INFLUENCE OF PORE STRUCTURES ON THE ELECTROLYTE BEHAVIOR IN EDLC BY ^{11}B SOLID STATE NMR

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Introduction

EDLC has been well acknowledged with its proven performance such as power density, rapid charge and discharge, cycle characteristic and lifetime and is expected to as energy storage media for electric vehicle etc.[1)]. Activated carbon with porous nature is already well adopted for use as electrodes in EDLC. However, influence of pore structure on electrolyte behavior and statement in pore has not been clarified yet.

In this study, therefore, we prepared activated carbon with controlled surface areas and pore size distributions clarify on the influence of surface area and pore size distributions in regards to behavior of electrolyte by ^{11}B solid state NMR analysis.. The prepared samples have surface area ranging from low to moderate (500-2000 m^2/g).

Experimental

1. Preparation of Activated Carbon.

Activated carbons were prepared from High Density Particulate Cokes (HDPC) by KOH activation. The porous structure was controlled by changing activation temperature and KOH amount.

2. Preparation of Electrode for EDLC.

As for the preparation of electrode, ativated carbon, Ketjen Black and plytetorafluoroethylene were mixed at the rate of 1:1:1 (wt%)

3. Preparation of EDLC

Et_4NBF_4(1M)/PC was used as an ectrolyte in EDLC. The capacitance was measured by charge up to 2.7 V and discharge at constant voltage and current.

4. ^{11}B solid state NMR measurement.

The electrodes of EDLC at impregnated, chaged and discharged states were measured by JEOL ECA400 11B solid state NMR ([11]B:128.3MHz).

Results and Discussion

1. Preparation of Activated Carbon

The activated carbons with surface area from 500 m^2/g to 2000 m^2/g were prepared by KOH activation. The samples were named as M500, M1000, M1500 and M2000 according to their surface area. Figs. 1 and 2 and show N_2 adsorption/desorption isotherms at 77K and the pore size distribution of each samples. It was found that the mesopore proportion tends to increase along with an increase of surface area.
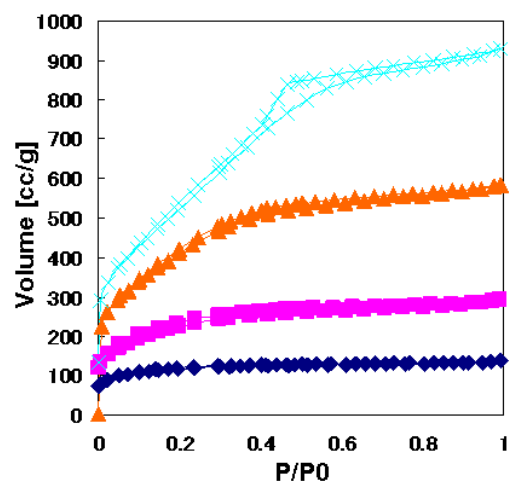

Fig. 1 N_2 adsorption/desorption isotherms at 77K of M series. ♦:M500 ■:M1000 ▲:M1500 ×:M2000
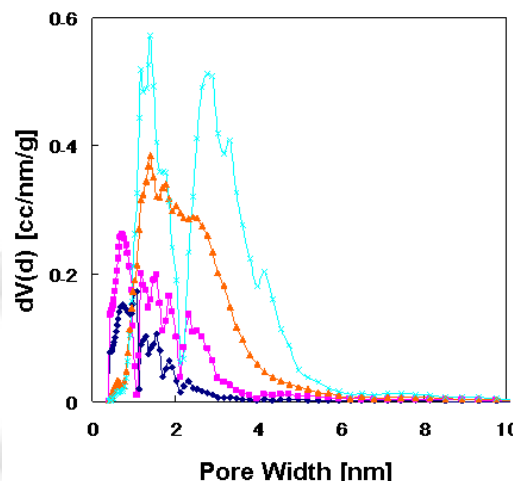
Fig. 2 Pore size distribution of M series. ♦:M500 ■:M1000 ▲:M1500 ×:M2000

2. ^{11}B solid NMR Measurement

Fig. 3 shows the ^{11}B solid state NMR spectra of BF_4^- for the positive electrodes at impregnated, charged, and discharged states. All samples showed two peaks, one sharp and one broad. The former was attributed to the free BF_4^- which shows only slight adsorption characteristics and the latter was due to BF_4^- represented by strong adsorption. The larger surface area, the bigger the broad peak was. Such phenomena are assumed to be due to an increase in the pore volume. As for the longitudinal relaxation time (T_1) of broad peak, the impregnated state showed the longest of the three states (Table. 1). Additionally, T_1 of impregnated state was raised by increasing pore volume, which presents the usefulness of narrow pore shapes in facilitating stronger interaction between anion and electrode. On the other hand, charging process gave dramatic drop, indicating the strong adsorption due to electrostatic interaction. Relaxation times had tendency to show similarities regardless of samples with the only exceptional trend of charged state where strong interaction can be found. When in discharge, the

prolongation of time was observed while not reaching as much as that in impregnated state. It is believed to be explained by strongly adsorbed ions remained in fine pores. By observing the relaxation time, the adsorption state of ions could be known. It could be very well assumed that ^{11}B solid state NMR shows highly corresponding result to the movement of anion in the charge and discharge process.

Conclusions

Activated carbons with arbitrary medium surface area were prepared by KOH activation. When the anion in EDLC was measured by ^{11}B solid state NMR, the result showed good correspondence to charge and discharge behavior. The ^{11}B solid NMR was useful for the behavioral analysis of the electrolytic ion.

Table 1. Longitudinal relaxation times (T_1) of about broad peak for M series.

Sample	State	T_1 [s]	Sample	State	T_1 [s]
M500	imp	0.986	M1500	imp	2.158
	ch+	0.235		ch+	0.239
	dis+	0.639		dis+	1.690
M1000	imp	1.377	M2000	imp	3.699
	ch+	0.247		ch+	0.344
	dis+	1.28		dis+	2.495

5. Reference

[1] Takeshi Morimoto,TANSO 2004 [No.214] 202-209.

[2] Yoshiharu Matsuda, TANSO 2005 [No.216] 41-46.
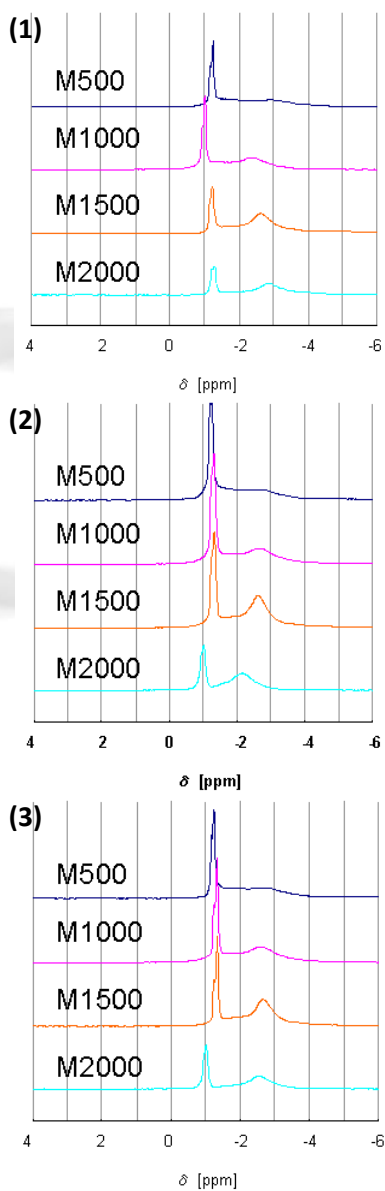
Fig. 3 ^{11}B solid state NMR spectra of BF_4^- on the positive electrode of M series. (1):impregnated (2):charged (3):discharged