Exfoliated Carbon fibers as Electrode For EDLC in H_2SO_4

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Abstract
Exfoliated carbon fibers (ExCFs) were prepared by rapid heating of intercalation compounds of pitch-based carbon fibers. After exfoliation, a single fiber was found to be converted to a bundle of thin filaments split along the original fiber axis. These ExCFs were examined as an electrode of electric double layer capacitor (EDLC) in H_2SO_4 electrolyte. The capacitance reached 117 and 555 in 1 and 18 mol/dm^3 H_2SO_4 electrolyte, respectively, even though ExCFs had relativity small surface area of about 300 m^2/g. Capacitance of ExCFs strongly depended on their specific surface area, but the relation on ExCFs between capacitance and specific surface area was quite different from that reported on activated carbon fibers.

INTRODUCTION

Marked exfoliation after heat-treatment of intercalation compounds of carbon fibers prepared through electrolysis was reported in our previous papers [1-6]. After rapid heating, a marked morphological change was observed, a single fiber being converted to a bundle of thin filaments split along the original fiber axis. A number of fissures extended along the fiber axis were observed on those filaments. On observation of its ExCFs in cross section, stacked graphite layers were recognized. This morphology of ExCFs, such as pores formed by exfoliation is expecting to develop new and functional applications, such as EDLC. In our previous paper [7-9] ExCFs were examined as EDLC electrode materials and the capacitance of 160 F/g and 117 F/g was obtained in 1 mol/dm^3 H_2SO_4 electrolyte from cyclic voltammogram and charge-discharge curve, respectively. The ExCFs with the largest surface area (ca.300m^2/g) showed the highest capacitance of 555F/g in 18 mol/dm^3 H_2SO_4 electrolyte [7-9]. Such a high capacitance was never observed by using activated carbon fibers and activated carbons. In the present work, therefore, the reasons of high capacitance for ExCFs electrodes were investigated.

EXPERIMENTAL

Mesophase-pitch-based carbon fibers heat-treated at 2800 ^{o}C were used in present study. The intercalation reaction was carried out by electrolysis in nitric and sulfuric acid by applying a constant current of 0.5 A between carbon fiber bundles and Pt counter electrode using the potentiostat/galvanostat at room temperature. A reference electrode employed was an Ag/AgCl one. The CF-GICs thus prepared were exfoliated by insertion into a tubular furnce. To obtain different degree of exfoliation *i.e.*, to prepare the ExCFs having different surface area, heat-treatment conditions such as exfoliation temperature and holding time were changed; the former from 300 to 1200 ^{o}C and the latter from 5 to 120 sec. The measurements of electrochemical behavior of ExCFs were performed using standard three-electrode cell with 1 mol/dm^3 H_2SO_4 electrolyte. The ExCFs were cut into 2.5 cm long and sandwiched with Pt mesh and glass micro filter between two PTFE plates to compose a working electrode (scan rate 1mV/s). Pt plate and Hg/Hg_2SO_4 were used as counter and reference electrode, respectively. The electric double layer capacitance was estimated from cyclic voltammogram. Specific surface area on ExCFs was calculated from BET plot based on the adsorption isotherm of nitrogen at 77 K.

RESULTS AND DISCUSSION

The dependences of EDLC capacitance in 1 mol/dm^3 H_2SO_4 electrolyte on specific surface area of two carbons electrode, ExCFs which were studied in the present work and the activated carbon fibers reported in the literature [10, 11] was discussed. Even though the dependences of BET surface area and EDLC capacitance on the preparation conditions could not be clearly obtained, the dependence of EDLC capacitance of ExCFs on their specific surface area is very clear, irrespective from preparation conditions such as intercalates used, either nitric or sulfuric acids, exfolaition temperature and holding time. This relation between BET surface area and EDLC capacitance could be extended by simple air oxidation, the increase in EDLC capacitance being very shrap with BET surface area. The activated ExCFs having a specific surface area around 400 m^2/g gave the EDLC capacitance of about 160 F/g. The present ExCFs give relatively large capacitance at relatively low specific surface area; the capacitance of about 150 F/g is possible to obtain by using ExCFs with the specific surface area of about 300 m^2/g, but for activated carbon fibers the specific surface area higher than 1000 m^2/g is required to get the same capacitance. These results might be suggested the existence of additional factor, which governs the capacitance of EDLC composed from carbon electrode. After exfoliation of the carbon fibers, all ExCFs were found to be split into a number of thin filaments along the original fiber axis. From TEM observation, these filaments were recognized to consist of thin sheets [2, 7]. In these sheets, hexagonal carbon layers were found to be oriented along the original fiber axis, and to give well-aligned long 002 lattice fringes. This structural feature having well-oriented graphite layers after exfoliation might be important for giving a large capacitance for EDLC, even though they have a small surface area. The intercalation of H_2SO_4 molecules into ExCFs in concentrated electrolyte might be responsible for resultant large capacitance of EDLC.

References

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