ELECTRIC DOUBLE LAYER CAPACITY OF ACTIVATED CARBON FIBER CONTAINING MESO/MACRO PORES

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Introduction

The electric double layer capacitor (EDLC) which has large capacity is expected for the sub-power source for electric vehicle. The EDLC is composed of activated carbon electrode and aqueous or nonaqueous electrolytes [1-3]. The high capacity of the EDLC is derived from large specific surface area due to many micropores in activated carbon material. Recently, however, it is found that the electric double layer capacity is not proportional to the specific surface area [4]. This problem may originate in the presence of the micropores which can not be used for the formation of the electric double layer. Therefore, the activated carbon materials having large pores such as mesopores and macropores can realized a higher electric double layer capacity. In this study, we prepared the Ni/NiO loaded activated carbon fiber (Ni-ACF) which has many mesopores and macropores. The relationship between the pore structure and electric double layer capacity was discussed here.

Experimental

The Ni/NiO-loaded activated carbon fiber (Ni-ACF) was prepared by blending method as described in the following. Novolac-type phenolic resin and $Ni(acac)_2$ are dissolved in methanol individually, where the percentage of nickel in raw materials is 0.5 wt %. The methanol was removed under a reduced pressure to obtain a mixture resin. The resin was spun centrifugally to prepare resin fiber. After stabilization of the resin fiber, it was heated to 800°C in nitrogen atmosphere and continuously activated in steam at 800°C. The activated carbon fiber without agent (pristine fiber) was also prepared in the same way as the above preparation process. The samples containing Ni species and without agent were named "0.5Ni-ACF (activation time)" and "Ref-ACF(activation time)",

respectively. The composite pellet electrode was made from ACF fiber (0.05 g), carbon black, and PTFE powder (90:10:5wt%). The standard three-electrode cell was used for the measurement of electric double layer capacity at galvanostatic condition (2mA, 0.0 V - 0.4 V vs. Ag/AgCl) in 1.0 mol dm^{-3} H_2SO_4 aqueous solution.

Results and Discussion

From the results of XRD and XPS analysis (not shown here), it was found that Ni and NiO particles were involved in carbon matrix of 0.5Ni-ACF. The Ni/NiO particles exposed on the surface were removed by the H_2SO_4 aqueous solution before the measurement of double layer capacity. Figure 1 shows the SEM image of 0.5 Ni-ACF(60). Many macropores with several 100 nm pore size were observed on the ACF. The results of the N_2 adsorption/desorption analyses indicated that the both ACFs had many micropores and that the specific surface areas were large. The BET specific surface area (BET-SSA) and the DH specific surface area (DH-SSA, corresponding to specific surface area of mesopores) were summarized in table 1. This indicates that the micropores are more developed with longer activation time in Ref-ACF series and that both of Ref-ACFs and 0.5Ni-ACF have about 50-150 m^2 $g^{-1}$of the specific surface area for mesopores. However, the pore-size distribution showed that 0.5 Ni-ACF (60) had many mesopores of relatively large size such as 10-20 nm radius. Therefore, from the results, it can been said that 0.5Ni-ACF (60) is an activated carbon fiber consisting of not only micropores but also large size mesopores and macropores. The dependence of electric double layer capacity on BET specific surface area was shown in Figure 3. In the case of the Ref-ACF series, the capacity did not increase when BET specific surface area was over 1500 m^2 g^{-1}. This may be caused by that the electrolyte can not penetrate into well-developed micropores. On the other hand,

0.5Ni-ACF (60) showed a large capacity (about143 F g⁻¹) compared with Ref-ACF(60) . Such differences are related to that in pore structure in ACF such as the presence of the large size mesopores and the macropores.

In this study, the Ni/NiO loaded ACF showed the high capacity of the electric double layer in the aqueous electrolyte. Thus, this fact suggests that large pores such as mesopores and macropores are effective for the formation of the electric double layer on ACF-electrode.

References

1. Endo M, Miyashita A, Ishibe S, Ueda M, and Yamashita M. Electric double-layer capacitor using aqueous electrolyte and cativated carbon fiber. Extend abstracts, the 24th annual meeting of the carbon society of japan. Matsuyama (Ehime, Japan) : the carbon society of japan, 1997 ; 272-273.

2. Tanahashi I, Yoshida A, and Nishino A. Electrochemical characterization of activated carbon-fiber cloth polarizable electrodes for electric double-layer capacity. J. Electrochem. Soc. 1990 ; 137 : 3052-3057.

3. Momma T, Liu X, and Osaka T, Ushio Y, Sawada Y. Electrochemical modification of active carbon fiber electrode and its application to double-layer capacitor. J. Power Sources 1996 ; 60 : 249-253.

4. Shiraishi S, Shi L, Hirano A, and Oya A. Application of chromium oxide-loaded activated carbon fiber for electric double layer capacitor. Extended abstracts, International Symposium on Carbon. Tokyo (Tokyo. Japan) : the carbon society of japan, 1998 ; 64-65.
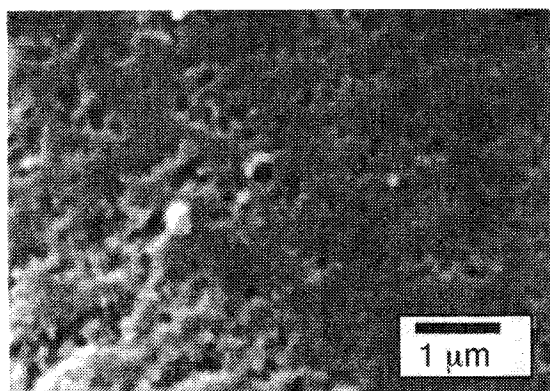
Figure 1 Scanning electron microscopic (SEM) image of 0.5 Ni-ACF (60).

Table 1 Relationship between activation time, BET specific surface area, and DH specific surface area of various ACFs.

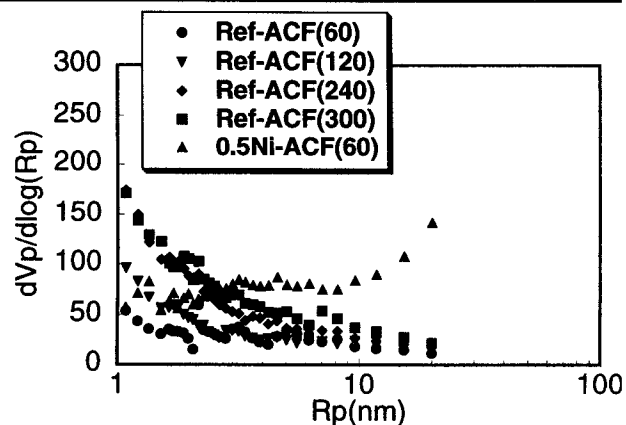|	Activation time [min]	BET-SSA [m² g⁻¹]	DH-SSA [m² g⁻¹]
Ref-ACF	60	916	49
	120	1175	85
	240	1450	153
	300	1771	163
0.5Ni-ACF	60	855	97

Figure 2 Pore size distribution (mesopore region) of Ref-ACF series and 0.5 Ni-ACF (60), calculated by the DH method.
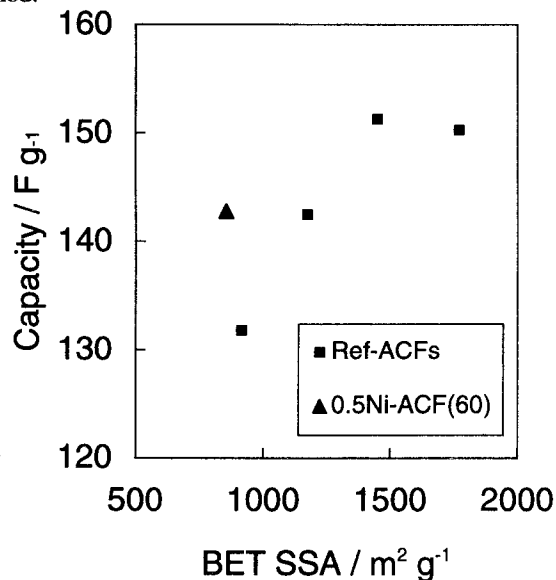
Figure 3 Relationship between BET-SSA and electric double layer capacity (at 0.3→0.1V vs. Ag/AgCl) for various ACFs.