

ELECTRIC DOUBLE LAYER CAPACITANCE OF MESOPOROUS ACF IN NONAQUEOUS ELECTROLYTES

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Introduction

The electric energy storage system utilizing charge-discharge process of an electric double layer on porous electrodes is called “Electric double layer capacitor (EDLC)” [1]. Recently, EDLCs have been proposed as the sub power source for hybrid electric vehicle (HEV) because of its higher power density. However, since the energy density of EDLC is only several Whkg^{-1} and therefore much lower than that of rechargeable batteries, the capacitance of EDLC has to be increased. The practical electrode material for EDLC is porous carbon such as activated carbons. The high capacitance is owing to high specific surface area owing to many micropores. In general, it is believed that there is a proportional relationship between the specific surface area and the electric double layer capacitance of activated carbons. However, some researchers have reported non-linearity of the double layer capacitance on surface area [2-5]. This may be due to the dimension of ion or solvent in electrolyte and the pore size distribution (PSD) of activated carbons. In the meantime, we recently prepared uncommon ACF containing many mesopores by blending an activation catalyst with phenolic resin or isotropic pitch. These mesoporous ACFs are a suitable material for investigating the influence of the mesopores on the double layer capacitance because the ACF prepared without an activation catalyst has a narrow pore size distribution of micropores without larger pores such as mesopores or macropores. Therefore, in this paper, the double layer capacitance of the mesoporous ACF is discussed in terms of a comparison with that of the microporous ACF without mesopores.

Experimental

2-1. Preparation and Characterization of ACF

Mesoporous ACF was prepared by a “blending method” [5] using nickel as the activation catalyst. The detailed procedure was done as follows. Novolac-type phenolic resin and $(\text{CH}_3\text{COCHCOCH}_3)_2\text{Ni}\cdot 2\text{H}_2\text{O}$ were dissolved in methanol. The percentage of nickel in the raw materials

was 0.1 wt %. The methanol was removed under reduced pressure to obtain a mixed resin. The resin was spun centrifugally to prepare the 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 ACF without an agent (pristine fiber) was also prepared in the same way as the above preparation process. The samples containing Ni species or without an agent were referred to as “0.1Ni-ACF (activation duration [min])” or “Ref-ACF (activation duration [min])”, respectively.

2.2. Measurement of double layer capacitance of ACF

A composite pellet electrode was prepared from ground ACF, acetylene black, and binder (86:10:4wt%). A standard three-electrode cell was used to measure the electric double layer capacitance of a single ACF electrode. The measurement of the double layer capacitance was conducted under galvanostatic conditions (40 mA g^{-1} , 2.0 V~ 4.0 V vs. Li/Li⁺) in propylene carbonate containing 1.0 mol dm^{-3} LiClO₄ electrolyte (1.0M LiClO₄/PC). In this paper, the process of electrons passing from (to) the carbon electrode is referred to as a positive (negative) process. The electric double layer capacitance was calculated by the amount of electricity passed during a positive or negative process according to the following equation.

$$C = i t / m \Delta V \quad (1)$$

where C ; electric double layer capacitance [F g^{-1}], i ; current [A], t ; positive (or negative) duration [s], m ; weight of ACF in the electrode [g], and ΔV ; potential change during positive (or negative) process [V] (= 2 V, in this study).

Results and Discussion

3.1. Characterization of ACF

The N_2 adsorption/desorption isotherms of both Ref-ACF (480) and 0.1 Ni-ACF (180) are shown in Figure 1. In the isotherm of the Ref-ACF (480), a large amount of N_2 was remarkably adsorbed at low relative pressure (< 0.1 P/Ps), while the N_2 adsorption was saturated at middle and high P/Ps. The drastic increment in adsorption at the low relative pressure is due to the micropore filling. The other Ref-

ACFs also showed the Type I isotherms. In the case of 0.1Ni-ACF (180), a drastic adsorption of N_2 was observed at low relative pressure as well as the case in Ref-ACF (480). However, the N_2 adsorption still increased even in the region of middle P/Ps and markedly increased again in the region of high P/Ps such as > 0.8 P/Ps. This result can be attributed to the capillary condensation of N_2 in the mesopores (or macropores) and multilayer adsorption on the mesopores or the macropores. The drastic adsorption in the region of middle and high P/Ps is also observed in the other 0.1Ni-ACFs.

The PSD of the mesopores for 0.1 Ni-ACF (180) and Ref-ACF (480) calculated by the adsorption isotherms using the Dolimore-Heal (DH) method are shown in Figure 2. The former has more mesopores than the latter. Especially, 0.1 Ni-ACF (180) had a relatively large size mesopore in the range of 10~40 nm pores. The BET specific surface area (corresponding to the total specific surface area of ACFs) and the DH pore volume (DH-PV, corresponding to the total pore volume of mesopores in the ACFs) are summarized in Table 1. In both of Ref-ACFs and 0.1Ni-ACFs, the BET specific surface area was increased as the activation duration was extended. This means that the pore structure in the ACFs is well developed with longer activation time. The 0.1 Ni-ACFs had larger mesopores volume compared with Ref-ACF having almost the same BET specific surface area. Additionally, the total micropore volume (W) and average micropore width (2χ) were estimated by the adsorption isotherms using the Dubinin – Radushevich (DR) equation. They are also summarized in Table 1. The micropore volume and the micropore width became larger with longer activation duration regardless of the Ref-ACF series and 0.1Ni ACF series. However,

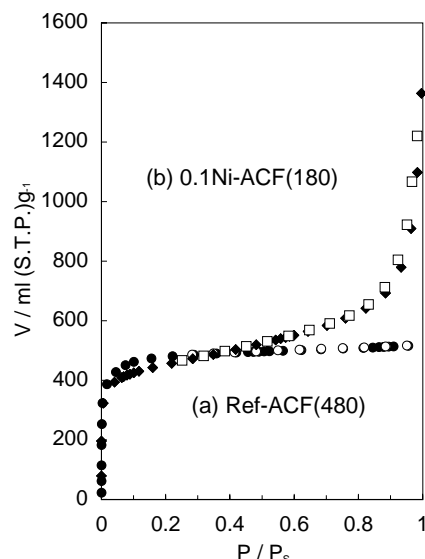


Figure 1. N_2 adsorption and desorption isotherms of (a) Ref-ACF (480) and (b) 0.1Ni-ACF (180). Filled symbols: adsorption isotherms, open symbol: desorption isotherms.

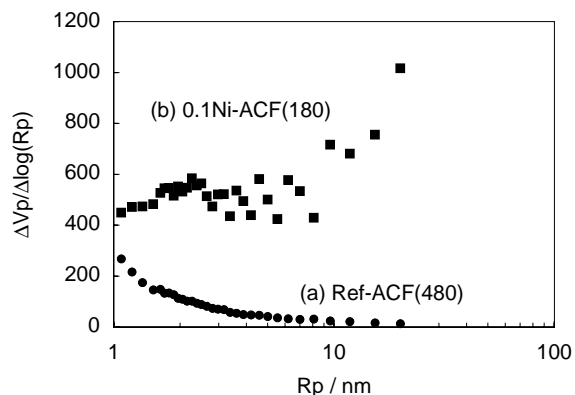


Figure 2. Pore size distribution for the mesopore region of Ref-ACF (480) and 0.1 Ni-ACF (180), calculated by the DH method. R_p ; pore radius, V_p ; pore volume.

Table 1. BET specific surface area, average micropore width, micropore volume, and mesopore volume of various ACFs.

Sample*	BET-SSA[m ² g ⁻¹]	W [ml g ⁻¹]	2χ [nm]	DH-PV[ml g ⁻¹]
Ref-ACF(10)	654	0.28	0.64	0.06
Ref-ACF(60)	934	0.37	0.80	0.03
Ref-ACF(120)	1151	0.47	0.85	0.08
Ref-ACF(240)	1475	0.60	0.94	0.09
Ref-ACF(480)	1776	0.73	1.07	0.16
0.1Ni-ACF(10)	706	0.28	0.70	0.10
0.1Ni-ACF(60)	957	0.38	0.83	0.21
0.1Ni-ACF(120)	1048	0.42	0.83	0.30
0.1Ni-ACF(140)	1287	0.52	0.88	0.35
0.1Ni-ACF(180)	1655	0.69	1.06	0.86

little difference was observed in the micropore volume and the average micropore width between Ref-ACF and 0.1 Ni-ACF with almost identical BET surface area. These results suggested that the micropore structure was independent of the mesopore structure using the activation catalyst.

3.2 Double Layer Capacitance of ACF

Figure 3 is the relationship between the BET specific surface area and the electric double layer capacitance in 1.0 M LiClO₄/PC. In the cases of both Ref-ACFs and 0.1Ni-ACFs, the double layer capacitance was not linearly proportional to the BET specific surface area. The very small capacitance of the ACFs with a small BET specific surface area is derived from the difficulty in forming an effective double layer or from the low mobility of the ion in the narrow micropores. However, the double layer capacitance of 0.1Ni-ACF was higher than that of Ref-ACF with almost the same BET specific surface area. Especially, the higher capacitance of 0.1Ni-ACFs was prominent in the region of 1000~1500 m²g⁻¹ BET specific surface area. In the previous section, it has already been revealed that the mesopores in the Ni-ACF series were developed much more compared with those in the Ref-ACFs, although there was little difference in the micropore structure for both series of samples from the viewpoint of the average micropore width and the micropore volume. Consequently, this advantage of the capacitance of 0.1N-ACFs can be attributed to the presence of many mesopores, which assists the permeation of electrolyte into the pores or the transfer of ions through the microporous structure.

Conclusions

Mesoporous ACF were prepared from a phenolic resin with 0.1 wt % of an organic nickel complex through carbonization and steam activation. In both cases, for the mesoporous ACFs and the microporous ACFs, the double layer capacitance of in 1.0 M LiClO₄/PC electrolyte was not proportional to the BET specific surface area. This is due either to the low permeability of nonaqueous electrolyte or the low mobility of the ions in the narrow micropores. However, the mesoporous ACF showed a higher double layer capacitance than the microporous ACF. This result suggests that the presence of many mesopores promotes the formation of an effective double layer or the transfer of ions in the micropore.

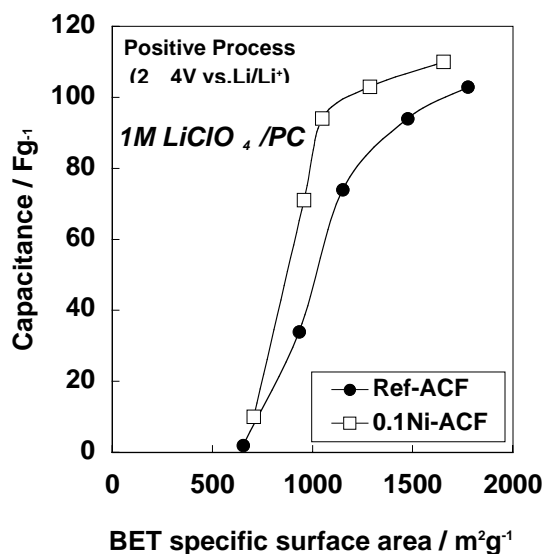


Figure 3. Relationship between BET specific surface area and double layer capacitance (positive process) for Ref-ACFs and 0.1 Ni-ACFs in 1.0 M LiClO₄/PC.

References

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