EDLC CHARACTERISTICS FOR FIBROUS MATERIALAS AND EFFECT OF ITS SURFACE CHARACTERISTICS

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Abstract

Electric double layer capacitors (EDLCs) using carbon electrodes are one of anticipated energy storage devices and have been employed for the microelectronics. Exfoliated carbon fibers (ExCFs) prepared from mesophase-pitch based carbon fibers heat treated from 1150 to 3000 ^{o}C revealed huge capacitance in sulfuric acid electrolyte, in spite of their small surface area. The relation between surface characteristics and capacitance of ExCFs was discussed to clear reason showing high capacitance. From N_2 adsorption/desorption isotherm at 77K for ExCFs, the presence of mesopores was indicated from isotherms of ExCFs showing hysteresis above P/P_0 of 0.5 and then difference of ratio for micropore and mesopore was recognized. Influence of pore for capacitance was discussed by dividing into capacitances with inner surface of pore and with external surface. It obviously indicated that capacitance per unit external surface area was higher than that with inner surface of pore. External surface of exfoliated carbon fibers is effective for EDLC. ExCFs prepared from heat-treating in atmosphere pressure have a lot of functional group on surface of ExCFs. Its functional group on surface depend on heat-treatment of exfoliation. And then it on surface of ExCFs was also effective for EDLC.

Introduction

Electric double layer capacitors (EDLCs) attracted attention as one of energy storage devices. Advantages of EDLCs are summarized as follows; 1) possible to charge/discharge quickly, 2) long cycle life because of no chemical reactions, 3) high efficiency for charge/discharge cycle and 4) possible to discharge in high current density. Marked exfoliation of carbon fibers were reported in author's previous papers. Its morphological changes were observed through rapid heating, 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 recognized on those filaments. From observation of cross sectional morphology in its ExCFs, some pores with exfoliation were recognized. The ExCFs showing unique morphologies and having pores were applied an electrode of the EDLC. In our previous paper, the ExCFs revealed high capacitance of 160 F/g and 117 F/g in 1 mol/dm^3 H_2SO_4 electrolyte from cyclic voltammogram and charge-discharge curve, respectively. Highest capacitance of 555F/g in 18 mol/dm^3 H_2SO_4 electrolyte was obtained in spite of a small surface area such as ca.300m^2/g. The relation between surface characteristics and capacitance of ExCFs was discussed to obtain the clear reason having high capacitance. From N_2 adsorption/desorption isotherm at 77K for ExCFs, difference of ratio for micropore and mesopore was recognized. Influence of pore on capacitance was discussed by dividing into capacitances with inner surface of pore and with external surface. In the present work, therefore, the reasons of high capacitance for ExCFs electrodes were investigated. Amount of functional group of surface on ExCFs was determined by using Bohem method.

Experimental

Mesophase-pitch-based carbon fibers heat-treated from 1150 to 3000 ^{o}C were used. Sizing agent on surface of these carbon fibers was removed through dipping in acetone solution, preliminarily. Electrochemical processing was carried out by electrolysis in acid electrolyte such as conc. HNO_3 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 with saturated KCl solution. After the electrolysis, their carbon fibers electrolyzed in nitric acid was dried at room temperature with water, and then dried at room temperature in air. Carbon fibers thus electrolyzed were exfoliated by insertion into a tubular furnace kept at a constant temperature. To obtain different degrees of exfoliation, *i.e.*, to prepare the ExCFs having different surface characteristics, pristine carbon fibers heat-treated at different temperature were treated different exfoliated temperature and with various holding time; the former from 300 to 1200 ^{o}C and the latter from 5 to 120 sec were employed. Nitrogen adsorption/desorption isotherms were measured on ExCFs at 77K and BJH surface area of ExCFs was calculated from the adsorption isotherm. The measurements of electrochemical behavior of ExCFs were performed using a standard three-electrode cell with 1 mol/dm^3 H_2SO_4 electrolyte. In order to characterize carbon materials as the electrode of EDLC, their specific capacitance was calculated from a half of the difference between charge and discharge currents at 0 mV on the CV curves observed.

Results and Discussions

Fig. 1 shows the adsorption/desorption isotherms of N_2 gas at 77 K for ExCFs. All of the isotherms of ExCFs were classified into type IV according to IUPAC, a large hysteresis above P/P_0 of 0.5 which indicated the presence of mesopores. A sharp rise of isotherms at very low P/P_0 suggests the presence of micropores, but it seems not to be a large amount because of relatively small amount of adsorbed gas.

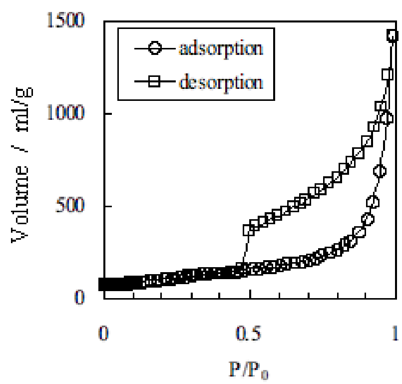

Figure 1. N_2 adsorption/desorption isotherm of exfoliated carbon fiber prepared from carbon fiber heat-treated at 2800 ^{o}C

Capacitance of the ExCFs as an electrode of EDLCs in H_2SO_4 electrolyte were examined and reported. Its capacitance reached 160 F/g in 1 mol/dm^3 and 555 F/g 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 applied to electrode of EDLC strongly depended on their specific surface area and pores, however, their relations on ExCFs between capacitance and surface characteristics were quite different from that reported on activated carbon fibers. ExCFs thin filaments showing unique surface characteristics with some pores derived from exfoliation might be related to this large capacitance .

Capacitance C_{obs} was analyzed by dividing into two parts, capacitance due to micropores (size of less than 2 nm) C_{micro} and that due to larger pores (mesopores and macropores up to 100 nm) C_{ext} as follows;

$$C_{obs.} = C_{ext.} \times S_{ext.} + C_{micro.} \times S_{micro,} \qquad (1)$$

where $S_{micro.}$ and $S_{ext.}$ were surface area due to micropores and other larger pores (external surface area and used $S_{ext.}$), respectively. The equation (1) was rewritten to

$$C_{obs.}/S_{ext.} = C_{ext.} + C_{micro.}(S_{micro.}/S_{ext.}) \qquad (2)$$

which suggests the linear relation between ($C_{obs.}/S_{ext.}$) and ($S_{micro.}/S_{ext.}$). $C_{micro.}$ and $C_{ext.}$ were calculated as the slope and the intercept of the linear relations, respectively.

Fig.2 was plotted the EDLC capacitance to the average pore diameter having the various ExCFs (ExCFs having different surface characteristics, pristine carbon fibers heat-treated at different temperature was exfoliated at different temperature and with holding time; the former from 300 to 1200 ^{o}C and the latter from 5 to 120 sec were employed) calculated from BJH method. Increasing of capacitance of the EDLC was recognized with increasing with the average pore diameter. It seems to be that an electrolyte ion is easy to infiltrate into the pores, as the pore is much larger, and the surface area of its pore could be used effectively. It was divided into pore interior surface area (S_{micro}) of 2 nm or less calculated from the BJH method and further the external surface area (S_{ext}) in order to examine the effect of the pore of the ExCFs having large capacitance.

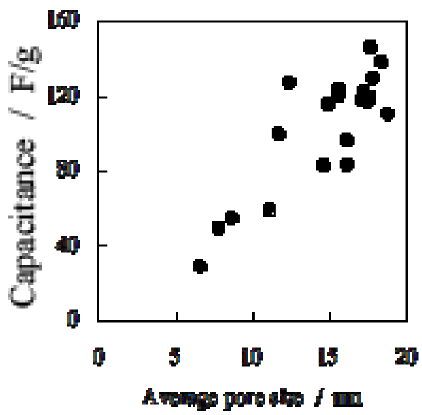

Figure 2. Dependence of EDLC capacitance on average pore size of ExCFs

From calculation of $C_{obs.}/S_{ext.}$ plots as a function of $S_{micro.}/S_{ext}$, its slope shows unit capacitance of pore interior surface area ($S_{micro.}$), and the intercept shows the external surface area (S_{ext}), from approximate straight line. For ExCFs, $C_{ext.}$ = 2.4 F/m^2 and $C_{micro.}$ =0.51 F/m^2 was obtained. These values suggest certain contribution of external surface area (*i.e*., mesoporous and macroporous surface areas) to observed capacitance and might be suggested the importance of morphology of ExCFs. Additionally, ExCFs prepared from heat-treating in atmosphere pressure have showed a lot of functional group on surface of ExCFs. Its amount of functional group on surface of ExCFs depend on heat-treatment of exfoliation. The ExCFs exfoliated at high temperature have shown a lot of surfaces functional group. From this results, it on surface of ExCFs was also related and effective for capacitance of EDLC.

Conclusion

Relationship of surface characteristics and capacitance of EDLC on fibrous carbon such as ExCFs was studied to make clearly. From N_2 adsorption/desorption isotherm at 77 K, the presence of mesopores was indicated by isotherms of these fibers showing hysteresis above P/P_0 of 0.5. These average pore size indicated 5-20 nm and capacitances depended on it. For investigation more clearly about influence of pores on capacitance, capacitance of EDLC was separated into capacitances with micropores and external surface. It obviously indicated that capacitance per unit surface area with external surface was higher than that with micropores. Additionally, amount of functional group on surface of ExCFs also related on capacitance of EDLC. The ExCFs exfoliated at high temperature have shown the large capacitance.

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