THE MORPHOLOGICAL CHARACTERIZATION OF ACTIVATED MESOPHASE PITCH-BASED CARBON FIBER (MPCF) AND ITS APPLICATION TO EDLC

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Introduction

MPCF pitch based carbon fiber has been used and investigated for an electric storage devices like Li ion secondary battery [1]. In this study, we studied the application for MPCF to electric double-layer capacitor. The chemical activation by hydrated potassium, KOH, was adopted as the activation method. Activated milled mesophase carbon fiber (AC-mMPCF, MP-series) shows the higher specific capacitance in spite of a smaller specific surface area than those of power type activated carbon (AC-series). The electric double layer capacitors (EDLC) behavior for the activated milled-mesophase pitch-based carbon fiber will be discussed, comparing with the granular type activated carbon made from coconut shell.

Experimental

The samples used in this study are of a series of activated carbon (AC) samples, each with a different surface area, and a milled fiber type activated carbon fiber (AC-mMPCF). These ACs were commercially prepared by Nippon Gaisi Co. by carbonizing and activating a coconut shell in steam/carbon dioxide. The AC-series used in this study were AC-a, AC-b, AC-c, and had BET specific surface areas (SSA) of 959.7 m^2/g, 1499.9 m^2/g, 1848.4 m^2/g, respectively. Petoca supplied MP series samples that were prepared by carbonizing and activating a mesophase carbon fiber (MPCF). Sample was nominated as MP-a and MP-b with 770.7 and 683.3 m^2/g of SSA. The capacitance measurements were performed with an unit cell system. Samples used ACs and ACFs mixed with 5wt % of PTFE as a binder. Then, the coin type electrodes were prepared by compressing with 1 ton/cm^2 pressure. Tetraethylammonium tetrafluoroborate (Et_4NBF_4)/ propylene carbonate (PC) was used as an electrolytic solution. The capacitor was charged at a constant voltage (2.5, 3.0, 3.5 V) for 2min and then discharged at a constant current from 1mA to 40mA.

Results and Discussion

Table 1 summarizes the Brunauer-Emmett-Teller (BET) properties. In both series of samples, the micropore volume increases as the specific surface area increases. AC-c shows specific surface area as high as 1848 m^2/g. And the MP-series shows a lower specific surface area of 683, 770 m^2/g than those of the AC-c sample.

Figure 1 shows HR-SEM photographs of AC-series carbons made from coconut shell at a magnification of × 50,000 (a, b, c) and ×100,000 (d, e, f), respectively. And, (a, d) are the photographs of AC-a, which (b, e) are photographs of AC-b, and (c, f) are photographs of AC-c. Generally, powder type activated carbons, such the AC-series show a tendency that the pore size as well as the number of pores increase as the surface area increases. Almost all the pore could be observed in GA-a and these pores show a size under the meso- size (below 500 Å), but a lot of macropores could be observed as the temperature of the activation process increases.

Figure 2 shows HR-SEM photographs of the center and periphery of an activated milled mesophase carbon fiber. Figs 2 (a), (d) show the overall features of the MP-series, which (b), (e) illustrate the periphery, and (c), (f) illustrate the center of the fiber. The structure of non-activated pristine MPCF was already observed and demonstrated by Endo et al. [1]. MPCFs have a different morphology at the center and the periphery of the cross section. That is, cross-sectional core region has a well-aligned layer structure, while the periphery of the core is distinguished as having a more wavy layered structure. Moreover, its original morphology remains preserved after the activation process. The postulated form of the porous structure of AC-mMPCFs is supported by its lamellae arrangement, where individual lamellae or their groupings are inter-bonded by cohesive forces. Owing to the unevenness of the surfaces of the lamellae, there remain free spaces of molecular dimensions between the contact points, which can be defined as slit-shaped micropores [2].

Figure 3 illustrates the accessibility of the MP-series and AC-series samples which is calculated by dividing the specific capacitance by the BET surface area, and the result was converted into a percentage against maximum value of the specific capacitance. The accessibility was obtained by the following equation:

$$\text{Accessibility} = (SC/S)/MSC \times 100 \qquad (1)$$

where, the accessibility is a relative dimensionless variable, SC is the specific capacitance, S is the specific surface area and, MSC is the maximum specific capacitance.

Table 1. BET properties of the samples

Sample I. D.	Surface area (cm^2/g)	Total pore volume (cc/g)	Average pore diameter (Å)
AC-a	959.73	0.52	14.67
AC-b	1499.91	0.82	14.70
AC-c	1848.37	0.98	14.15
MP-a	770.73	0.42	14.68
MP-b	683.33	0.37	14.52

In this figure, the accessibility of many MP-series samples are shown altogether. The AC-series have from 43 to 70% of relative accessibility assuming that the sample has the maximum capacitance. Therefore, this work confirms that MP-series samples have excellent capacitance properties, such as high conductivity, high specific capacitance, etc, in spite of their small surface area.

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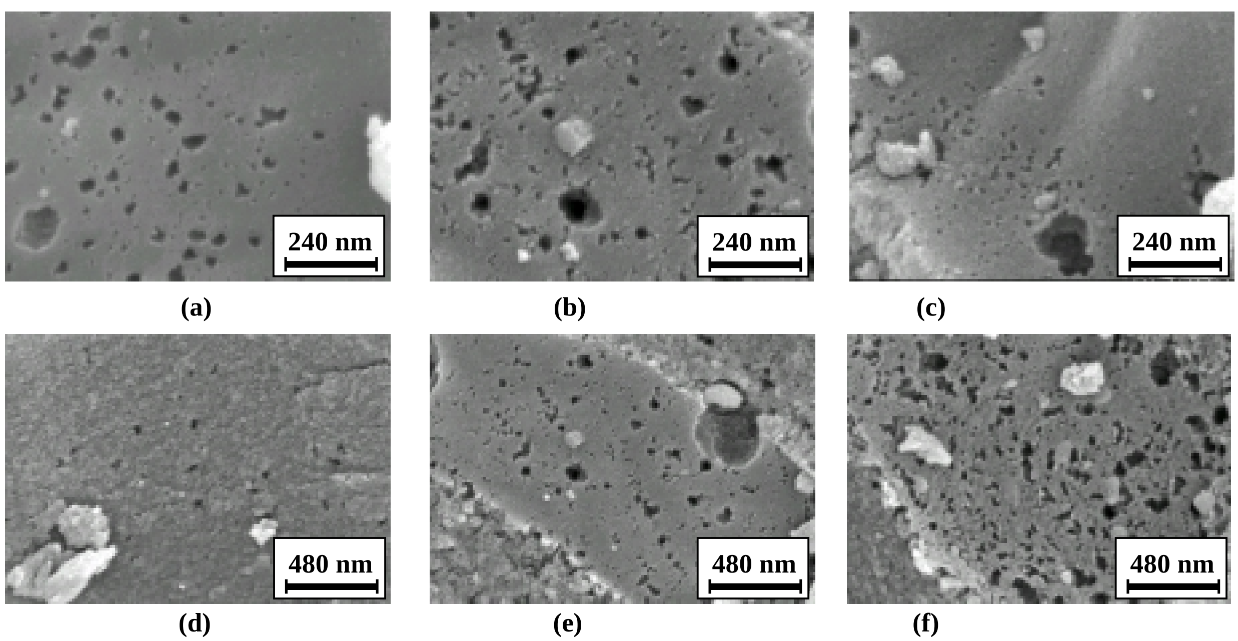

Figure 1. HR-SEM photographs of AC-series made from coconut shell; (a, d) is the photographs of AC-a. (b, e) is AC-b, (c, f) is AC-c. The picture was taken at magnification of ×50,000, ×100,000 in each sample.

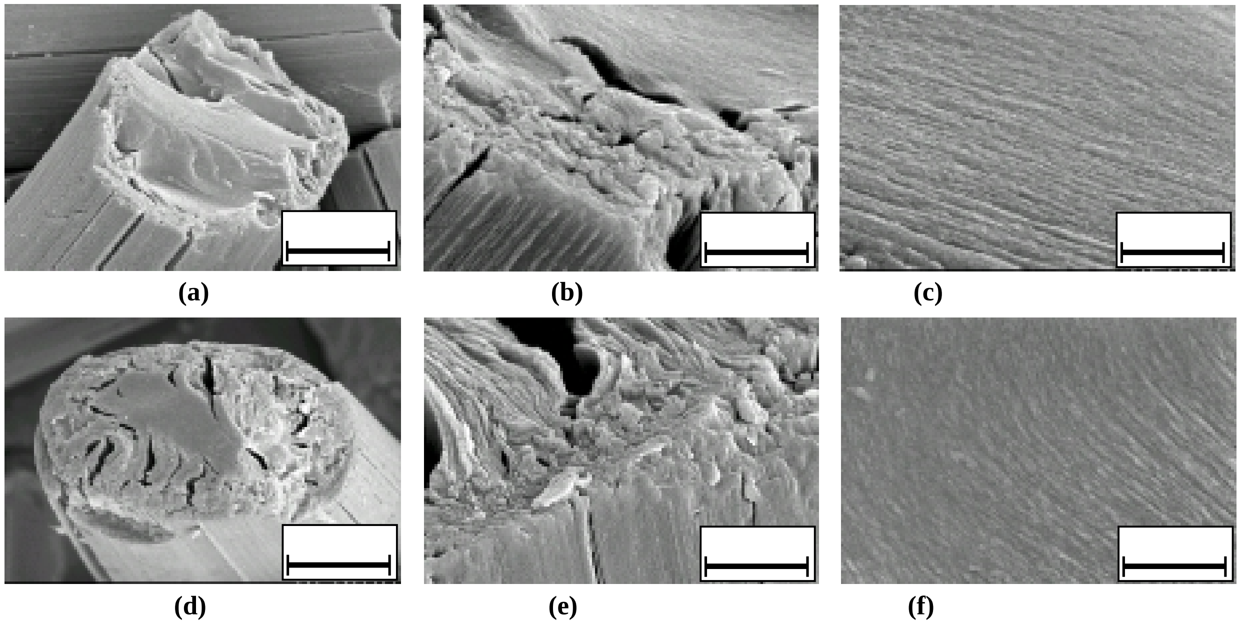

Figure 2. HR-SEM photographs of MP-series made from mesophase carbon fiber; (a, b, c) is the photographs of MP-a, and taken at the magnification of ×4,000, ×30,000, ×50,000 in order. (d, e, f) is the photographs of MP-b, and taken at the magnification of ×5,000, ×20,000, ×50,000 in order.

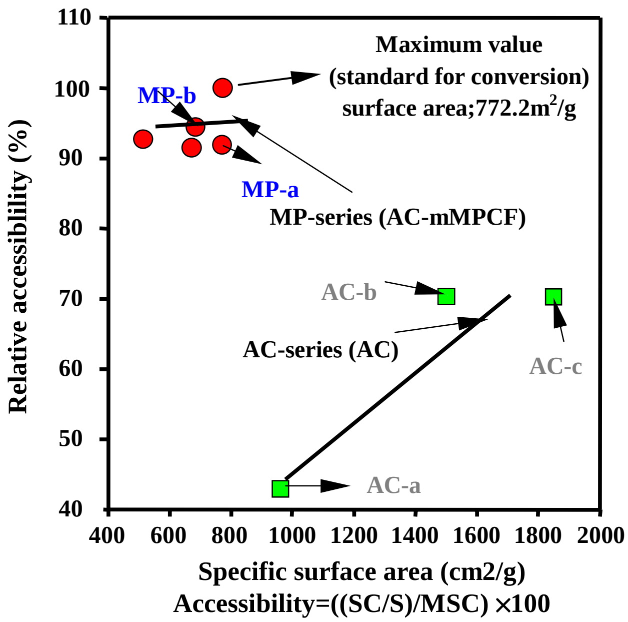

Figure 3. Relative accessibility per surface area on the basis of the maximum value