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KMFC™ Graphite Powder of High Capacity for Negative Electrode Material of Lithium Ion Secondary Batteries†

1. Introduction

Lithium ion secondary batteries are widely used as a power source for mobile devices such as a smartphones, laptop PCs, etc., taking advantage of their high energy density. As development to on-board automotive applications such as electric vehicle (EV) and hybrid electric vehicle (HEV) is also progressing, large growth is expected in the future. In general lithium ion secondary cells, lithium cobalt oxide is used as the positive electrode material and graphite is used as the negative electrode material, and charge/discharge proceeds by migration of lithium ions between the two electrodes. In order to realize long-time operation and large current charge/discharge as a battery, two types of performance are required in the graphite of the negative electrode material, namely, (1) high lithium occlusion capability (capacity) and (2) high speed charge/discharge performance (rate property). JFE Chemical developed a mesophase sphere graphite as a high performance negative electrode material responding to these requirements[1-3]. This report introduces the features and performance of the developed material.

2. Mesophase Spheres

JFE Chemical is one of the world's leading tar distillation manufacturers using coal tar produced as a byproduct of iron and steel production as a feedstock, and is also involved in the development of high value-added tar pitch products[1-5]. When heat treatment is applied to coal tar pitch, layers of aromatic rings, which spreads as a result of condensation and polymerization, form a laminated structure, and small spheres (mesophase spheres) with sizes from several micrometers to several 10 μm are generated. Coal tar pitch which is not heat-treated is optically isotropic, but in contrast, mesophase spheres display optical anisotropy. **Photo 1** shows an example of a polarized micrograph of mesophase spheres generated by heat treatment.

Mesophase spheres can be separated from the pitch matrix by using an appropriate solvent. Due to the structural feature of mutually-aligned crystallite, mesophase spheres have the property of easy graphitization by high temperature heat treatment, and thus are classified as graphitizable carbon. In general, the shape of graphite materials tends to become flat as crystallinity increases. From this viewpoint, mesophase spherical graphite can be called a unique material, as it develops a crystal structure while retaining a spherical shape.

Photo 2 shows a transmission electron microscope (TEM) image of the cross section of a particle of meso-

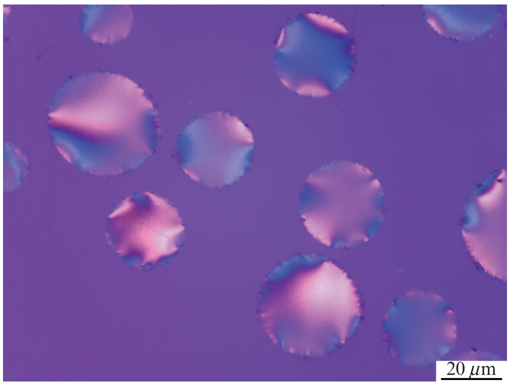

Photo 1 Polarized micrograph of mesophase spheres formed in coal-tar pitch

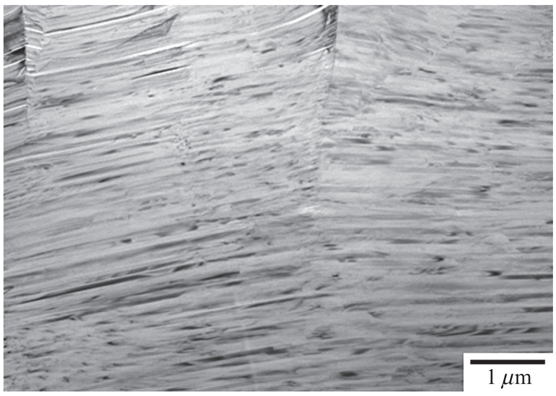

Photo 2 Transmission electron microscope (TEM) image of cross section of KMFC™ graphite powder

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phase spherical graphite (graphite powder). The striped pattern extending to the right and left shows that hexagonal carbon layers, which are the fundamental structural unit of the graphite crystal, are stacked in layers over a wide area. From this, it can be understood that a crystal structure has formed internally in the spherical body.

The mesophase sphere manufacturing process comprises heat treatment, solvent extraction and filtration, drying and calcination, and classification processes[4,5]. Graphite powder is manufactured by further graphitization of the mesophase spheres obtained by this process. JFE Chemical was the first in the world to succeed in industrial production of mesophase spheres (KMFC™: Kawasaki Mesophase Fine Carbon) using its own proprietary technology, and began manufacture and sale of this product as a raw material for high density/high strength carbon materials in 1987. In 1991, the company also began manufacture and sale of graphitized mesophase spheres as a negative electrode material for lithium ion secondary batteries.

3. Features of KMFC™ Graphite Powder as Negative Electrode Material

3.1 Discharge Capacity

The interlayer spacing of graphite, $d_{(002)}$, obtained by X-ray diffraction is generally used as an index of the crystallinity of graphite. Interlayer spacing decreases as crystallinity becomes higher and is 0.335 4 nm in perfect graphite crystals. During charge, lithium ions are inserted between layers and form graphite intercalation compounds expressed by the composition LiC_6. The theoretical value of the discharge capacity calculated from this is 372 mAh/g.

The relationship between the interlayer spacing in graphite powder and its discharge capacity is shown in **Fig. 1**. In order to increase the crystallinity of graphite powder, JFE Chemical selected the optimum raw material from its abundant tar sources and made repeated improvements in manufacturing conditions, resulting in the development of a new high capacity type[1-3]. Although the interlayer spacing of the initial product was 0.336 8 nm, this has been reduced to 0.335 7 nm in the most recently-developed product. Accompanying this improvement, the discharge capacity has also improved, achieving 360 mAh/g, or an increase of 50 mAh/g in comparison with the 310 mAh/g of the original product. Thus, high capacity corresponding to approximately 97% of the theoretical value has been realized.

3.2 Other Features

The spherical particle shape of KMFC™ is an advantage for use in electrodes, as the packing density in electrodes is increased, side reactions with the electrolyte are minimal due to the small specific surface area of the particles, etc. Moreover, as one distinctive feature of KMFC™, because a good balance of pores of an appropriate size can be secured in the electrode, the electrolyte can permeate the electrode without over- or under-supply, thereby enabling smooth movement of lithium ions.

As an example of that effect, **Fig. 2** shows the results of measurements of the discharge rate property of high capacity type KMFC™ graphite powder and natural graphite powder, when the electrodes were arranged so that their densities were the same. Here, 1 C is defined as the current value which enables discharge of 100% of capacity in 1 hour. Since natural graphite achieves a high order of crystallinity, it shows a discharge capacity approaching the theoretical value at low discharge rates. However, because the particle shape is flat, natural graphite is easily oriented, and as a result, the discharge

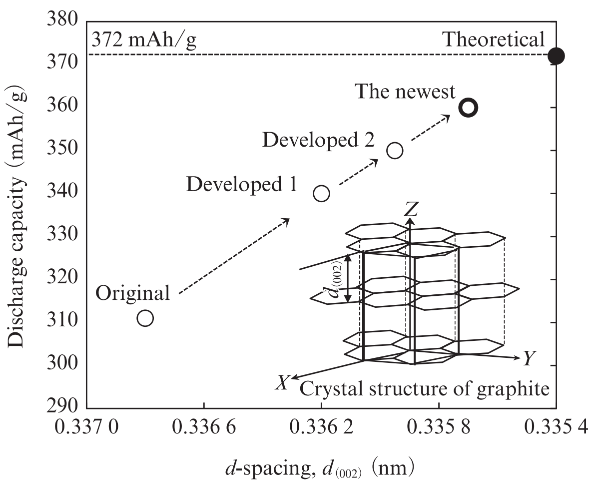

Fig. 1 Relation between *d*-spacing $d_{(002)}$ and discharge capacity of developed and conventional KMFC™ graphite powders

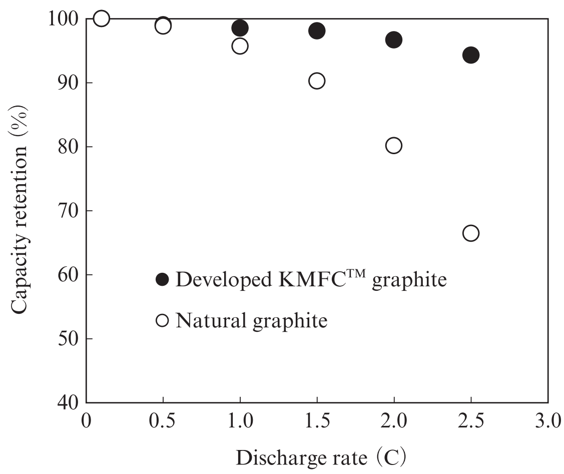

Fig. 2 Comparison in discharge rate property of developed KMFC™ graphite powder and natural graphite powder

capacity decreases rapidly when the discharge rate exceeds 1 C. In contrast, high capacity KMFC™ graphite powder maintains a discharge capacity of approximately 95% even at a high discharge rate of 2.5 C.

4. Conclusion

The new high capacity KMFC™ graphite powder developed by JFE Chemical realizes a high capacity of 360 mAh/g, which corresponds to approximately 97% of the theoretical value. Furthermore, because the particles are spherical in shape, this material displays totally high performance as a negative electrode material, including an excellent discharge rate property, etc. Longer time operation and larger current charge/discharge are required in lithium ion secondary batteries, and the developed graphite powder is a negative electrode material which satisfies these expectations.

JFE Chemical has continued to produce mesophase spherical graphite over a long period since beginning commercial production in 1987. In the future, the company will conduct research and development to achieve further improvements in performance so as to deliver products that meet the needs of the times with stable quality.

References

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