

Multi-nuclei NMR study on behavior of organic electrolyte at charged and discharged states on activated carbon as an electrode for EDLC

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1. Introduction

The electric double-layer capacitor (EDLC) using activated carbon as electrodes has been recognized as an efficient storage device for the electric power because of its better rate capability and longer cycle life as compared to secondary batteries in spite of its low energy density [1,2]. Recently new applications utilizing such performances have been attempted as an energy storage device for electric vehicle or pulse-current supply. In order to meet the specification for new application, it is necessary for particular activated carbon to have higher energy density per weight or volume than the conventional one.

Activated carbons with the specific surface areas beyond 2000m²/g have been prepared from the various carbon precursors by chemical or gas-phase activation, resulting in high capacitance per weight [3-5]. Nevertheless, they still suffer from low electrode density and capacitance per volume which lower the compactness of EDLC. Their effectiveness per surface area and pore volume stays rather low. Many researchers

have correlated the capacitance with one of carbon properties to find the dominant factor which may influence the capacitance directly, although their success was very limited [6-8].

In the present study, activated carbon was obtained from optically anisotropic spherical carbon by NaOH activation, and the electrode from the activated carbon was impregnated, charged or discharged using 1M Et₄NBF₄ in PC as an organic electrolyte. Behaviors of electrolyte and solvent in the negative and positive electrodes of the electric double layer capacitor were investigated at the impregnated, charged and discharged conditions by ¹³C and ¹¹B solid NMR. Solid NMR is thought to be a sole and powerful method to solve the chemical and dynamic behaviors of ion and solvent present in the pore or adsorbed on the wall of the pore [9-11].

2. EXPERIMENTAL

2.1. Preparation of samples in the form of electrode for NMR

In the present study, spherical carbon pre-calcined at 800°C was activated with 4times of NaOH in weight at 700°C for 1h, giving the specific surface area of 500m²/g by nitrogen isotherm. Its specific capacitance was measured at 25°C in a two-electrode galvanostatic system using 1M Et₄NBF₄ in PC as an electrolyte, resulting in specific capacitance of 36F/g and 35F/ml. The disc-type electrode (about 25mg) was composed of activated spherical carbon (80wt%), PTFE as a binder (10%), and carbon black as a conductive (10%). The electrode was impregnated (No.1) in the electrolyte under vacuum for 3h. The test cell was charged to 2.7V (No.2 and 3) at a current density of 200mA/g, and then discharged (No.4 and 5) to 0V at the same current density.

2.2. Solid NMR

2.2.1. ^{11}B -MAS, multiple quantum (MQ) MAS NMR

Disc-type electrodes at the impregnated, charged and discharged conditions were cut into pieces, loaded in the sample tube of 4mm in diameter, and spun at 12 kHz. All ^{11}B -NMR spectra were obtained at 96.423MHz by a Chemagnetics CMX-300, and referenced to saturated aqueous boric acid (19.5ppm). Relaxation time (T_1) was determined by the saturation recovery method.

3. RESULTS AND DISCUSSIONS

Figure 1 shows ^{11}B -MAS NMR spectra of electrodes in various states. All spectra showed a sharp peak (peak A) at 0ppm and broad one (peak B) ranging from about -3ppm to -11ppm, although the broad peaks of No.2 and 3 were rather sharper than those of other samples. The chemical shift of the particular species present in pore of activated carbon has been reported to shift to low field by π -electron shielding on the graphene planes of activated carbon [11,12]. Also adsorption of anion, BF_4^- , restricted its mobility, resulting in broadening the peak. Therefore, we could assign the sharp peak and broad one to the non-adsorbed anion staying over the outer surface and the adsorbed one in the pore of activated carbon, respectively.

Although it is difficult to conduct a quantitative experimental through NMR, in this study optimal 90° pulse for each sample was investigated to enhance the quantification among the samples. Also flip angle of 18° was used to reduce the difference in sensitivity between the sharp peak and broad one. Signal to noise ratio of each spectrum enables us to estimate that the total amount of anion (A+B) is in the following order; No.2>>No.4=No.5>No.3>No.1. ^{11}B -MAS NMR spectra were smoothed to

deconvolute into two peaks and the integration ratio (peak B/peak A) is summarized in

Table 1. Samples and integration ratio (IntR) of peak A to B.

Sample	Treatment	IntR (B/A)
No.1	Impregnated	4
No.2	Charged (+) Electrode	23
No.3	Charged (-) Electrode	5
No.4	Discharged (+) Electrode	5
No.5	Discharged (-) Electrode	5

Table 1. The ratio was also in the same order as that of total amount of anion. This means that the large amount of anions enter the pore of the positive when the electrode was electrochemically charged.

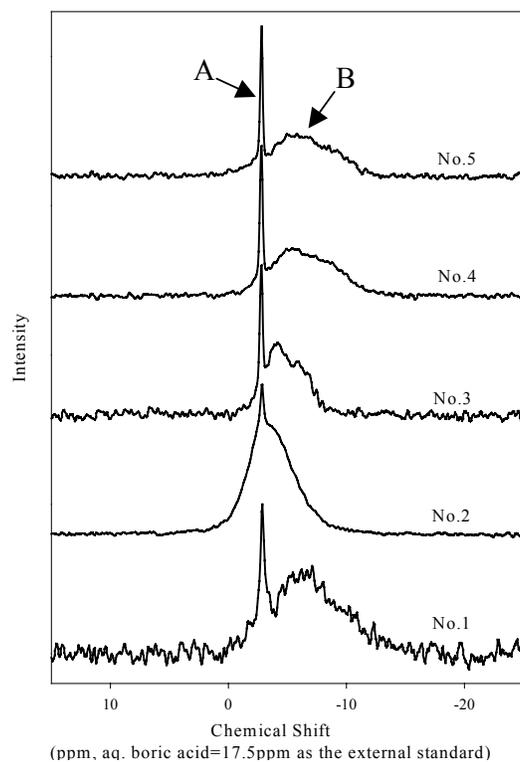


Figure 1. ^{11}B -MAS NMR spectra of the impregnated, charged and discharged electrodes.

^{11}B is a quadrupolar nucleus with half-integer spin number ($I=3/2$). Line broadening and splitting of the central transition ($-1/2, 1/2$) in ^{11}B -MAS spectrum result from the second-order interaction of the nuclear quadrupolar moment surrounded by the local electric field gradient [13,14]. It is often difficult to characterize chemically inequivalent boron sites, when distinct boron sites are overlapped each other under the regular MAS condition. One among the techniques overcoming the second-order quadrupolar interaction is multiple quantum magic-angle spinning (MQMAS) NMR.

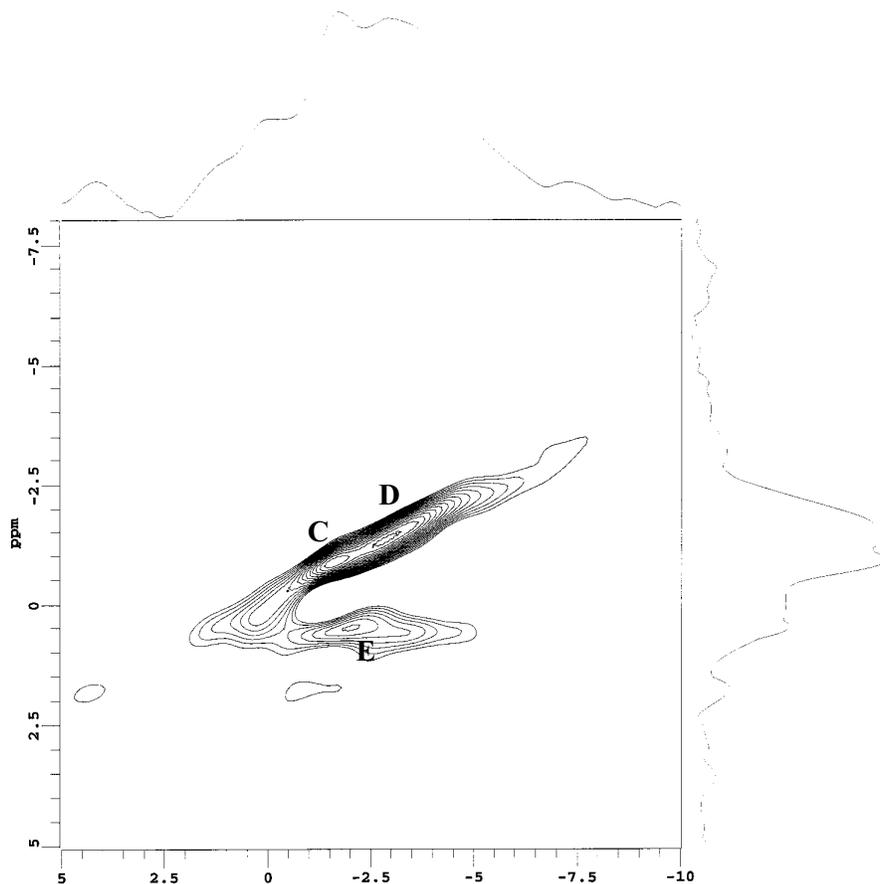


Figure 2. ^{11}B -MQMAS spectrum of the charged positive electrode, No.2.

Figure 2 and Figure 3 show ^{11}B -MQMAS NMR spectra of the charged positive electrode (No.2) and discharged positive electrode (No.4), respectively. Although there were two peaks (sharp and broad peaks) in MAS spectrum of Figure 1, MQMAS spectra showed that the broad peak (B) in MAS spectrum consisted of two distinct sites. This is the first direct observation of ^{11}B ion present in activated carbon electrode treated electrochemically.

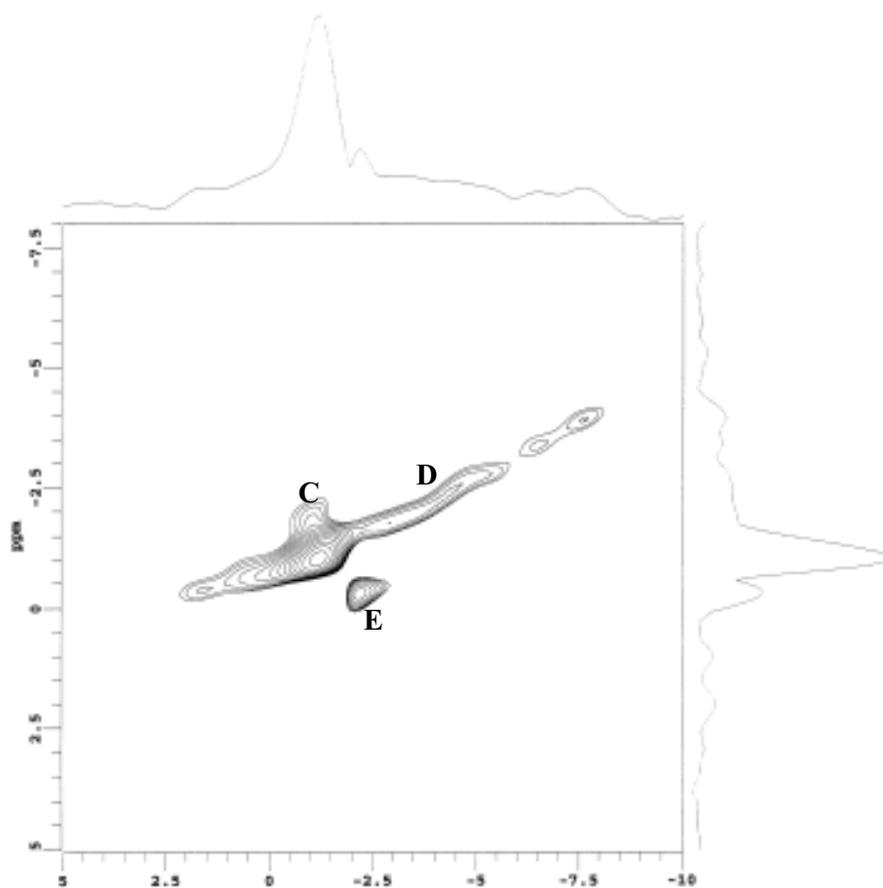


Figure 3. ^{11}B -MQMAS spectrum of the discharged positive electrode, No.4.

Table 2. Chemical shift and quadrupole constant of each site from ^{11}B -MQMAS spectra of sample No.2 and No. 4.

Sample	Chemical shift (ppm)			C_Q		
	Site C	D	E	Site C	D	E
No.2	-1.2	-2.0	-0.5	0.16	0.30	0.51
No.4	-1.1	-2.3	-0.8	0.04	0.25	0.42

Chemical shift and quadrupolar constant (C_Q) of site C, D and E are summarized in Table 2. From chemical shift and quadrupolar constant, site C is assigned to be the non-adsorbed anion staying over the outer surface (peak A in ^{11}B -MAS), and site D and E correspond the adsorbed anions in the pore of activated carbon (peak B in ^{11}B -MAS). The C_Q of site E was larger than that of site D, implying that boron of site E has the higher extent of nucleus deformation. Although there were no significant changes in chemical shift and quadrupolar constant according to discharge, there was the quantitative change. Site E kept its intensity of peak after discharge, but site D lost its intensity in the state of charge. This indicates that anion of site D experiences the quantitative change such as coming and going from the pore.

Relaxation time (T_1) was determined by the saturation recovery method on the basis of chemical shift of three sites in MQMAS spectrum, and summarized in Table 3. After charging, at the positive electrode (No.2) T_1 of three sites decreased significantly, but T_1 at the negative electrode (No.3) increased.

Table 3. Relaxation time (T_1) of each sample obtained by saturation recovery method.

Sample	T_1		
	Site C	D	E
No.1	2.00	0.90	0.90
No.2	0.09	0.05	0.03
No.3	4.40	2.10	1.70
No.4	0.78	0.35	0.26
No.5	2.10	0.40	0.30

It is remarkable that T_1 of the non-adsorbed anion staying over the outer surface (site C) is influenced simultaneously. T_1 for the discharged electrodes (No.4 and 5) was almost same, though slightly different for site C. Some researchers have reported that T_2 of the adsorbate on the activated carbon pore is shorter than that of the non-adsorbed, resultantly making the peak broader. However, the peak (peak B) of the adsorbed ion in the pore became sharper after charging, and the discharging recovered its broadness. Especially, it must be noticeable that the peak of the charged positive electrode (No.2) with the largest amount of BF_4^- ions and likely the strong adsorption is sharper than those of other electrodes. However, T_1 informs us that anion in the charged positive electrode is the most restricted and one in the charged positive is the most mobile among the electrochemically treated electrodes (No.2 – No.5). MAS NMR combined by MQ technique will open the window to the behaviors of ions in the electrolyte in the pore according to the electrochemical treatment.

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