became also lower with increasing reaction temperature higher than 973 K. This may be due to a change in the shape of the formed carbon, since SEM observation shows that almost no tubular carbon was contained in the specimens synthesized at 1173 K.

TEM observation of the as-synthesized carbon tube suggests the Ni catalysts exist at the tip of carbon tube. Therefore, the carbon tube seems to be grown by using Ni catalyst as a nuclear. Figure 3 shows the BET surface area of the obtained carbon tube as a function of Ni particle size. It is evident that the BET surface area monotonously decreased with increasing the Ni particle size at same temperature and with increasing reaction temperature at the same Ni particle size. Consequently, it is expected that the diameter of the carbon tube can be controlled by the size of Ni particle and the reaction temperature.

Figure 4 shows the Li intercalation capacity of the graphite tube as a function of BET surface area. It is generally believed that the carbon with the smaller BET surface area exhibits the larger reversible capacity for Li intercalation.¹¹⁾ However, relationship between the Li intercalation capacity and the surface area of carbon was not thoroughly made clear in the previous study. This is because the shape or the structure of carbon materials was always changed with changing BET surface area in the previous study. Therefore, in this study, Li intercalation capacity in the similar structured carbon nanotube with the different BET surface area was compared. It is evident that the Li intercalation capacity increased monotonously with increasing BET surface area of the carbon tubes and it attained to a value higher than 600 mAh/g. On the other hand, the reversible capacity was also increased with increasing BET surface area and attained to a maximum value at $40 \text{ m}^2/\text{g}$. The larger surface area of carbon leads to more formation

Fig. 1 TEM observation results of the carbon tube obtained by decomposition of CH_4 on Ni at 773 K. (a) low magnification, (b) high magnification.

Fig. 3 BET surface area of the obtained carbon tube as a function of the Ni particle size and the synthesis temperature.

Fig. 4 Initial capacity and reversible capacity of Li intercalation into carbon tube as a function of BET surface area.

of so-called "Solid Electrolyte Interface (SEI)" layer. Therefore, the larger surface area of carbon lead to a larger Li intercalation capacity, however, irreversible Li intercalation capacity which was mainly used for the formation of SEI was also increased. Consequently, large surface area is not preferable as the anode of Li ion rechargeable battery. This is also exhibited clearly on the carbon tube with the surface area higher than 50 m²/g. On the other hand, the initial Li intercalation capacity decreased with decreasing surface area. Therefore, the reversible capacity also decreased with decreasing surface area in the range smaller than 40 m²/g. The maximum reversible capacity was obtained at the graphitic tube with the medium surface area of 40 m²/g. Consequently, the optimized condition of synthesis of carbon tube for anode exists at 873 K and Ni metal with 70 nm particle size for temperature and catalyst, respectively. This carbon was obtained with Ni metal catalyst (70 nm size) at 873 K. On this carbon tube, the overall Li intercalation and the reversible intercalation capacity were 384 and 266 mAh/g, respectively.

Post heat treatment effect was further studied to improve the reversible capacity. Figure 5 shows the initial Li intercalation and the reversible intercalation capacities of the graphitic carbon (40 m²/g surface area) which was obtained at 873 K as a function of post annealing temperature. It is clear that the initial capacity was hardly dependent on the post annealing temperature, since the almost theoretical intercalation capacity for the formation of LiC₆ was reached. However, the reversible intercalation capacity increased with increasing post anneal temperature and it attained to a maximum value of 286 mAh/g when the post anneal was performed at 1873 K. XRD measurement suggests that crystallinity of graphitic phase was greatly improved by the post annealing treatment. However, it was shown by the TEM observation that the tubular structure of graphitic carbon was sustained after annealing at 1873 K and furthermore, the surface area was also hardly decreased. Therefore, the carbon tube prepared by CH₄ decomposition was highly stable against the heat treatment, however, it is likely that defects in the carbon plane or residual hydrogen could be removed by the post anneal treatment. Consequently, the post anneal treatment is effective for decreasing the amount of Li trapped at the disordered point in lattice resulting in the improved coulomb efficiency as shown in Fig. 5.

The charge and discharge characteristics of the tubular carbon after the post anneal at 1873 K were shown in Fig. 6. It is obvious that the Li charge-discharge curve exhibited the typical pattern reported for the graphitic carbon⁴⁾ and the potential was drastically increased at the final stage of intercalation, which is suitable characteristic for a rechargeable battery. The initial capacity for Li intercalation of the carbon tube was 376 mAh/g which corresponds to the theoretical capacity and the large reversible capacity of 286 mAh/g was also exhibited. In addition,

Fig. 5 Initial capacity, reversible capacity, and coulomb efficiency as a function of post annealing temperature. Post annealing was performed at the set temperature for 6 h. (○) Initial capacity, (□) reversible capacity, (△) coulomb efficiency.

Fig. 6 Charge-discharge curves of the carbon tube obtained by decomposition of CH_4 at 973 K followed by annealing at 1873 K for 6 h.

tion, this reversible capacity was stably sustained over few 10 cycles in the charge and discharge measurement. After 20 cycles, the reversible capacity was still sustained a value of 265 mAh/g. Consequently, comparing with a bulk graphitic carbon, this study revealed that graphitic carbon nanotube obtained by the catalytic decomposition of CH_4 with Ni catalysts exhibited a fairly large Li intercalation capacity and it could be used as the anode of Li rechargeable battery.

4 Conclusion

Although the bulk shaped graphitic carbon is generally investigated as the anode material of Li ion rechargeable battery, this study shows that the tubular carbon is also attractive as the anode material since a large Li intercalation capacity was exhibited. Decomposition of CH_4 into C and H_2 over Ni catalyst is also interesting from the hydrogen synthesis point of view, since this reaction proceeded at low tempera-

ture. The reversible capacity of Li intercalation was increased by post thermal treatment, however, as-synthesized carbon tube at 873 K also exhibited a good reversible capacity. The detail structure of the intercalated lithium into tabular carbon is currently under investigation and the results will be published somewhere else.

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