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The microstructure of milled mesophase pitch-based carbon fibers (mMPCFs) that have been developed as an anode material for Li ion batteries have been studied as a function of heat treatment temperature (HTT), by SEM, X-ray diffraction, and Raman spectroscopy. And the results obtained are compared with those by X-ray diffraction (XRD) and SEM observations, for the characterization of specific structural features of mMPCFs as a promising anode material.

Keywords: Carbon fibers; Raman spectroscopy; Microstructure; Li ion batteries

INTRODUCTION

Recently, in order to enhance the cell performance with regard to specific capacity and coulombic efficiency, milled mesophase pitch-based carbon fibers (mMPCFs) heat-treated at high temperature have been developed, and it has been shown that they have superior anode performance[1]. As a result, mMPCFs have been evaluated as one of the most suitable practical materials for use in graphitized anode systems because their fibrous form presumably gives rise to high battery

performance, which could be comparable to those of common mesocarbon microbeads (MCMBs) or of natural graphite. Furthermore, a high degree of battery performance could be expected for mMPCFs because of the homogeneity of their macroscopic morphology as well as microscopic structure. Intensive work has already been reported on the structural characterization of conventional mesophase pitch-based carbon fibers (MPCFs) from the view point of their mechanical properties as they relate to structural aspects, because of their wide use in applications to composite materials[2]. In the present paper, the structural changes of mMPCFs heat-treated at different temperatures have been evaluated regarding their structure from a different view point, specifically as a functional material that is tailored for application to Li ion batteries.

EXPERIMENTAL

The milled mesophase pitch-based carbon fibers (mMPCFs) were prepared using a melt-blow method for fiber synthesis from a petroleum mesophase pitch material. Oxidation of the pitch precursor was performed in air at 300°C. The fibers were then milled to be in lengths ranging several tens of μm, and the milling was followed by heat treatment at 650°C for pre-carbonization. The samples of these processed materials were subsequently heat-treated at 700°C~3000°C. X-ray diffraction (XRD) and field emission (FE) SEM observations, and Raman characterization were carried out for all the samples. Electrochemical measurements were performed by using three-electrode test cells made of pyrex glass. The working electrodes were prepared by mixing the carbon samples at 95 weight percent (wt.%) with poly(vinylidene fluoride) (PVDF) at 5wt.%, using 1-methyl-2-pyrrolidinone as a solvent. The electrode used was a *1M* solution of $LiClO_4$ in a propylene carbonate (PC, HTT$\leqq$1500°C) and EC(ethylene carbonate)+DEC(diethylene carbonate) (volume ratio=1:1, HTT$\geqq$2000°C), respectively. The current density was 30mA/g-carbon.

RESULTS AND DISCUSSION

Representative interlayer spacings, d_{002}, and crystallite thicknesses, $L_{c(002)}$, are plotted as a function of HTT in Fig. 1 for the mMPCFs used. The mMPCFs show an increase in $L_{c(002)}$ and a decrease in d_{002} with

increasing HTT. By heat treatment at 3000 °C, d_{002} contracts by about 4% from that of HTT=1000 °C. The interlayer spacing of mMPCFs heat-treated at 3000 °C approaches that of highly oriented pyrolytic graphite (HOPG) (3.354 Å). This graphitization behavior could be due to the high degree of graphitizability of the fibers caused by molecular mobility and the structural rearrangement that occurs with increasing HTT. Fig. 2 shows typical FE-SEM images of mMPCFs heat-treated at 1000 and 3000 °C. It is also noteworthy that the cross sectional core region has a well-aligned layer structure, as demonstrated by the high magnification micrograph shown in Fig. 3(a), while at the periphery (Fig. 3 (b)), we see a more wavy layered structure, where the layers are arranged like bamboo shoots along the surface of the fiber. The cross sectional morphology of the present fiber is schematically demonstrated in Fig. 3 (c). These structural features with different morphologies in the cross section of the present mMPCFs might contribute to their superior properties as an anode material for a Li inserted host material in Li ion batteries, while a homogeneous cross sectional morphology might be important for high performance in mechanical properties.

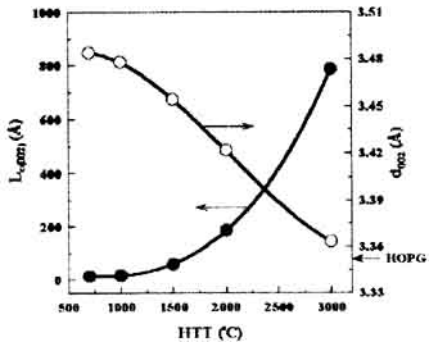

FIGURE 1. Crystallite thickness, $L_{c(002)}$ and interlayer spacing, d_{002} as a function of HTT.

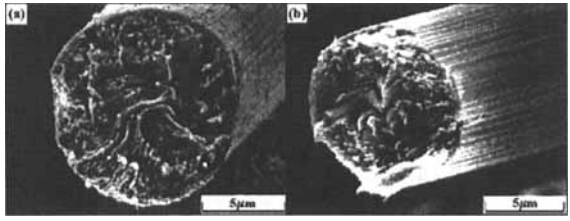

FIGURE 2. FE-SEM photographs of a mMPCFs heat treated at (a) 1000°C and (b) 3000°C.

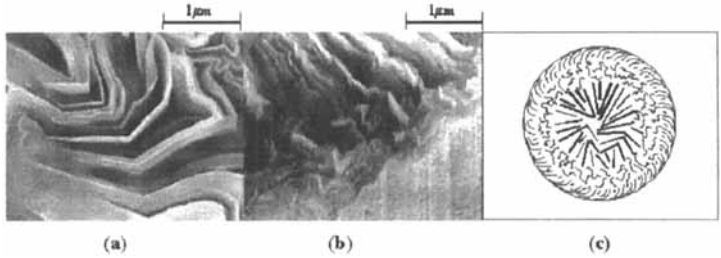

FIGURE 3. FE-SEM photographs of the (a)center, (b)periphery of mMPCFs, and (c) a schematic layer model for the fibers.

Figure 4 shows the first- and second-order Raman spectra from the cross section of mMPCFs with HTT ranging from 700°C to 3000°C. With increasing heat treatment temperature (HTT), the mMPCFs show an increase in the Raman intensity and a decrease in the linewidth of the graphite Raman-allowed 1580cm^{-1} band (G-band), and a decrease in the intensity and linewidth of the disorder-induced 1330cm^{-1} band

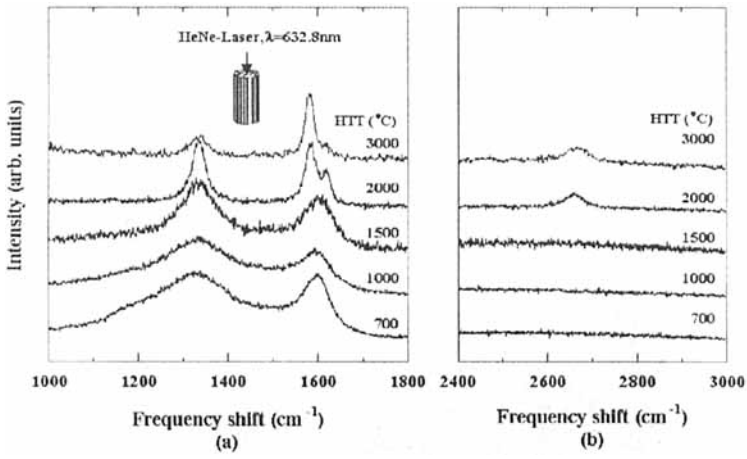

FIGURE 4. The first-(a) and second-order (b) Raman-spectra of the cross-section of mMPCFs as a function of HTT.

(D-band). At a heat treatment temperature of 2000°C and 3000°C, the cross section also shows Raman peaks corresponding to the second-

order line near 2660cm^{-1} and also a very weak peak at 1620cm^{-1}. These phenomena are associated with the development of graphite microcrystallites in mMPCFs with HTT above 2000°C. In the case of the samples heat-treated at 2000 and 3000°C, the peak at 1620cm^{-1} is due predominantly to midzone phonons which have energies corresponding to peaks in the density of phonon modes[3]. By heat treatment at 3000°C the peak near 1620cm^{-1} decreases, and the 2660cm^{-1} band increases in intensity which is associated with the second-order spectra of well-ordered graphite[4]. This similarity in the behavior of the peak demonstrates the disorder induced origin of the feature at 1620cm^{-1} peak and the disorder-induced line near 1330cm^{-1}. A HTT of ≈2000°C corresponds to the temperature at which the graphite structure is established from turbostratic carbon. This result is also consistent with the change in d_{002}. Namely, at HTT=2000°C d_{002} becomes smaller than 3.44Å, indicating that the three-dimensional graphite structure is starting to grow.

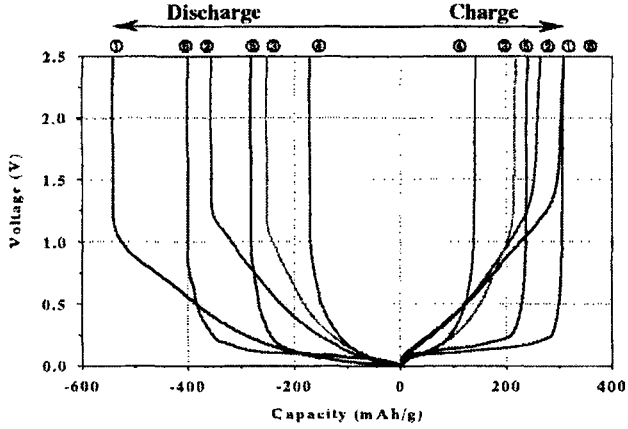

FIGURE 5. Discharge/charge curves of mMPCFs as a function of HTT. ①HTT=700°C, ②HTT=1000°C, ③HTT=1500°C, ④ HTT=2000°C, ⑤HTT=2500°C, and ⑥HTT=3000°C.

Fig. 5 shows the discharge and charging curves of mMPCFs as a function of HTT. It is can be seen, the high and low temperature heat-treated mMPCFs (HTT=3000, 700°C) have a larger capacity, but

mMPCFs heat-treated at 2000℃ possess minimum capacity. These results may be related to the crystallite domain size, $Lc_{(002)}$. Namely, for HTT above 2000℃ the Li intercalation and deintercalation processes mainly occurs. However, in the low HTT region the Li doping and undoping process mainly occurs. Especially, at HTT=2000℃, both reaction processes mainly occur incompletely, which might cause a minimum in the discharge and charge capacity. Also, previous researchers already reported the same kind of dependency on discharge and charging capacity as a function of HTT and $Lc_{(002)}$ [5-6].

CONCLUSIONS

Milled mesophase pitch-based carbon fibers for Li ion batteries have been characterized as a function of HTT by a variety of experimental techniques. In particular, we have attempted a structural characterization of the mMPCFs using the 632.8nm HeNe laser line as an excitation source. The present mMPCFs have a characteristic cross-sectional morphology, especially at the periphery of the fiber, which looks like as bamboo shoots. These specific structural features can contribute to the high performance of the electrochemical properties of the present mMPCFs for use in anode materials in Li ion batteries.

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