

APPLICATIONS OF EXFOLIATED CARBON FIBER FOR ELECTROCHEMICAL CAPACITOR ELECTRODE

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Introduction

Electric double layer capacitor (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 its carbons was recognized to be very important [1-3]. On the other hand, when the electrode material shows faradic reactions at the electrode surface in wide range of potential window under the capacitor-like working conditions, 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 reaction with carbons, and called as the electrochemical capacitor [4].

In our previous papers [5, 6], carbon fibers were exfoliated by rapid heating of their intercalation compounds prepared in either nitric acid or formic acid, single fiber splitting into a number of thin filaments. These exfoliated carbon fibers (ExCFs) were found to give huge capacitance in concentrated sulfuric acid [7]. In the present work, the electrochemical capacitor behavior of ExCFs was studied in different concentration of sulfuric acid electrolyte and the mechanism to give large capacitance was discussed.

Experimental

Mesophase-pitch-based carbon fibers heat-treated at 3000 °C were used as starting materials. The carbon fiber were oxidized by electrolysis in 13 mol/dm³ nitric acid; electrode of carbon fibers (5 cm) fixed to platinum plate by using PTFE sealing tape were immersed into concentrated nitric acid electrolyte and then applied 0.5 A of DC current for 40 min. After electrolysis, carbon fibers were rinsed with distilled water and dried at room temperature in air. The carbon fibers treated were rapidly inserted into a tubular furnace kept at 1000 °C for 5 s to be exfoliated. The detailed exfoliation procedure and behavior for carbon fibers were reported in previous papers [5, 6]. For the comparison, H₂SO₄-intercalation compound with natural graphite (400 μm) was prepared and thus heat treated to form exfoliated natural graphite (ExNG).

The measurements of electrochemical behavior of ExCFs and ExNG were performed using standard three-electrode cell with 1 to 18 mol/dm³ sulfuric acid electrolyte. ExCFs were cut into 2.5 cm long and sandwiched with current collector (Pt mesh) and glass micro filter between two PTFE plates to compose a working electrode. Pt plate and Hg/Hg₂SO₄ were used as counter and reference electrode, respectively. The measurement cell was poured with electrolyte under vacuum and purged with nitrogen flow during the experiment. The electric double layer capacitance was estimated from cyclic voltammogram with a constant rate of potential sweep of 1 mV/s and charge-discharge curve between 0 and 0.5 V vs. Hg/Hg₂SO₄ with a current density of 20 mA/g.

Results and Discussion

Fig.1 shows the dependence of specific capacitance per unit surface area for ExCFs and ACFs obtained from the 50th discharge curve of galvanostatic cycling with the concentration of sulfuric acid electrolyte. The capacitance value for ExCFs increased gradually with the concentration of the electrolyte up to 10 mol/dm³ and suddenly to huge value in higher concentration region of electrolyte and reached about 1.4 F/m² (450 F/g), although the value for ACFs does not give any tendency to the electrolyte concentration and rather constant at small value (ca. 0.1 F/m²). The dependence on the acid concentration seemed to suggest the intercalation reaction of H₂SO₄ molecules into graphite structure [8]. For the H₂SO₄ intercalation reaction, it has been known the strong dependence of the host structure (texture and crystallinity) and the concentration of acid solution; the higher graphitization degree for host carbon materials and the concentration of sulfuric acid were necessary to promote the intercalation reaction [9, 10].

Fig. 2 shows the cyclic voltammograms of ExCFs in different concentrations of H₂SO₄ electrolyte. Though the electrode currents during potential cycling increase with the concentration of electrolyte, there were no redox peaks concerning the intercalation-deintercalation reaction. This observation implies that the stage structure due to the intercalation of H₂SO₄ molecules was not clearly recognized with ExCFs. On the other hand, the cyclic voltammograms for the exfoliated natural graphite (ExNG) with the same conditions were changed drastically with the concentration of H₂SO₄ electrolyte (Fig.3). The change of the curves for ExNG indicates that the intercalation of H₂SO₄

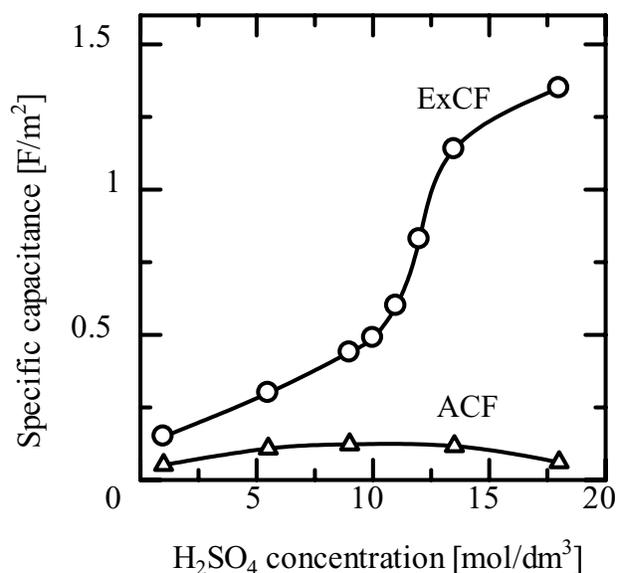


Fig. 1 Dependence of specific capacitance on the concentration of H₂SO₄ electrolyte. Capacitance was calculated from the 50th discharge curve in galvanostatic charge-discharge measurements (20mA/g).

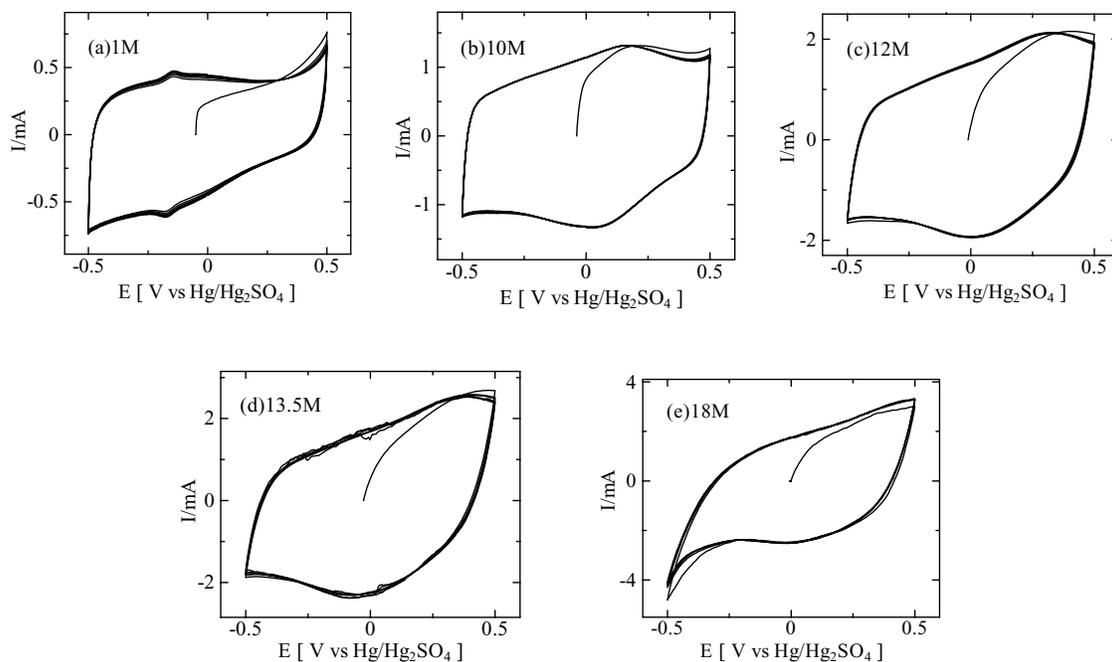


Fig. 2 Cyclic voltammogram of ExCFs in H_2SO_4 electrolyte. Concentration [mol/dm^3] of (a) 1, (b) 10, (c) 12, (d) 13.5 and (e) 18.

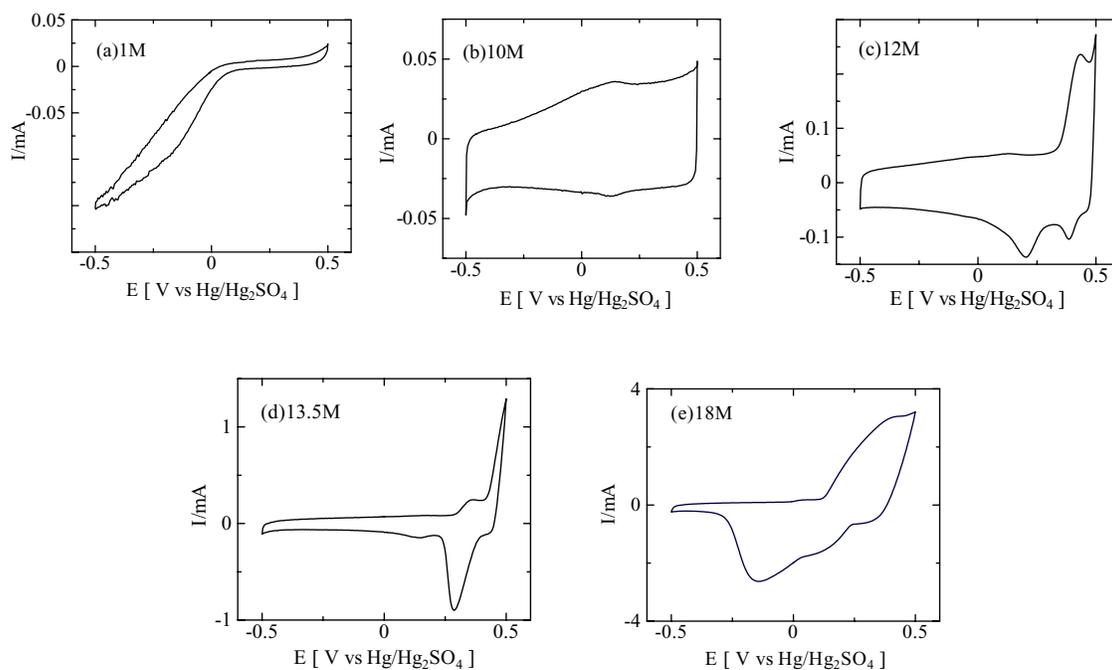


Fig. 3 Cyclic voltammogram of ExNG in H_2SO_4 electrolyte. Concentration [mol/dm^3] of (a) 1, (b) 10, (c) 12, (d) 13.5 and (e) 18.

molecules proceeded and the stage structure was formed in the H₂SO₄ electrolyte more than 12 mol/dm³.

From these results, the increase in the specific capacitance of ExCFs with increase in the electrolyte concentration does not accompany staging by the intercalation reaction, though there might have strong interaction between electrode surface and H₂SO₄ molecules. This behavior is more favorable than obvious intercalation reaction such the case of ExNG, since the formation of low stage structure introduces the volume change in the electrode, resulting the collapse of the electrode at short cycling.

Conclusions

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. From the cyclic voltammometry in concentrated acids, ExCFs did not show apparent stage formation by the intercalation of H₂SO₄ molecules, but exfoliated natural graphite did. The present results suggest that the origin of pseudo-capacitance to give huge capacitance-value for ExCFs is the intercalation of sulfuric acid into the electrode materials.

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