Plasma-Modified MCMB Powders for Anode of Li Ion Secondary Battery

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A kind of artificial graphite powder, so called as mesocarbon microbeads (MCMB) powder, was treated in various reactive plasma atmospheres, such as Ar-H₂, Ar-N₂, Ar-H₂-CO₂ and Ar-N₂-CO₂. The influence of the plasma modification on the electrochemical properties was clarified comparing them with that by the mechanical milling, a conventional treatment, to modify the surface structure and shape of the particle. Plasma treatment of MCMB gave rise to the improvement of electrochemical properties as the anode of lithium secondary battery. When the surface area is almost the same, the efficiency of the plasma treated MCMB is higher than that of the original MCMB. The modification of MCMB subject to the surface chemical composition maybe also gave the formation of more stable SEI as less heat was generated in DSC.
Key words: graphite, MCMB, thermal plasma, anode material, lithium ion battery

1. INTRODUCTION

In recent years, the miniaturization, lightening and making to high performance in mobile electronic equipments are remarkable. Higher energy density and better safety characteristics are indispensable for the secondary battery which is the power supply of these equipments. The lithium ion secondary battery using the carbon material for a negative electrode and lithium cobalt oxide for a positive electrode is the most typical case.

Many types of carbonaceous materials have been investigated extensively as an anode material of lithium secondary batteries, in order to obtain high performance such as high capacity, high efficiency at first charge/discharge cycle, good cycle characteristics and so on. Carbonaceous material anodes always have an irreversible capacity at the first charge/discharge cycle and this irreversible capacity loss originates from the decomposition of the electrolyte to form a solid-electrolyte interface (SEI) layer [1-3]. To reduce this irreversible capacity loss, surface modification of carbon materials, such as oxidation [4,5], coating of amorphous carbon by thermal vapor decomposition [6] has been tried.

Under the mechanically, thermally and electrically tough conditions caused by abuses (crushing, heating in hot oven, short circuit and so on), exothermal chemical reactions between the electrode materials and the electrolyte in a lithium ion battery take place at high temperature. And it is reported that the thermal stability of the SEI on the carbonaceous material is strongly related to the heat evolution, and plays an important role in determining battery safety [7-11].

Thermal plasma is characterized by its very high temperature (>10,000 K) and high concentration of chemistry reactive species in it. The powders introduced into the plasma are modified in shape, surface morphology, chemical composition and crystal structure in a moment [12]. The present authors have reported the thermal plasma treatment of glassy carbon and phenolic resin powder, and their electrochemical properties [13-15]. The plasma treated carbon powder subjected to modifications in chemical composition, morphology on the surface, and graphitzation in the bulk, and the modification gave rise to the higher capacity than the untreated powders as an anode of lithium secondary battery.

In this work, in order to modify the surface characteristics, mesocarbon microbeads (MCMB) powder, which is known as a kind of artificial graphite, was treated in various reactive plasma atmospheres, such as Ar-H₂, Ar-N₂, Ar-H₂-CO₂ and Ar-N₂-CO₂. The influence of the plasma modification and the electrochemical properties was examined by comparing with the mechanical milling which has been modified the surface structure and shape of the carbon particle.

2. EXPERIMENTAL

The induction plasma torch and reactor chamber was described in the previous work [16]. MCMB powder (Osaka gas, 10-28, 10 μ m in average particle size) was treated in Ar-H₂, Ar-N₂, Ar-H₂-CO₂ and Ar-N₂-CO₂ induction thermal plasmas generated at the power level of 40kW and pressure of 27 and 53 kPa. The plasma

Table I   Plasma generating and powder feeding conditions

Sample	1 a	b	2 a	b	3 a	b	4 a	b
Plasma gas flow rate / L/min								
Central gas	Ar / 15		Ar / 15		Ar / 15		Ar / 15	
Seath gas	Ar-H_2 / 60+3		Ar-N_2 / 60+3		Ar-H_2 / 60+3		Ar-N_2 / 60+3	
Powder carrier gas	Ar / 10		Ar / 10		Ar-CO_2 / 9.5+0.5		Ar-CO_2 / 9.5+0.5	
R.F. Frequency / MHz	2		2		2		2	
Plate power / kW	40		40		40		40	
Reactor pressure / k Pa	27	53	27	53	27	53	27	53
Powder feed rate / g/min	4		4		4		4	

generating and powder feeding conditions are summarized in Table I. Mechanical milling was carried out for different durations in a ball mill. The plasma treated and mechanically milled MCMB powders were characterized by the measurement of Brunauer-Emmett-Teller (BET) surface area and the particle size distribution, X-ray diffractometry (XRD), and Raman scattering spectroscopy.

Electrochemical measurement was performed galvanostatically. Sample electrodes for lithium secondary batteries were prepared as follows. Poly vinylidene fluoride as a binder, and sample powders were mixed in N-methyl-2-pyrolidione and the slurry was spread on copper foil, and dried at 150℃ under vacuum for an hour. A 1 mol·cm^{-3} solution of $LiClO_4$ in a 50:50 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) was used as an electrolyte. A counter lithium electrode and reference lithium electrode were employed. The electrochemical cells were set up in a dry box under an argon atmosphere and charged/discharged galvanostatically at a current density of 0.25mA· cm^{-2} between 0 to 3V vs. Li/Li^{+} at 25℃.

Thermal stability of the plasma treated and the mechanically milled MCMB was examined by the differential scanning calorimetery (DSC). Fully charged half cell was decomposed in the dry glove box, and samples of several mg were collected. The collected sample was immediately pressed against the inner wall of the resisting pressure SUS holder to make good heat conduction, and it was sealed up in the DSC holder. The scanning speed was 10℃/min and the range of the measurement temperature was from the room temperature to 400℃.

3. RESULT AND DISCUSSION

3.1 BET and particle size distribution

Table II shows the BET surface area of the plasma treated, mechanically milled and original MCMB powders. The BET surface area of the Ar-N_2 plasma treated MCMB particles was more than two times as larger than that of original MCMB particles. The Ar-H_2 and Ar-H_2-CO_2 plasma treatments of MCMB caused slight increase in the BET surface area, while the Ar-N_2-CO_2 plasma treatment of MCMB gave slight decrease in the BET surface area. The BET surface area of the mechanically milled MCMB increased corresponding to the milling duration.

Table II   BET surface area of plasma treated and mechanically milled MCMB

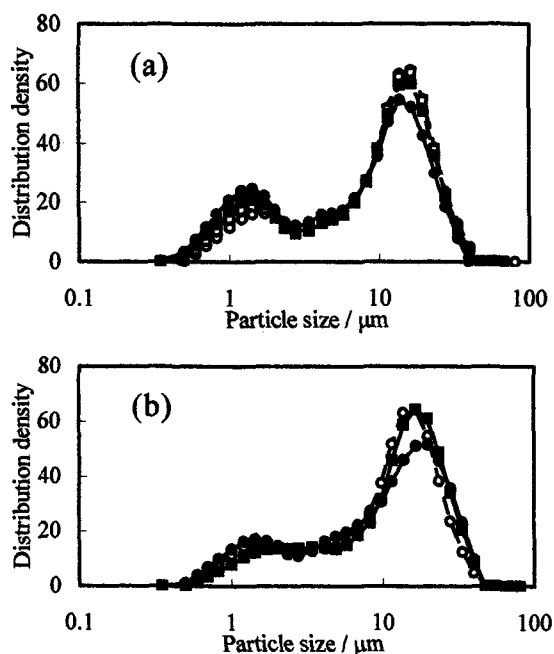| Sample	Surface area / m^2/g
Original	1.80
Plasma treated	
Ar-H_2 1a	2.22
Ar-H_2 1b	1.86
Ar-N_2 1a	3.63
Ar-N_2 1b	6.41
Ar-H_2 -CO_2 1a	1.49
Ar-H_2 -CO_2 1b	1.67
Ar-N_2 -CO_2 1a	1.41
Ar-N_2 -CO_2 1b	2.68
Mechanically milled	
1 h duration	2.15
3 h duration	2.59
5 h duration	2.89
10 h duration	3.47
24 h duration	5.44
48 h duration	7.51

Fig.1   The particle size distribution of (a) mechanically milled MCMB (○ original, □ 3h, ■ 10h, ● 48h) and (b) plasma treated MCMB (○ original, ● Ar-N_2 1a, ■ Ar-N_2 -CO_2 1a).

Figure 1 shows the particle size distribution. The peak size of the coarse particles decreased in proportion to the milling duration, and number of the fine particles increased in proportion to the milling duration at the mechanical milling (Fig.1(a)). As can be seen from Fig. 1(b), the number of the fine particles somewhat increased by $Ar-H_2$ and $Ar-N_2$ plasma treatments, and decreased by plasma treatments containing CO_2. The peak size of the coarse particles increased in the $Ar-H_2$ and $Ar-N_2$ plasma treatments, where the surface of MCMB particles was attacked by plasmas and became rough, and then fine condensates were formed through coagulation from a vapor phase and covered on the surface of the particles. On the other hand, in the atmospheres containing CO_2 , fine particles and coarse particles were attacked by oxygen atoms formed from CO_2 , and some fine particles were burned off.

3.2 XRD measurement and Raman spectra

XRD data showed that the lattice parameters and half width of plasma treated MCMB were the same as that of the original MCMB. The plasma treatment did not give rise to the further graphitization in the bulk. Also, no appreciable change was observed in XRD of mechanically milled powders.

In the Raman, two peaks were observed at about $1580cm^{-1}$ and at about $1350cm^{-1}$. The $1580cm^{-1}$ band is assigned to the Raman active E_{2g2} mode of graphite lattice vibration. The $1350cm^{-1}$ band is originated from disordered structure of carbon. Thus, the ratio of the $1580cm^{-1}$ band intensity (I_{1580}) and the $1350cm^{-1}$ band intensity (I_{1350}), I_{1350} / I_{1580} (=R) can be the indicator of the graphitization. Fig.2 shows R value of the original, mechanically milled and the plasma treated powders. Upon increasing the milling duration, R value increases indicating the increase of defects on the surface. Even for short duration such as one hour, R value became twice value of original. R value of all plasma treated samples became larger than that of the original MCMB, and tended to be larger than that of the mechanically milled MCMB. As the information obtained from Raman spectra is limited to the
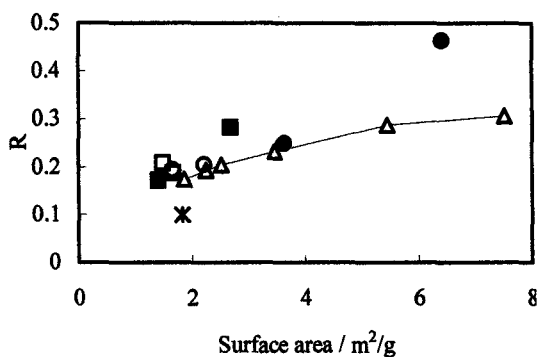
layer structure of several nm underneath surface, surface on the MCMB particles can be recognized to have the disordered carbon structure.

3.3 First discharge/charge efficiency

In Table III, discharge capacity of thermal plasma-modified MCMB was larger than that of original MCMB in our study. On the other hand, there was a little decrease in the discharge capacity of mechanically milled MCMB at short duration (<10h).

First charge/discharge efficiency obtained through the galvanostatic charge/discharge measurements were shown in Fig.3. The efficiency decreased as the relative surface area increased in mechanically milled and plasma-modified MCMB. When the surface area of the plasma-modified MCMB was almost the same, the efficiency of the plasma-modified MCMB was higher than that of the original MCMB. The efficiency of all MCMB milled for short duration was higher than that of the original MCMB. Suzuki et al. [17] proposed the model that turbostratic texture resists drastic swelling of interlayer spaces arising from co-intercalation reaction of solvated ion because of interactions among randomly configured crystallites. Raman spectra data of plasma-modified and mechanically milled MCMB suggested also the turbostratic surface structure.

Table III   Discharge capacity of plasma-modified and mechanically milled MCMB

Sample	Capasity / mAh/g
original	280
Plasma-modified	
$Ar-H_2$ 1a	300
$Ar-N_2$ 1a	297
$Ar-H_2$ -CO_2 1a	302
$Ar-N_2$ -CO_2 1a	301
Mechanically milled	
1 h duration	279
3 h duration	269
5 h duration	270
10 h duration	268
24 h duration	289
48 h duration	289

Fig.2   The relation between R value and the surface area of MCMB (* original, △ mechanically milled, ■ $Ar-H_2$,● $Ar-N_2$,□ $Ar-H_2$ -CO_2,○ $Ar-N_2$ -CO_2).
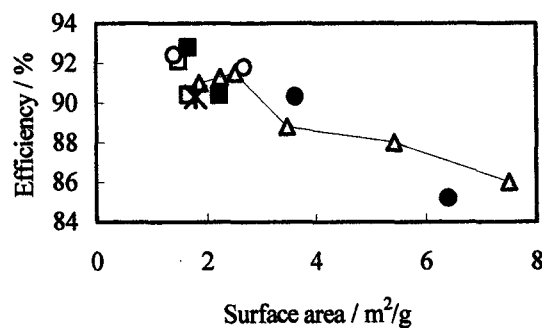

Fig. 3   Relation between the surface area and first charge/discharge efficiency of MCMB (* original, △ mechanically milled, ■ $Ar-H_2$, ● $Ar-N_2$,□ $Ar-H_2$ -CO_2,○ $Ar-N_2$ -CO_2).

Our result agreed with the model reported by them.

3.4 Thermal stability

Figure 4 shows typical DSC curves of MCMB negative electrodes containing the electrolyte at full charging state. Heat generation from 100 to 200℃ corresponds to the thermal behavior [9-11] concerning the reaction of the SEI formed with the first charge. This heat generation of mechanically milled and plasma-modified MCMB increased depending on the increase of surface area (Fig. 5). However, there is a tendency that the heat generation of the plasma-modified MCMB with the surface area of *ca.* 2 m²/g, is smaller than their original and milled MCMB with the similar surface area.

This reaction of the SEI associated with decomposition of metastable component of the SEI, followed by reaction of intercalated lithium with electrolyte [9,10]. It is reported that the coke sample shows a lower self-heating rate, in other words, higher thermal stability than expected, based on its surface area [11]. These results suggests that lower heat generation of plasma-modified MCMB may be related to the formation of more stable SEI, which could attribute to the modification of the surface chemical composition by the plasma treatment. Plasma treatment of MCMB can give rise to the improvement of stability as the anode of lithium secondary battery.
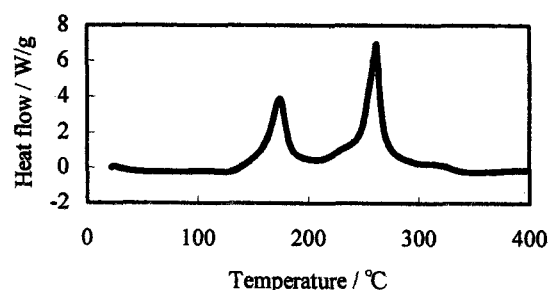

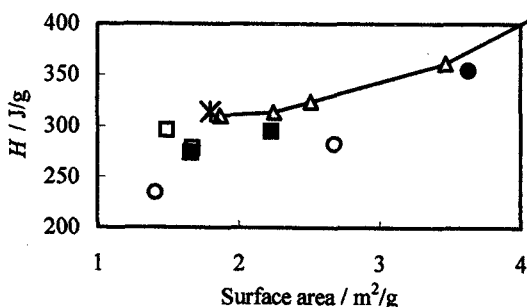Fig. 4 Typical DSC curve of MCMB electrode with 1M LiClO₄ / EC+DEC (1:1) (24h milling sample).

Fig. 5 Relation between the surface area and Heat generation (*H*) from 100 to 200℃ of MCMB (* original, △ mechanically milled, ■ Ar-H₂,● Ar-N₂ ,□ Ar-H₂ -CO₂,○ Ar-N₂ -CO₂).

Summary

The influence of the plasma modification on the electrochemical properties was investigated comparing them with that by the mechanical milling to modify the surface structure and shape of the particle. When the surface area is almost the same, the efficiency of the plasma-modified MCMB is higher than that of the original MCMB. The modification of MCMB subject to the surface chemical composition maybe also gave the formation of more stable SEI as less heat was generated in DSC. Plasma modification of MCMB gave rise to the improvement of electrochemical properties as the anode of lithium secondary battery.

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