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High voltage, rechargeable lithium batteries using newly-developed carbon for negative electrode material

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Abstract

Carbon is a good candidate for negative electrodes because it can take the form of lithium intercalation compounds. We discussed the characteristics of typical carbon materials which have been studied as negative electrode materials. We have found that the mesophase pitch-based carbon microbead (MCMB) of high graphitization stage which have been graphitized at a high temperature such as 2800 °C gives good characteristics as a negative electrode for rechargeable lithium batteries.

The cylindrical 'AA-size' batteries of our trial products using $LiCoO_2$ as the positive electrode and the MCMB graphitized at 2800 °C as the negative electrode have been found to provide large capacities of 500 mA h and high voltages of 3.7 V with high energy densities of 240 W h/l, 100 W h/kg.

Introduction

Recently, rechargeable lithium batteries have been awaited as power sources with high energy densities. Early rechargeable batteries with metallic Li negative electrodes were studied in expectation of high energy density. However, they have a poor cycle life, and there is considerable difficulty in preventing internal short circuits caused by dendrite penetration of the separators. The risk of dendrite penetration increases as the charge current is increased. In addition, the safety of the batteries with metallic Li negative electrodes are presently less than satisfactory. Various kinds of negative electrode materials have, therefore, been proposed as substitutes for metallic Li. Among them, carbon which can take the form of Li intercalation compounds as good candidates for negative electrodes. There is a great variety of carbons, and their suitability as negative electrodes may be dependent on their form or their method of fabrication.

Here we discuss the characteristics of carbon materials which have been found to have appropriate characteristics for negative electrodes. The performance of batteries, using the carbon as negative electrode materials and $LiCoO_2$ as positive electrode materials, is also discussed.

Experimental

Artificial graphite (AG), acetylene black (AB), mesophase pitch-based carbon microbead (MCMB), vapor-grown carbon fiber (VGCF) and polyacrylonitrile-based carbon fiber (PANCF) were examined as typical carbon samples. Carbon fibers were

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used after being reduced to powder. The examinations were carried out in coin cells. A mixture of each carbon material and a binder of acrylic acid resin was molded into a tablet electrode. 50 mg of carbon material was used with a binder of 5 wt.%. Lithium metal was used as a counter electrode and organic solvents containing Li salts were used as electrolytes. The cells were galvanostatically cycled at 0.3 mA/cm^2 to 0 and 2.0 V (or 1.0 V) cutoff voltages for charge and discharge, respectively. Crystalline parameters of the carbon materials were measured by X-ray diffraction method using Cu radiation.

Results and discussion

Characteristics of typical carbon materials

The charge and discharge curves of the cells using some carbon materials are shown in Fig. 1. The charge and discharge capacities, average discharge voltages, measured values of crystalline parameters (002d-spacing d002, crystallite size *Lc* and *La*) of the carbon materials are arranged in Table 1. MCMB and VGCF whose

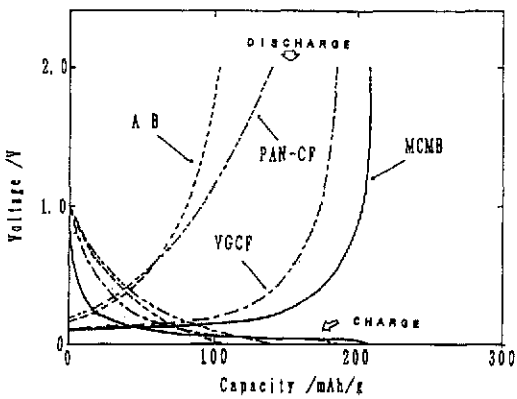

Fig. 1. Charge and discharge curves of typical carbons from coin cell with Li metal counter electrode and 1 M $LiClO_4$/PC+EC, cycled at 0.3 mA/cm^2, and cutoff voltages of 0 to 2.0 V.

TABLE 1

Charge and discharge capacities, average discharge voltages, crystalline parameters, and bulk density of some carbon materials[a]

Carbon materials	Capacity (mA h/g)	Average discharge voltage (V)	d002 (Å)	*Lc* (Å)	*La* (Å)	Bulk density (g/cm^3)
AG	10		3.37	278	776	
AB	103	0.47	3.47	36		0.02
MCMB	208	0.15	3.37	150	705	0.60
VGCF	185	0.17	3.41	126	347	0.02
PANCF	140	0.70	3.54	16		0.56

[a]Charge and discharge were carried out in coin cell with Li metal counter electrode and 1 M $LiClO_4$/PC+EC cycled at 0.3 mA/cm^2 and cutoff voltages of 0 to 2.0 V.

graphitization stages are comparatively high (d002 values are small and *Lc* and *La* values are large) give large capacities, and low average discharge voltages. In addition, their charge and discharge voltages corresponding to Li intercalation/deintercalation potentials lie flatly below 200 mV versus the potential of Li counter electrodes. On the other hand, PANCF and AB, whose graphitization stages are not so high, give relatively small capacities; their charge and discharge voltage profiles are not so flat and vary largely from 0 to over 1.0 V. It is supposed that the characteristics of carbon materials as negative electrodes are related to the stages of graphitization. AG, however, gives a small capacity in spite of having the highest graphitization stage among the examined materials. In the case of AG, it is supposed that the structure is too rigid to carry out the intercalation smoothly. The exceptionally-small capacity of AG shows the characteristics of carbon materials for negative electrodes must be depended on not only the crystalline parameters but also on other factors such as their structure, morphologies or their method of fabrication.

Requirements of carbon materials for negative electrodes

Carbon materials must be adopted as a negative electrode for rechargeable Li batteries. They require a large capacity per weight (mA h/g). In addition, their average discharge voltage must be low to give a higher battery because of the advantage on operating voltage. Finally, they must have low bulk, because there is a limit to the amount of packing volume available in a battery. From these perspectives, MCMB would be the best candidate among the carbon materials mentioned above.

Characterization of MCMB

We investigated MCMB samples graphitized at 1000, 2000, 2500 and 2800 °C. The above-mentioned MCMB, shown in Table 1, was the sample graphitized at 2500 °C. Precursors of graphitized MCMB are carbon spherules which deposited in melted pitch by heating at a relatively low temperature, 400 °C. The graphitizations are carried out by heating at high temperatures (> 1000 °C) after gathering the carbon spherules.

The graphitized MCMB also consist of spherical particles as shown in scanning electron microscopy (SEM) picture of Fig. 2. We suppose that the shapes must be

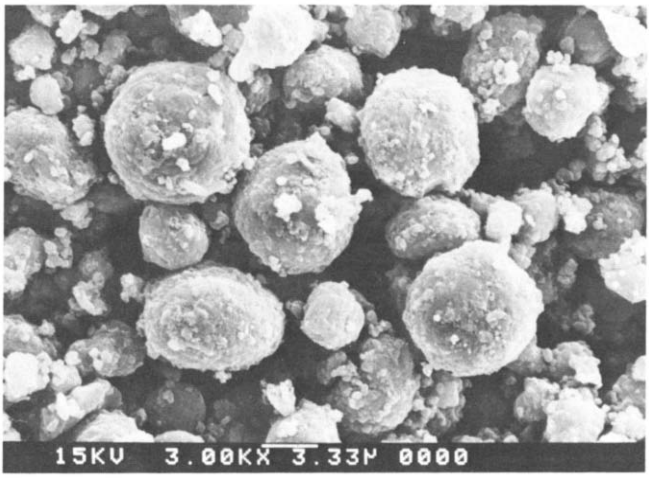

Fig. 2. Scanning electron microscopy picture of MCMB (×3000).

advantageous for high-packing density, and that the particle which has a lamellar structure must be advantageous for smoothly intercalation.

The charge and discharge curves of the cells using the MCMB samples graphitized at above-mentioned temperatures are shown in Fig. 3. Charge and discharge capacities, average discharge voltages, and measured values of crystalline parameters of the samples are arranged in Table 2. The graphitization stage of MCMB progresses as the graphitization temperature increased. The capacity increases and the average discharge voltage decreases as the graphitization stage is developed. The X-ray diffractograms of the samples graphitized at 1000, 2000 and 2800 °C are shown in Fig. 4. The X-ray patterns of the samples after charge and discharge are shown in Fig. 4. It is obvious that the sample of 1000 °C is not graphitized entirely as shown by its broad pattern. Besides the formation of Li intercalation compound it cannot be recognized clearly from its X-ray pattern of the sample after charge although the peak corresponding to 002 shifts slightly after charge. In the case of the sample graphitized at 2800 °C, the original peak of 002 vanishes and two peaks appear at the low angle side after charge.

The appearance of the two peaks shows the formation of Li intercalation compound of graphite; and the peaks at lower and higher angle correspond to the first stage

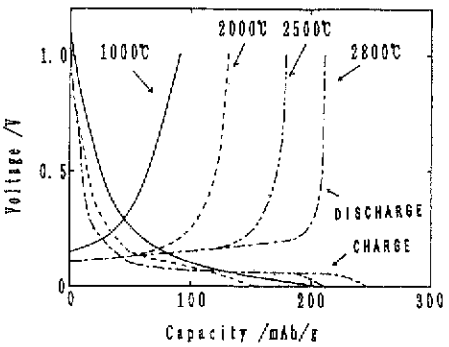

Fig. 3. Charge and discharge curves of MCMB graphitized at various temperatures from coin cell with Li metal counter electrode; 1 M $LiPF_6$/EC+DEC cycled at 0.3 mA/cm^2, and cutoff voltages of 0 to 1.0 V.

TABLE 2

Charge and discharge capacities, average discharge voltages and crystalline parameters of MCMB graphitized at various temperatures[a]

Graphitization temperature (°C)	Capacity (mA h/g)	Average discharge voltage (V)	d002 (Å)	*Lc* (Å)	*La* (Å)
1000	91	0.31	3.53 ~ 3.56	17 ~ 21	
2000	128	0.17	3.40	150	424
2500	178	0.15	3.37	150	705
2800	212	0.15	3.37	300	1163

[a]Charge and discharge were carried out in coin cell with Li metal counter electrode and 1 M $LiPF_6$/EC+DEC, cycled at 0.3 mA/cm^2, and cutoff voltages of 0 to 1.0 V.

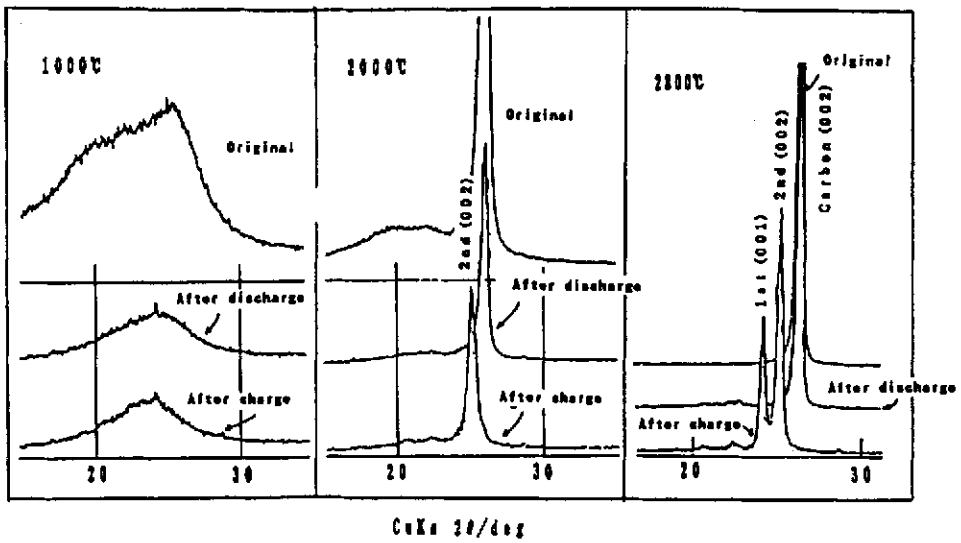

Fig. 4. X-ray diffractograms of MCMB of samples graphitized at various temperatures.

TABLE 3

Retention capacities (capacity losses at the first charge) of MCMB graphitized at various temperatures using PC+DEC or EC+DEC as a solvent of electrolyte containing $LiPF_6$

Solvent of electrolyte	Graphitization temperature (°C)	Retention capacity (mA h/g)
EC+DEC	1000	111
	2000	31
	2500	33
	2800	35
PC+DEC	1000	108
	2000	46
	2500	[a]
	2800	

[a]It is impossible to charge and discharge.

and to the second stage of intercalation level, respectively. In the case of sample graphitized at 2000 °C, the original peak of 002 also vanishes and a peak corresponding to the second stage appears at the low angle side after charge. It is supposed that the utilizable intercalation level is relative to the graphitization stage. The X-ray patterns of the samples after discharge show that almost all the intercalated Li are deintercalated by discharge, and the materials return to their original states. Almost all the charge capacities are larger than the discharge capacities only at the first charge and discharge. We call this capacity loss at the first charge 'retention capacity'. Typical data of retention capacities are shown in Table 3. It is found that the retention capacities depend on not only the kind of electrolytes but also the graphitization stages

of MCMB. When using EC (ethylene carbonate) + DEC(diethyl carbonate) as electrolyte solvents, the retention capacities are not so large, except for the MCMB sample graphitized at 1000 °C. In the case of PC (propylene carbonate) + DEC, however, the samples with high graphitization stages (graphitized at 2500 and 2800 °C) had no discharge capacities at all, in spite of having charge capacities. The X-ray diffractograms after charge in this case also showed no Li intercalation. The charge current in this case must be consumed by electrolysis of the electrolyte containing PC.

We conclude from the results about the capacity, the average discharge voltage, and the retention capacity, that the MCMB graphitized at 2800 °C is most suitable material for the negative electrode among the MCMB samples. In addition, electrolyte containing EC must be more favorable for the suitable MCMB than the electrolyte containing PC.

Trial production of cylindrical-type battery using MCMB

We tried to make cylindrical-type batteries using the MCMB graphitized at 2800 °C as negative electrodes material. In that case, we used $LiCoO_2$ as a positive electrode material.

The negative and positive electrodes which are made into films are wound spirally with the separator of polyethylene membrane. Electrolytes were EC-based solutions containing $LiPF_6$ as Li salts.

Typical discharge curves under various load of the 'AA-size' batteries are shown in Fig. 5. This battery has a capacity of over 500 mA h (at 0.2 C or 1 C rate) and an average operating voltage of over 3.7 V (0.2 C) or over 3.5 V (1 C). This battery has a good cycleability, cycle life is over 300 cycles as shown in Fig. 6. It was also possible to discharge at low temperature (−20 °C) and to charge quickly within 1 h.

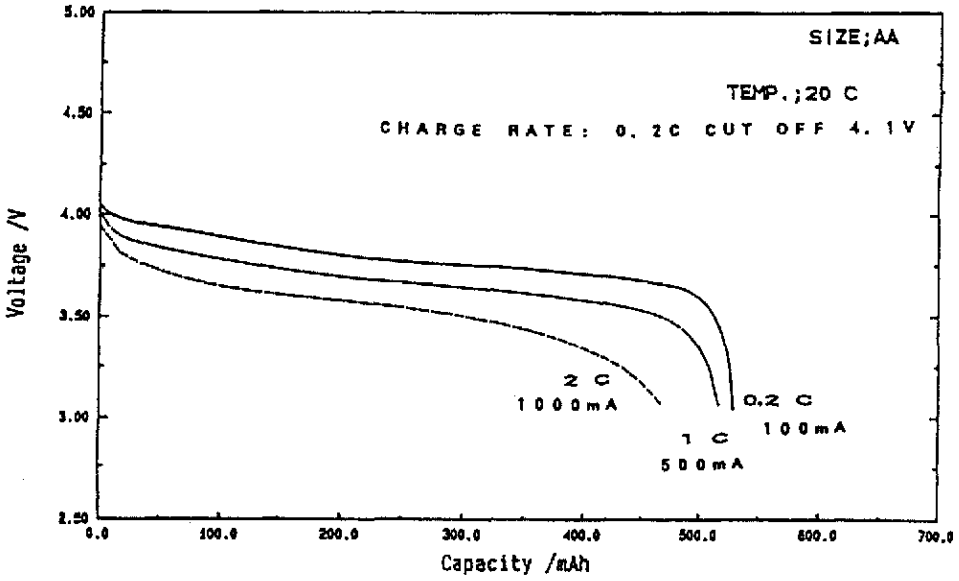

Fig. 5. Discharge curves under various load of 'AA-size' battery using $LiCoO_2$ and MCMB.

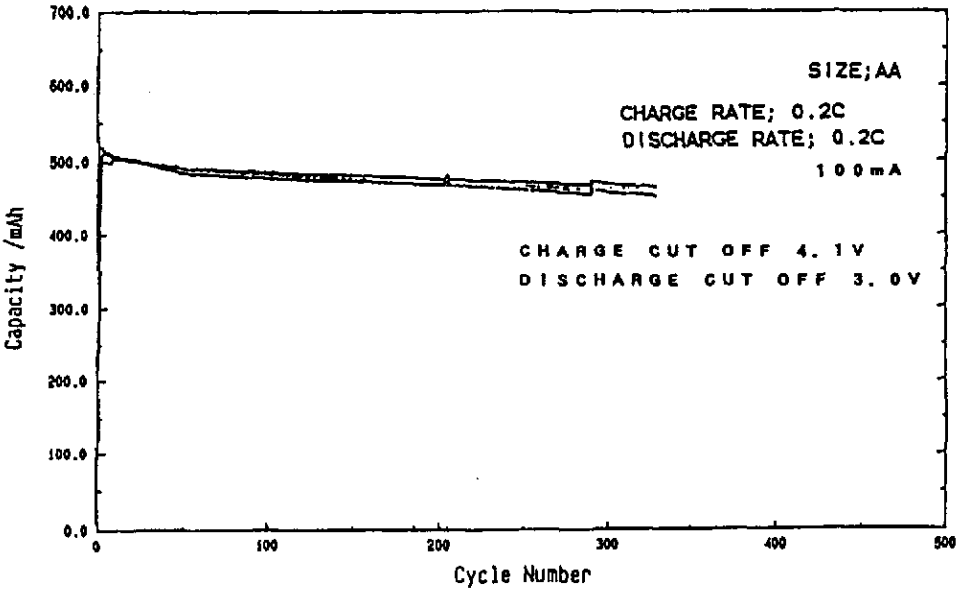

Fig. 6. Cycle-life characteristics of 'AA-size' battery using $LiCoO_2$ and MCMB.

Conclusion

We have found that the MCMB, with a high graphitization level which functions as a Li intercalation compound, has good characteristics for a negative electrode material. The cylindrical 'AA-size' batteries of our trial using $LiCoO_2$ as positive electrode materials and the MCMB graphitized at 2800 °C as negative electrode materials gave large capacities of over 500 mA h and high operating voltages of 3.7 V high energy densities of 240 W h/l and 100 W h/kg.