JFE TECHNICAL REPORT
No. 6 (Oct. 2005)

High-performance KMFC Graphite Powder for Lithium Ion Secondary Battery†

1. Introduction

Lithium ion secondary batteries are widely used as a power source for mobile equipment such as cellular phones and personal computers owing to their high energy density. **Figure 1** shows the working principle of the lithium ion secondary battery. Lithium cobalt oxide is generally used as the positive electrode material, and graphite as the negative electrode material. Lithium moves in ionic form from the positive electrode to the negative electrode during the charging period of the battery, and moves from the negative electrode to the positive electrode during the discharging period. The graphite used for the negative electrode is required the characteristics of (1) large lithium occlusion capacity, (2) high charge/discharge efficiency, (3) good charge/discharge rate, and (4) high capacity retention after many cycles. JFE Steel and JFE Chemical (hereafter "JFE Steel Group") have developed a spherical graphite as a high-performance negative electrode material which satisfies these requirements. This paper describes the characteristics of the developed KMFC graphite powder and its performance as a negative electrode material.

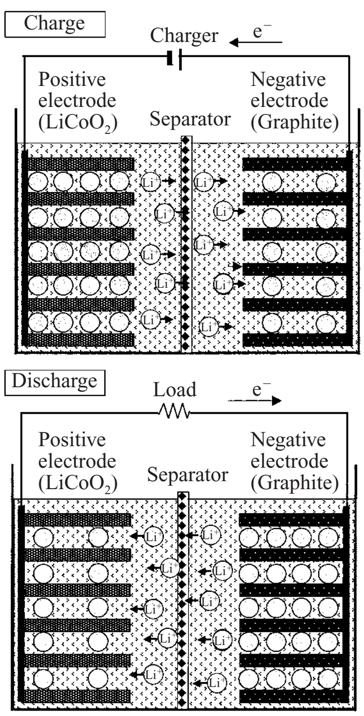


Fig. 1 Principle of the lithium ion secondary battery

† Originally published in *JFE GIHO* No. 8 (June 2005), p. 71–73

2. Development of KMFC

JFE Steel Group has been developing KMFC (Kawasaki Mesophase Fine Carbon) to add value to coal-tar. KMFC is an easily graphitized spherical carbonaceous powder, which is prepared by extracting optically anisotropic small spheres (mesophase spheres) formed by heat treatment of coal-tar pitch using a tar-based solvent, and then by separating the mesophase spheres. In 1977, the Government Industrial Research Institute, Kyushu reported that the separated spheres show excellent self-sintering property[1]. Based on these results, JFE Steel Group conducted studies from basic research to commercialization, and succeeded in manufacturing the KMFC on an industrial scale for the first time in the world by using an exclusive technology.

In 1987, JFE Steel Group began to manufacture and sell the KMFC as a raw material for high-density, high-strength carbon materials. In addition, the graphitized KMFC was found to have excellent performance as the negative electrode material for lithium ion secondary batteries, and application in this field began in 1991.

3. Manufacturing Process of KMFC and KMFC Graphite Powder

Figure 2 shows the Manufacturing process of KMFC and KMFC graphite powder. The KMFC is manufactured from coal-tar pitch as the raw material, through the steps of heat treatment, solvent extraction and filtration, drying and calcination, and classification. The KMFC is then baked, pulverized and classified into specified particle sizes. After classifying, graphitization is performed to obtain KMFC graphite powder[2,3]. The KMFC is used as a raw material for high-density, high-strength carbon materials, and KMFC graphite powder is used as the negative electrode material for lithium ion secondary batteries[4,5].

Photo 1 shows a typical polarized micrograph of

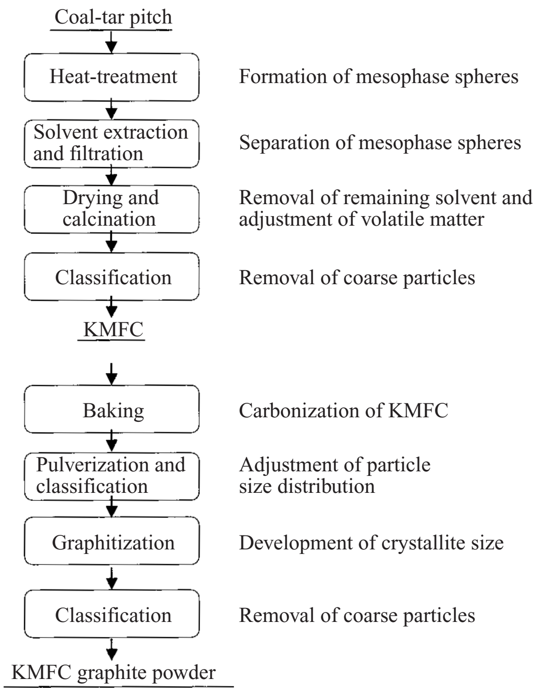


Fig.2 Manufacturing process of KMFC and KMFC graphite powder

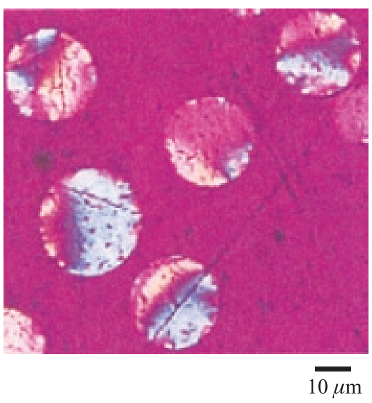


Photo 1 Polarized micrograph of mesophase spheres formed in coal-tar pitch

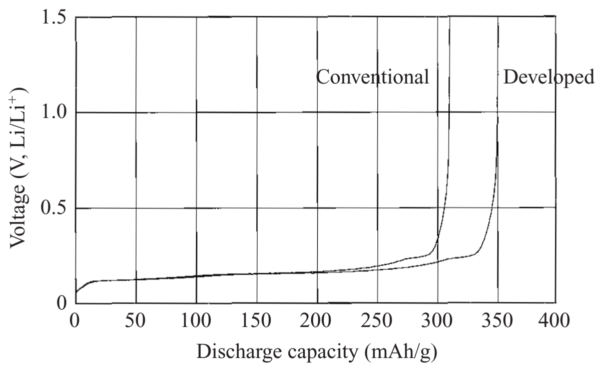
mesophase spheres formed during the heat treatment step. The quality of coal-tar pitch as the raw material significantly affects the quality of KMFC graphite powder so strict quality control is required for stable manufacturing. JFE Steel Group has established technology for controlling the quality of pitch as the raw material of carbon materials in the binder pitch manufacturing process, and so applied it to the quality control of raw material of KMFC.

4. Charge/Discharge Characteristics of KMFC Graphite Powder

The use of KMFC graphite powder as the negative electrode material gives flat charge/discharge potential, which is a feature of graphite-based materials. Furthermore, KMFC graphite powder has excellent performance as a negative electrode material, giving high charge/discharge efficiency and good discharge rate. To increase the capacity of KMFC graphite powder, it is important to increase its crystallinity and thus increase the number of sites for intercatation and deintercalation of lithium ions. JFE Steel Group has conducted R&D to improve the crystallinity without affecting the favorable performance. Since the crystallinity of KMFC graphite powder is affected by both the raw material quality and the manufacturing conditions, optimization of the combination of these variables increases the capacity of KMFC graphite powder. JFE Steel Group generates various types of coal-tar in the iron-making process and so carefully selected the optimum coal-tar as the raw material. By investigating manufacturing conditions that fully utilize the selected coal-tar to improve the crystallinity, the Group succeeded in developing high-capacity KMFC graphite powder.

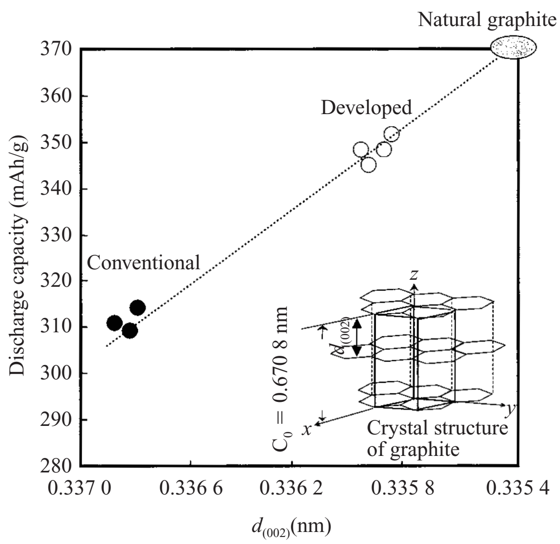
Figure 3 shows the discharge capacity of the conventional product A1500 and that of the developed high-capacity KMFC graphite powder as the negative electrode material, while applying lithium metal as the counter electrode. Both cases give flat potential which is a feature of graphite-based materials. However, the high-capacity KMFC graphite powder generates a discharge capacity of 350 mAh/g which is higher than that of the conventional grade by about 40 mAh/g. **Figure 4** shows the relation between the discharge capacity and the graphite layer distance (*d*-spacing), $d_{(002)}$ as an index of the crystallinity of graphite, measured by X-ray diffraction. The conventional type had a *d*-spacing of about 0.336 8 nm, and the high-capacity type gave a small *d*-spacing of 0.335 8 nm, thereby improving the crystallinity. As a result, the high-capacity type has a significantly higher discharge capacity than the conventional type. Generally, graphite-based materials have a flatter shape as the crystallinity increases. Nevertheless, KMFC graphite powder provides high capacity without affecting the spherical shape of the mesophase spheres. Therefore, the particle orientation of the electrode using KMFC graphite powder can be suppressed. **Figure 5** shows the discharge rate characteristics measured on a KMFC graphite powder (high-performance type) electrode and a natural graphite electrode, their densities being adjusted to the same value.

The discharge characteristic of the natural graphite significantly deteriorates as the discharge rate increases from 0.1*C* to 0.5*C*, 1*C*, 1.5*C*, and 2.5*C*. On the other hand, the developed high-capacity type KMFC graphite powder showed excellent discharge rate characteristics, and maintained the discharge capacity of about 90% even at 2.5*C*.



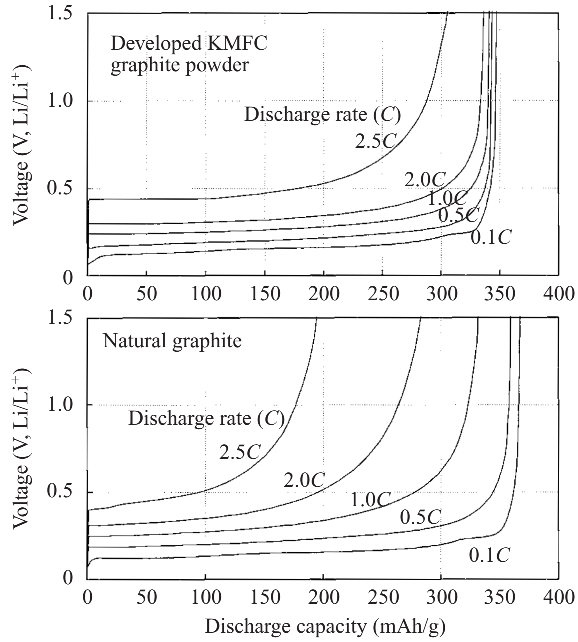
Measurement conditions of discharge capacity:
Electrolyte; 1 M $LiPF_6$ in EC/EMC (1:2 volume)
Discharge; Constant current to 1.5 V (1.5 V cut off)
(Discharge rate: 0.1 C)
EC: Ethylene carbonate
EMC: Ethyl methyl carbonate

Fig. 3 Discharge capacity of developed and conventional KMFC graphite powders



Measurement conditions of discharge capacity:
Electrolyte; 1 M $LiPF_6$ in EC/EMC (1:2 volume)
Discharge; Constant current to 1.5 V (1.5 V cut off)
(Discharge rate: 0.1 C)
EC: Ethylene carbonate
EMC: Ethyl methyl carbonate

Fig. 4 Relation between *d*-spacing $d_{(002)}$ and discharge capacity of developed and conventional KMFC graphite powders



Measurement conditions of discharge capacity:
Electrolyte; 1 M $LiPF_6$ in EC/EMC (1:2 volume)
Discharge; Constant current to 1.5 V (1.5 V cut off)
EC: Ethylene carbonate
EMC: Ethyl methyl carbonate

Fig. 5 Comparison in discharge rate property of developed KMFC graphite powder and natural graphite powder

5. Conclusion

The KMFC developed by JFE Steel and JFE Chemical is a distinctive carbon material having a spherical shape and is easily graphitized. With these characteristics, the developed KMFC can be used as a raw material for high-density, high-strength carbon materials, and the KMFC graphite powder can be used as the negative electrode material for lithium ion secondary batteries. Demand for higher capacity lithium ion secondary batteries is increasing year after year, and so a higher capacity negative electrode material is required. In response, JFE Steel Group has increased the capacity by improving the raw material and manufacturing conditions, and has developed a KMFC graphite powder that has a discharge capacity of 350 mAh/g, which is about 40 mAh/g greater than that of the conventional type. This high-capacity KMFC graphite powder also shows excellent discharge rate characteristics.

JFE Steel Group has the world's largest KMFC manufacturing facilities which assure stable supply of products, and the operating period of the facilities is also the longest in the world. JFE Steel Group is continuing R&D to ensure the delivery of products with stable quality that meet customers' requirements.

References

1) Yamada, Y. Shibata, K.; Honda, E. Tanso. vol. 88, 1977, p. 2.
2) Fukuda, N. Honma, S. Nagasawa, K.; Muranichi, Y.; Abe, H. Kawasaki Steel Giho. vol. 18, no. 3, 1986, p. 289.
3) Fukuda, N.; Nagayama, K.; Honma, S.; Kawasaki Steel Giho. vol. 21, no. 4, 1990, p. 335.
4) Hatano, H.; Fukuda, N.; Aburaya, T.; Kawasaki Steel Giho. vol. 29, no. 4, 1997, p. 233.
5) Hatano, H.; Nagayama, K.; Tajima, H. Kawasaki Steel Giho. vol. 34, no. 3, 2002, p. 140.

For Further Information, Please Contact to:

Division of Carbon Materials, JFE Chemical
Phone: (81) 3-5820-6533 Fax: (81) 3-5820-6539