KMFC Graphite Powder for Negative Electrode Material of Lithium Ion Secondary Battery*

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1 Introduction

Aromatic constituents in coal-tar pitch were thermally polymerized by a heat-tretmet at 350°C to 400°C to form optically anisotropic spheres, of up to several tens of μm in diameter, called mesophase spheres. The spheres, which are separable from the pitch matrix by an adequate solvent, were found by Yamada et al. in 1977 to be a suitable raw material with self-sinterability for carbon block of high density and high strength[1]. Kawasaki Steel is one of the largest coal-tar distilleries in Japan, using its own coal-tar from the steel-making process. During its development of new carbon materials from coal-tar pitch, Kawasaki Steel focused on research and development of the commercial production of mesophase spheres. Ultimately, Kawasaki Steel succeeded in the commercial production using its own technology and began to supply the spheres under the name KMFC (Kawasaki mesophase fine carbon) for carbon blocks of high density and high strength in 1987. In 1991, KMFC was accepted as a raw material for the negative electrode of lithium ion secondary batteries, and its market should now grow even further.

2 Manufacturing Process

The KMFC manufacturing process consists of heat-treatment of coal-tar pitch, solvent extraction, filtration, drying, calcining and classification (**Fig. 1**)[2,3].

The quality of the raw coal-tar pitch is strictly controlled, since it has a strong influence on KMFC quality. In the heat-treatment process, the coal-tar pitch is treated at 350°C to 400°C to form the mesophase spheres. Since the particle size distribution and the graphitizability of KMFC are mostly determined in this process, batch heat-treatment is applied to stabilize of these properties. In the solvent extraction and filtration, pitch matrix is extracted by a tar-solvent and mesophase spheres are fil-

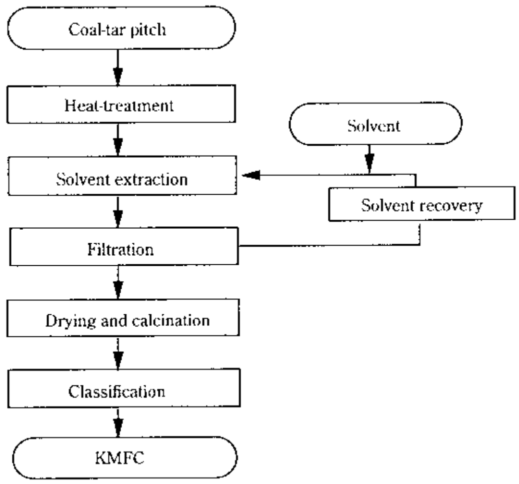

Fig. 1 Process flow diagram for KMFC manufacturing

tered for separation. In order to leave some β-resin (toluene insoluble-quinoline soluble component) around the spheres from the pitch matrix, a tar-solvent with an adequate capability to dissolve pitch was selected. The β-resin around the spheres gives KMFC the self-sinterability which is necessary to the production of carbon blocks of high density and high strength. In the drying and calcining process, the separated spheres are further heat-treated at 300°C to 400°C in order to remove the existing solvent and light component. β-resin is thermally converted in the process into α-resin (quinoline insoluble component) and its self-sinterability is controlled. Finally, in the classification process, narrow distribution of particle size was achieved by shifting out large spheres, and purity was improved by removing ash.

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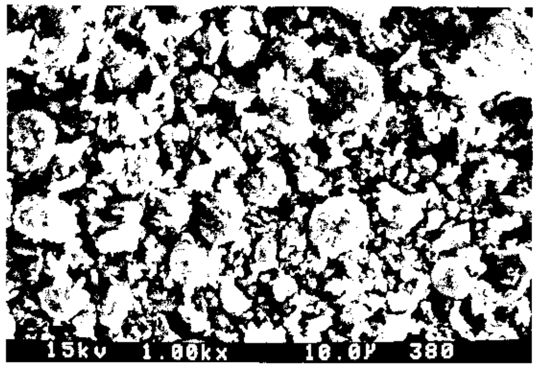
Table 1 Properties of KMCF graphite powder

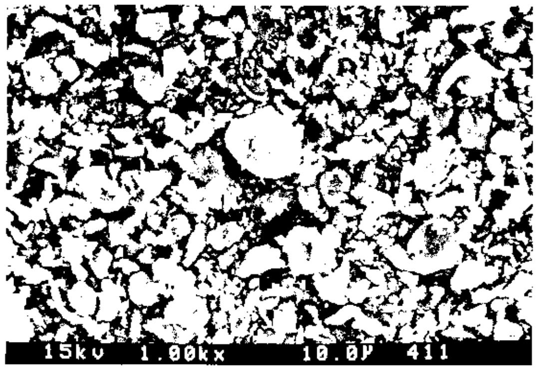
			KMFC-A	KMFC-B
True density		(g/cm^3)	2.18~2.22	2.18~2.22
Ash		(%)	< 0.1	< 0.1
Specific surface area		(m^2/g)	3.8~4.2	4.6~5.2
Bulk density		(g/cm^3)	0.52~0.48	0.42~0.38
Lattice constant	C_0 (002)	(Å)	6.740	6.740
	L_c (002)	(Å)	750	750
Average particle diameter* dp50		(μm)	17.1	5.3

*Measured by the Coulter counter



10 μm

Photo 1 Scanning electron micrograph of KMFC-A graphite powder



10 μm

Photo 2 Scanning electron micrograph of KMCF-B graphite powder

3 Application of KMFC

3.1 Carbon Material for Negative Electrodes of Lithium Ion Secondary Batteries

Since lithium ion batteries have higher voltage and energy density than conventional Ni-Cd and Ni-MH batteries, they are increasingly being used as an electric power supply for cellular phones and notebook personal computers. The graphite or carbon used in the batteries as a negative electrode requires the the following properties.

(1) Large discharge capacity
(2) Good charge-discharge cyclability
(3) Steady discharge voltage vis-a-vis lithium
(4) Small retention, which is the difference between charge capacity and discharge capacity in the first cycle

Although KMFC was originally developed for carbon blocks of high density and strength, the graphitized KMFC was found to be highly suitable for a negative electrode material of the batteries, since KMFC is spherical fine powder consisting of graphitizable mesophase as a basic structure. Kawasaki Steel has two kinds (A and B) of graphitized powder which are differentiated by their respective particle size. Both powders satisfy the reuired properties described above. The properties of KMFC-A and -B are summarized in **Table 1**, and their scanning electron micrographs are shown in **Photos 1** and **2**. As shown in Table 1, the true density of the powders is 2.18 to 2.22 g/cm^3 which is much higher than that of hard carbon materials. This means that KMFC powder gives high discharge capacity per unit volume. Because of the sphericity (Photos 1 and 2), KMFC is packed on the current collector much more densely than fibrous or flaky material. **Figures 2** and **3** show the charge-discharge curves of the powder measured in a glass cell having lithium metal as a reference and working electrode. For the charge curve, a larger irreversible loss, possively caused by the decomposition of electrolyte, is found in KMFC-B than in KMFC-A, because KMFC-B contains smaller particles, *i.e.*, higher specific surface area, than KMFC-A. For the discharge, both A and B show steady voltage as is typically observed in graphite materials and show almost the same discharge capacity of about 300 mAh/g.

It is reported that lithium ions are doped in the graphite and turbostratic structures of KMFC graphitized powder and then is undoped from these sites during the charge and discharge cycle[4]. In graphite structure, the hexagonal aromatic sheets are located in a highly ordered position. The theoretical composition becomes LiC_6 at maximum doping of lithium ion and 372 mAh/g is calculated from the LiC_6 structure. The discharge voltage from graphite structure is 0.25 V below that of lithium metal. On the other hand, in turbostratic structure, the stacking order of the aromatic sheets is at random and less lithium ions are stored than in graphite structure. Therefore, charge and discharge capacities of this part, corresponding to the voltage over 0.25 V, become smaller than the theoretical value of graphite. The ratio of graphite structure in KMFC changes depending on heat-treatment temperature. The graphite structure appears at about 2 000°C and its ratio increases with increasing in heat-treatment temperature. Increasing heat-treatment temperature gives higher

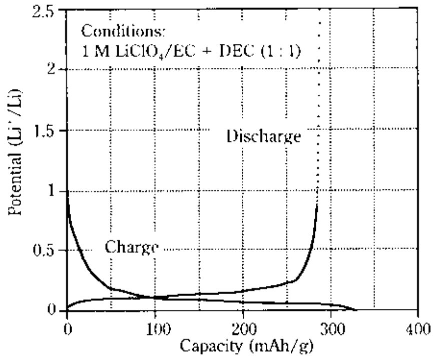


Fig. 2 Charge and discharge curves of KMFC-A graphite powder

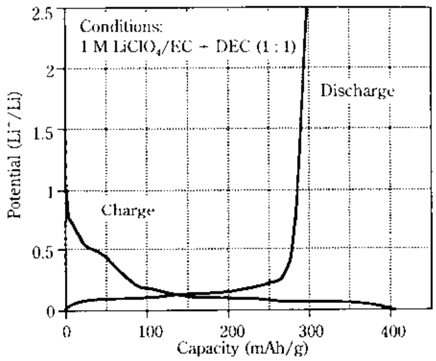


Fig. 3 Charge and discharge curves of KMFC-B graphite powder

capacity of the flat voltage. Oppositely, with the growth of graphite structure, the ratio of turbostratic to graphite structure, as well as the capacity over 0.25 V, decrease.

It is reported that almost 100% of efficiency can be achieved with KMFC graphitized powder after the second cycle, although irreversible loss caused by the decomposition of electrolyte has been observed in the first cycle[5]. It is also reported that KMFC graphitized powder shows superior properties of charge and discharge capacity, compared with other carbon or graphite materials such as petroleum coke and CVD grown carbon fiber[6].

Since KMFC is suitable as a raw material for the negative electrode for lithium ion batteries as described above and has high stability in the manufacturing process, demand of KMFC has been increasing and further growth is expected.

3.2 Carbon Blocks of High Density and High Strength

Carbon materials, used as jigs in semiconductor production and electrodes in electro-discharge machining, are conventionally produced by the method, which consits of mixing binder and coke as a filler, forming and baking. If necessary, the blocks thus produced, are further heat-treated at 2 000°C to 3 000°C. In this method, almost no carbon blocks of sufficient density and strength have been obtained, since the blocks became porous during the baking due to the vaporization of decomposed product from the binder. However, unlike the conventional method, KMFC needs no binder to produce carbon blocks because of its self-sinterability as described earlier, and carbon blocks of high density and high strength are easily produced[7]. Due to its excellent properties, demand for KMFC has been growing in many applications such as jigs in semiconductor production, electrodes in electro-discharge machining, carbon for machinery and carbon materials for atomic energy power plants.

4 Conclusions

Although KMFC was first developed as a raw material for high-density, high-strength carbon, demand for it as a raw material for negative electrodes of lithium ion batteries has been growing in recent years. In both applications customers' evaluation of KMFC has been high. We lead the world in production capacity of mesophase spheres and in operational experience. We supply KMFC with highly stable quality and expect further growth in a wide range of applications and fields.

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