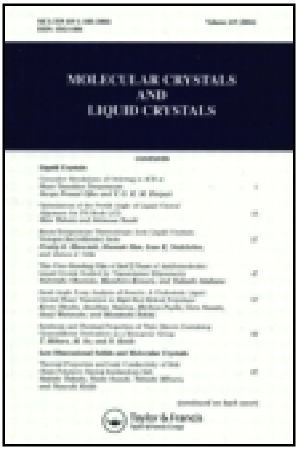

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Graphitization Behaviors of Vapor-Grown Carbon Fibers with Different Diameters as Studied by Raman Spectroscopy

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VGCFs have been used as the anode materials as well as conductive additives in Li-ion batteries due to these special chemical and physical properties. Three types of VGCFs with different diameter sizes from 10μm to 30nm were characterized by Raman spectroscopy to monitor the microstructure based on the size effect.

Keywords: vapor-grown carbon fibers; Raman spectroscopy; size effect

INTRODUCTION

Vapor-grown carbon fibers (VGCFs) obtained by the thermal decomposition of hydrocarbons using transition metal catalysts have a high potential for applications as an anode material in Li-ion batteries due to their graphitization properties and excellent electrical and mechanical properties [1-2]. Therefore, it is very important to understand the variation of the microstructure based on the diameter, which would affect the anode performance. In this study, we prepared three types of VGCFs with different diameters of ~10μm (so called VGCFs), ~0.2μm (so called Submicron VGCFs and denoted S-

VGCFs) and ~30nm (so called Nanofibers), and characterized the graphitization behaviors of the respective fibers as a function of HTT (heat treatment temperature) by microprobe Raman spectroscopy. Present results can contribute to further development of the Li-ion battery performance as an additive in anode materials.

EXPERIMENTAL

The original carbon fibers were prepared by pyrolyzing a mixture of benzene and hydrogen, and the diameters were controlled by reducing the temperature, time, and benzene partial pressure in hydrogen, relative to the normal conditions for common VGCFs using the same apparatus [3]. Graphitization of the fibers was performed at various temperatures from 1000 to 3000°C, using a graphite-resistance furnace operating in a high purity Ar atmosphere. Raman spectra for the polarized beam in the direction perpendicular to the fiber axis were taken under ambient conditions using a Renishaw Image Microscope System 1000, equipped with a CCD (Charge Coupled Device) multichannel detector. The excitation source was a 514.5nm Argon-ion laser line, and the optical power at the sample position was maintained at 25mW. The scattered light was collected in a backscattering configuration.

RESULTS AND DISCUSSION

Figure 1 shows the first-order Raman scattering of (a) VGCFs, (b) S-

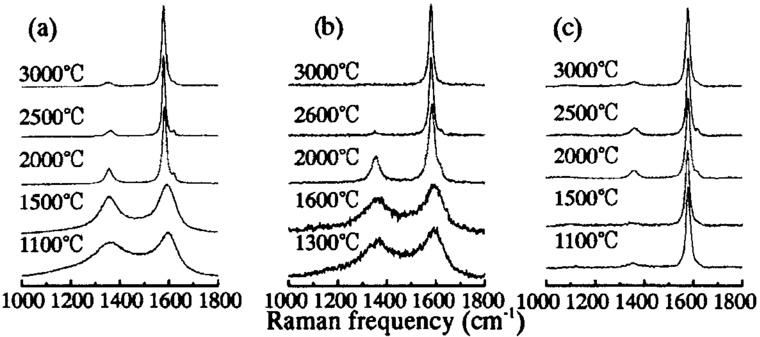

FIGURE 1 The first-order Raman spectra of (a) VGCFs, (b) S-VGCFs and (c) Nanofibers as a function of HTT.

VGCFs and (c) Nanofibers as a function of HTT. All samples exhibit mainly two Raman bands at about 1580cm^{-1} and 1335cm^{-1}, respectively, the former corresponding to the Raman-allowed E_{2g2} mode called the graphite mode (G-band) and the latter to the defect-induced Raman band called the D-band[4]. Also, a D'-band at around ~1620cm^{-1} due to the maximum in the phonon density of states[3] is clearly observed above HTT= 2000°C for all samples. In the case of the S-VGCFs, the general features of the Raman spectra are almost similar to those for the normal VGCFs; the shape of the D and G bands become sharper, and the bandwidth of the D band decreases with increasing HTT. On the other hand, Nanofibers show a very different behavior as compared with those of the former two types of fibers. The intensity of the D bands is increased for the Nanofibers sample above 2000°C, and decreased for this sample at 3000°C. Namely, the Nanofibers should consist of stacked multitubes, which have a nearly perfect cage structure of carbon atoms already in the as grown state. No evident effect in the Raman spectra occurs even by heat treatment at a temperature as high as 3000°C, which is reflected in the almost constant Raman results as a function of HTT, as shown in Fig. 2. The D band behaviors mentioned above should result from the lattice strain between each graphene layer caused by heat treatment. In-plane ordering starts for VGCFs and S-VGCFs at around 2000°C, because the relative intensity and Raman frequency of the G bands show a larger variation at this temperature. As a result,

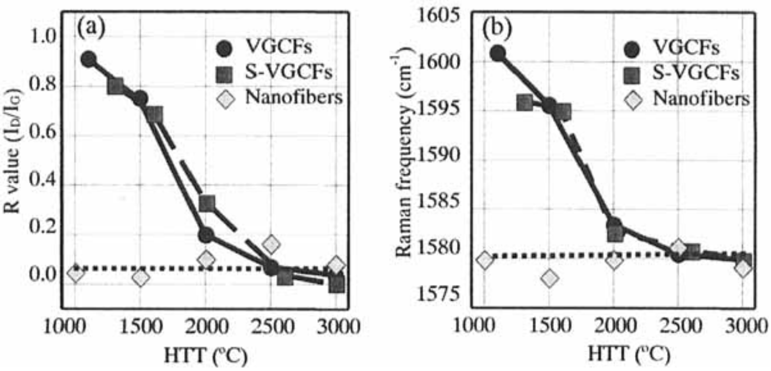

FIGURE 2 The variation of (a) the relative intensity (R value) (I_D/I_G) and (b) Raman frequency of G-peaks as a function of HTT.

the behavior of VGCFs with diameters of ~10μm and S-VGCFs with diameter of ~0.2μm are characterized as typical graphitizable carbons within the optical skin depth, showing a transformation from turbostratic carbons to highly graphitic materials. But, in the case of Nanofibers, the general trend of the Raman peaks are not changed much. Therefore, it is possible to say that the graphitization behavior of Nanofibers with smaller diameters would show no variation of D band structures as a function of HTT.

It is well known that the second-order of Raman spectra show high sensitivity to the three-dimensional stacking by observing the shape of the 2D peaks at around 2710cm^{-1} [5]. Generally, asymmetric features are observed for VGCFs and S-VGCFs above 2500°C, whereas all samples of Nanofibers show these phenomena. To estimate the degree of three-dimensional stacking, curve-fittings using Lorentzian distribution functions were performed. Even though the distances between fitted peaks are known to reflect the three-dimensional ordering [6], in our samples, the relative intensities or R\` value (I_{2700}/I_{2725}) shows a definitive relation with interlayer spacing, as shown in Fig. 3. Generally speaking, with decreasing interlayer spacing, the R-value of the 2D peaks shows tendency to decrease with increasing HTT. Also, higher R-values for S-VGCFs as compared with VGCFs would be ascribed to the size effect as reported previously [7]. Even though as-grown Nanofibers already show relatively high graphitic properties as compared with those of VGCFs and S-VGCFs, heat-treated samples at 3000°C show a

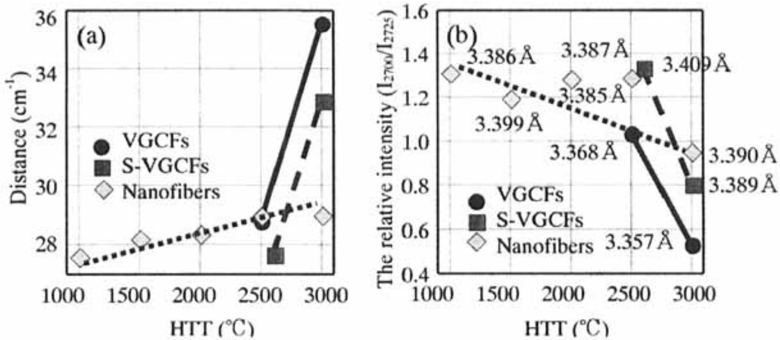

FIGURE 3 The variations of (a) distance and (b) the relative intensity of peak at 2725cm^{-1} to the peak at 2700cm^{-1}.

comparatively larger R-value (interlayer spacing) due to severe size effects arising from the cylindrical shape of the Nanofiber cross section.

CONCLUSIONS

The first-order Raman spectra of VGCFs and S-VGCFs show similar graphitization behavior, transforming turbostratic carbon into graphite, whereas those of Nanofibers shows no large differences for all samples except a little variation of the D bands, which might be due to the characteristic tubule structure. Regarding the second-order Raman spectra, the R` value (I_{2700}/I_{2725}) show a definitive relation with the degree of three-dimensional stacking, that is, the interlayer spacing for all samples. The above results can be explained by two effects: the first is based on a catalytically grown tubular carbon layers in the as-grown materials, and the second is due to the strain energy caused by the curvature. The variation of the microstructure for the respective fibrous carbons obtained by pyrolyzing hydrocarbon would greatly affect the anode performance when used as the anode material or as additives in Li-ion batteries.

References

[1] M. Endo, *Chemtech*, **8**, 568 (1988).
[2] M. Endo, K. Takeuchi and M. S. Dresselhaus, *J. Phys. Chem. Solids*, **58**, 1707 (1997).
[3] M. Endo, K. Takeuchi, K. Kobori, K. Takahashi, H. W. Kroto and A. Sarkar, CARBON NANOTUBES (Elsevier Science Limited,1996) pp.1–10.
[4] R. J. Nemanich and S. A. Solin, *Phys. Rev. B* **20**, 392 (1979).
[5] T. C. Chieu, M. S. Dresselhaus and M. Endo, *Phys. Rev. B* **26**, 5867(1982).
[6] K. Angoni, *J. Mater. Sci.* **33**, 3693 (1998).
[7] J. S. Speck, M. Endo and M. S. Dresselhaus, *J. Crys. Growth.* **94**, 834(1989).