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Pseudo-capacitance on exfoliated carbon fiber in sulfuric acid electrolyte

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ABSTRACT The specific capacitance of exfoliated carbon fibers (ExCF) which were synthesized from pitch-based carbon fibers showed a strong dependence with the concentration of sulfuric acid electrolyte and reached $1.4\,F/m^2$ in $18\,M\ H_2SO_4$ solution. Since the capacitance value is quite large compared with the case of conventional activated carbons, faradic reactions (charge transfer reactions) are the cause of pseudo-capacitance. ExCF, however, gave a featureless cyclic voltammogram in $18\,M\ H_2SO_4$ solution. In the case of exfoliated natural graphite, the intercalation of H_2SO_4 molecules is evidenced by redox peaks observed in the voltammograms in the same conditions. Therefore, a strong interaction between the H_2SO_4 molecules and the ExCF surface might be the reason for the origin of pseudo-capacitance with ExCF in H_2SO_4 electrolyte.

1 Introduction

Electric double layer capacitors (EDLC) using carbon electrodes have been anticipated as an energy storage device for electric vehicle, distributed energy system applications and so on. High surface area carbons were employed for the electrode materials of EDLC to store energy in the electric double layer, and the control of pore size distribution of carbon was recognized to be very important [1–3]. On the other hand, when the electrode material shows Faradic reactions in a wide range of potential window, the energy stored by the charge transfer can be accounted as pseudo-capacitance. This type of energy storage is found in transition metal oxides, conducting polymers and intercalation reactions with carbons, and called the electrochemical capacitor [4].

In our previous papers [5–7], carbon fibers were exfoliated by rapid heating of their intercalation compounds prepared in either nitric acid or formic acid, splitting single fibers into a number of thin filaments. By controlling the synthesis conditions, exfoliated carbon fibers (ExCFs) with a specific surface area of $120–420\ m^2/g$ were obtained and thus a specific capacitance of $40–160\,F/g$ resulted in $1\ mol/dm^3$ sulfuric acid [8]. From the capacitance depen-

dence with surface area, the specific capacitance per unit surface area reached $0.4\,F/m^2$, which is larger than most of the conventional activated carbons [9]. Moreover, it was found that ExCFs give a specific capacitance that is as large as $450\,F/g$ in $18\ mol/dm^3$ sulfuric acid [10]. In the present work, the electrochemical capacitor behavior of ExCFs was studied in different concentrations of sulfuric acid electrolyte and the mechanism to give large capacitance was discussed by comparison with exfoliated natural graphite and activated carbon fibers.

2 Experimental

Exfoliated carbon fibers (ExCFs) were prepared from mesophase-pitch-based carbon fibers heat-treated at $3000\,^{\circ}C$. Raw carbon fibers were electrochemically oxidized in $13\ mol/dm^3\ HNO_3$ solution; carbon fibers (5 cm) were fixed on to a platinum plate using PTFE sealing tape and immersed into electrolyte, then they were intercalated with a DC current of $0.5\,A$ for 40 min. After electrolysis, the carbon fibers were rinsed with distilled water and dried at room temperature in air. The treated carbon fibers were rapidly inserted into a tubular furnace kept at $1000\,^{\circ}C$ for 5 s to be exfoliated. The detailed exfoliation procedure and behavior for carbon fibers were reported in previous papers [5–7]. For comparison, exfoliated natural graphite (ExNG) was prepared from the H_2SO_4-graphite intercalation compounds (GIC), which was synthesized by chemical oxidation of flaky natural graphite (400 µm) with nitric acid. The exfoliation conditions are the same as in the case of ExCF. Commercial activated carbon fibers (ACF, Gun-Ei Chemical Industry Co., Ltd., Japan) were also used as electrode material for comparison.

The electrochemical behavior of ExCF, ExNG and ACF was measured using a standard three-electrode cell with 1 to $18\ mol/dm^3$ sulfuric acid electrolyte. The electrode materials were pulverized and mixed with PTFE binder in a mortar, and then the mixture was molded to form a pellet at $30\,MPa$ for 15 min at room temperature. The pellet thus obtained was dried at $110\,^{\circ}C$ for 1 hr and cooled under vacuum. The weighed pellet was sandwiched with a current collector (Pt mesh) and a glass micro filter in between two PTFE plates to compose a working electrode. The measurement cell containing the working electrode was evacuated for 1 hr at room temperature and filled with electrolyte under vacuum. A Pt plate

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and Hg/Hg_2SO_4 were used as counter and reference electrode, respectively. The measurement cell was purged with nitrogen flow during the experiment.

The specific capacitance was estimated from cyclic voltammetry with a constant rate of potential sweep of 1 mV/s and galvanostatic charge–discharge curve between 0 and 0.5 V vs. Hg/Hg_2SO_4 with a current density of 20 mA/g. All the electrochemical measurements were performed using VMP-1 potentiostat/galvanostat (Biologic. Inc.).

The ExCF samples pulverized were characterized by X-ray diffraction measurement (XRD, Cu K_α) using a non-reflective sample holder. The morphology and nanotexture of the samples were also observed by scanning electron microscopy (SEM, acceleration voltage of 2 kV) and transmission electron microscopy (TEM, acceleration voltage of 300 kV). For the TEM observation, the sample was sonicated in ethanol and hold on the cupper grid mesh.

3 Results and discussion

3.1 Textural and structural characteristics of ExCFs

Figure 1 shows scanning electron microscopy (SEM) images of exfoliated carbon fibers (ExCF) prepared at 1000 °C. Through the exfoliation process, a monofilament
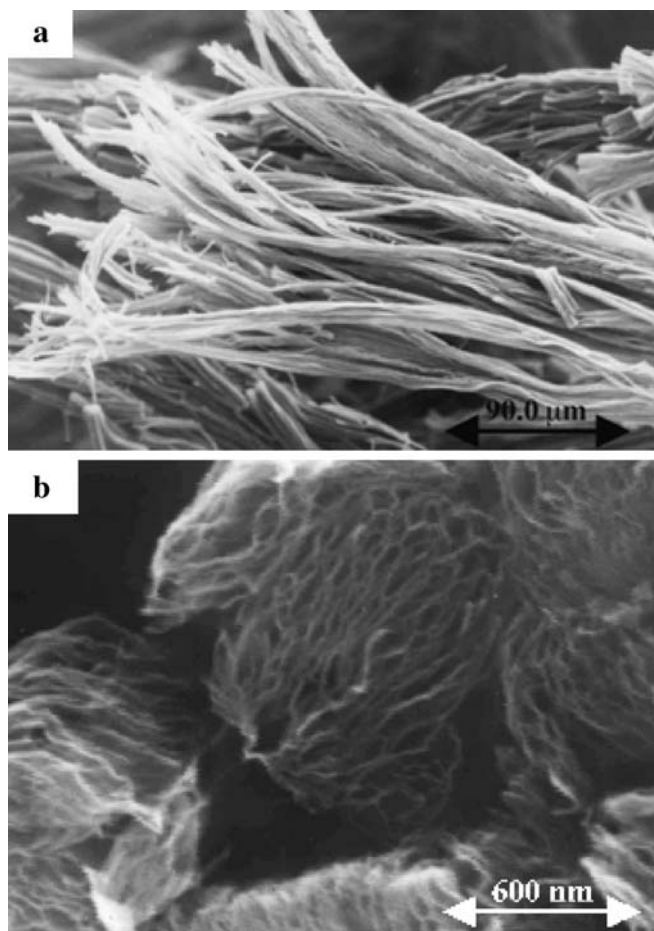

FIGURE 1 Scanning electron microscopy (SEM) observation of exfoliated carbon fiber (ExCF). The sample was exfoliated at 1000 °C for 30 s. (**a**) bundle of thin filaments resulted from the fibril texture, (**b**) balloon-like morphology developed by exfoliation
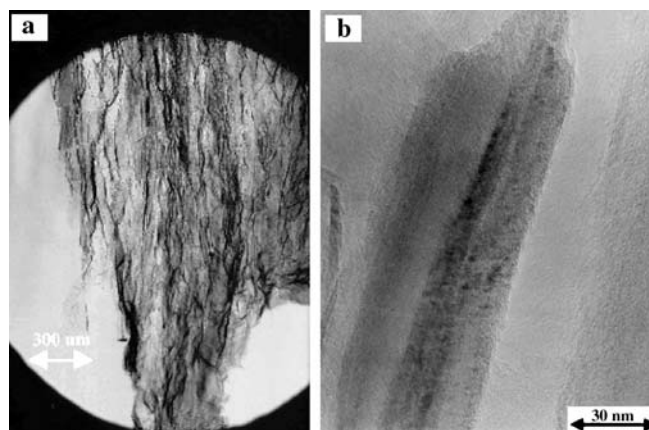

FIGURE 2 Transmission electron microscopy (TEM) image of ExCF. (**a**) Spreading thin carbon sheet, (**b**) preserved carbon layer stacking giving 002 lattice fringes

of carbon fiber (ca. 8 μm) was split into a bundle of thin filaments along the longitudinal direction of the fiber (Fig. 1a), which reflects the fibril texture of the pristine carbon fiber. The apparent diameter (a bundle of thin filaments) became 30 to 50 μm. The SEM observation at high magnification indicates a unique worm-like morphology (Fig. 1b) which is a typical characteristics of well-exfoliated graphite [11]. Transmission electron microscopy (TEM) observations showed that ExCF was composed mainly of thin and wrinkled carbon sheets. 002 lattice fringes from carbon layers stacking were also observed (Fig. 2).

X-ray powder patterns of raw and exfoliated carbon fibers are compared in Fig. 3. The 002 diffraction line of the carbon layered structure from ExCF (Fig. 3b) is composed of a sharp peak and a broad band, indicating a large distribution of inter layer spacings and crystallite size along *c*-axis. The position of the strong diffraction line is unchanged from the raw carbon fiber (Fig. 3a) and locates at 0.337 nm. Therefore, the exfoliation process introduce significant amount of structural defects into the carbon fiber, but the high crystallinity of the raw materials is preserved partly. These results are consistent with the SEM and TEM observations. On the nitrogen adsorption/desorption isotherm at 77 K of ExCF (Fig. 4),
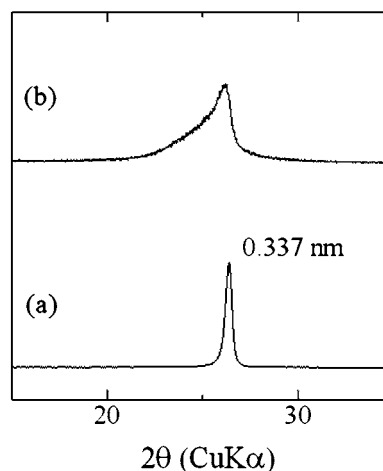

FIGURE 3 X-ray diffraction patterns of (a) pristine and (b) exfoliated carbon fibers (ExCF)
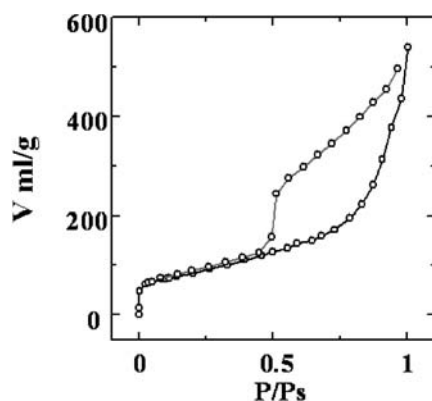
FIGURE 4   Nitrogen adsorption/desorption isotherm at 77 K on exfoliated carbon fibers (ExCF). BET surface area was ca. 300 m^2/g

a large hysteresis loop is observed above 0.5 of relative pressure which indicates the existence of developed mesopores. The specific surface area of ExCF is ca. 300 m^2/g from the BET plot. These results imply that the ExCF has structural characteristics of relatively high graphitization degree with a moderate pore texture, which are different from conventional activated carbons.

3.2   *Electrochemical characteristics of ExCFs*

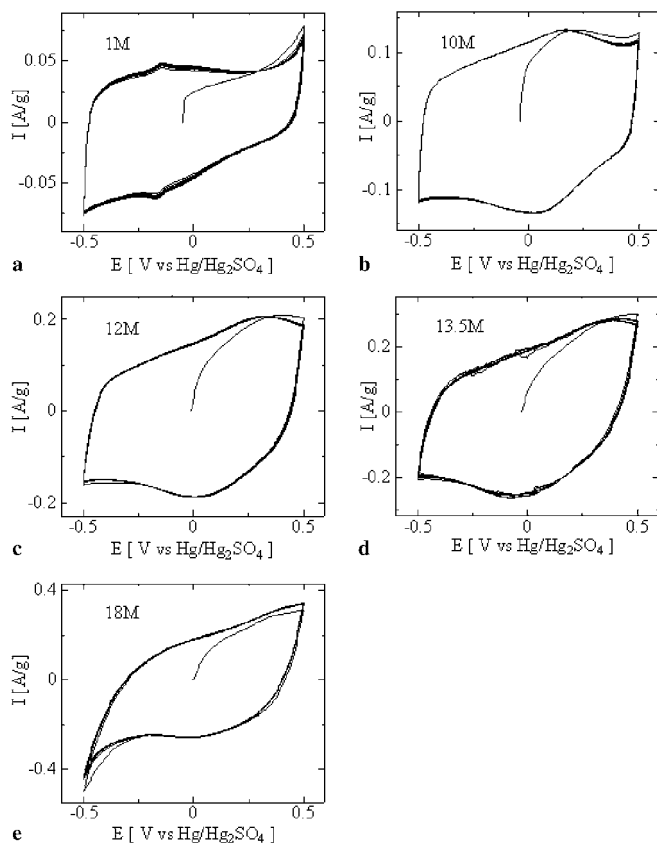Figure 5 shows the cyclic voltammograms (CV) of ExCFs in different concentrations of H$_2$SO$_4$ electrolyte. As indicated by the value of current during the potential sweep, the specific capacitance of the electrode materials increases with the increase in electrolyte concentration. This result suggests that a Faradic reaction (pseudo-capacitance) is superimposed on the double layer capacitance in concentrated H$_2$SO$_4$ electrolyte. However, a distinct redox peak resulting from the Faradic reaction was not observed in any concentration of electrolyte.

On the other hand, the cyclic voltammograms for the exfoliated natural graphite (ExNG) in the same conditions changed drastically with the concentration of H$_2$SO$_4$ electrolyte (Fig. 6). An oxidation peak at 0.43 V and a marked current at the limit potential of 0.5 V, and the corresponding reduction peaks at 0.39 and 0.2 V, were observed for H$_2$SO$_4$ concentrations above 12 mol/dm^3, although the CV curve in 10 mol/dm^3 H$_2$SO$_4$ had the typical box shape for an electric double layer capacitor without redox reaction. These changes of CV curves for ExNG indicate that the intercalation of H$_2$SO$_4$ molecules proceeded and a stage structure was formed above 12 mol/dm^3 of H$_2$SO$_4$ electrolyte. The voltammogram in 18 mol/dm^3 H$_2$SO$_4$ has the same characteristics as reported for graphite materials [12, 13].

The redox reaction in concentrated H$_2$SO$_4$ solution is most probably the intercalation of H$_2$SO$_4$ and is clearly observed as peaks on the CV curves with the ExNG electrode. In the case of ExCF, however, no important discontinuity of the observed current is observed on the CV curve in the whole potential region and redox peaks characterizing the intercalation-

FIGURE 5   Cyclic voltammograms of ExCF in H$_2$SO$_4$ electrolyte. Concentration [mol/dm^3] of (**a**) 1, (**b**) 10, (**c**) 12, (**d**) 13.5 and (**e**) 18. Scan rate of 1 mV/s
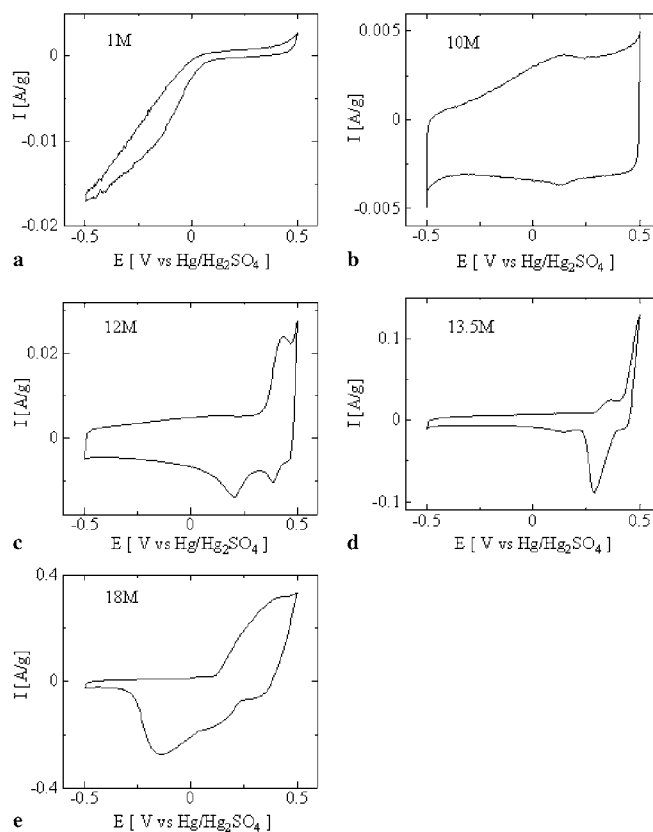
FIGURE 6   Cyclic voltammograms of ExNG in H$_2$SO$_4$ electrolyte. Concentration [mol/dm^3] of (**a**) 1, (**b**) 10, (**c**) 12, (**d**) 13.5 and (**e**) 18. Scan rate of 1 mV/s

H_2SO_4	[mol/dm^3]	1	5.5	9	12	13.5	18
ExCF		0.15	0.30	0.44	0.83	1.14	1.35
ExNG	[F/m^2]	0.01			0.81	3.63	11.90
ACF		0.05	0.11	0.12		0.12	0.06

TABLE 1   Specific capacitance per unit surface area in different concentration of H_2SO_4 electrolyte

deintercalation reaction (0.4 V in anodic and 0.2 V in cathodic sweep) were scarcely observed even in the concentrated H_2SO_4 electrolyte. Therefore, the formation of stage structure and its transformation due to the intercalation of H_2SO_4 molecules was not evidenced apparently with ExCFs.

The specific capacitances per unit surface area for ExCF, ExNG and ACF in different concentrations of H_2SO_4 electrolyte are listed in Table 1. The capacitance values are calculated from the 50th discharge curve of galvanostatic cycling. The specific capacitance for ExCFs increased gradually with the electrolyte concentration reaching about 1.4 F/m^2 (450 F/g). The ExNG shows a similar trend with the electrolyte concentration, but abnormally large capacitances were obtained in 12 and 18 mol/dm^3 because of the distinct intercalation reaction of H_2SO_4 molecules and the smallest specific surface area (16 m^2/g). Since ExNG is synthesized from flaky natural graphite, the sample has higher crystallinity and smaller surface areas than ExCF. On the other hand, the specific capacitance of ACFs is almost constant in different concentrations of electrolyte, and the capacitance value (ca. 0.1 F/m^2) is similar to the reported one for activated carbons [14, 15].

Considering the above observation, the enhancement of the specific capacitance for ExCFs with electrolyte concentration does not accompany the formation of stage structure caused by the intercalation reaction, though there might have strong interaction between electrode surface and H_2SO_4 molecules. The large capacitance of ExCF in concentrated electrolyte implies a charge transfer reaction (Faradic reaction) at the electrode surface, since the intercalation of H_2SO_4 is obvious for the case of ExNG. The disappearance of stage formation for ExCF may due to the less crystallinity and more distorted texture than graphite. The behavior of ExCF is more favorable than the case of ExNG, since the formation of stage structure introduces volume change in the electrode, which results in the collapse of the electrode at short cycling.

4   Conclusion

Exfoliated carbon fibers (ExCFs) synthesized from pitch-based carbon fibers showed huge capacitance in concentrated sulfuric acid electrolyte. The capacitance for ExCFs depended strongly on the concentration of the electrolyte, though the one for ACFs used for comparison remained almost unchanged. The specific capacitance of ExCF exceed 500 F/g in 18 mol/dm^3 H_2SO_4 electrolyte, though ACF showed 150 F/g because of the absence of pseudo-capacitance. From the cyclic voltammometry in concentrated H_2SO_4, ExCFs did not show apparent intercalation reaction of H_2SO_4 molecules, but the exfoliated natural graphite (ExNG) showed distinct stage structure formation. The present results suggest that the origin of pseudo-capacitance to give huge capacitance-value for ExCFs is a strong interaction between H_2SO_4 and the surface of the ExCF electrode. The lack of stage structure change by the intercalation reaction on ExCF is advantageous compared to ExNG (or expanded graphite), giving a stable cycling during long charge-discharge. A better rate performance than the intercalation reaction on ExNG (or expanded graphite) could be expected, if the surface reaction is the major contribution for pseudo-capacitance in ExCF.

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