Non-porous Carbon for a High Energy Density Electric Double Layer Capacitor

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Apparently non-porous activated carbon with a specific surface area less than 100 m²/g(BET) prepared from calcined carbon of petroleum coke is studied as the polarized electrode for an Electric Double Layer Capacitor(EDLC). The non-porous carbon makes negligibly small electric double layer when it is dipped into an electrolyte solution in the beginning. During the initial charging process, however, "solvent co-intercalation of ions" builds double layers in the positive and the negative electrodes, and during the discharging process, the excess ions go out, while the opposite ions come in, to maintain the double layers electrically neutral. After that, the electrodes behave like conventional activated porous carbon electrodes with an extra high dense capacitance. The observed phenomenon is discussed from the viewpoints of the inter-layer distance in graphite-like structure, the molecular volume of solvent for electrolyte, the residual functional groups such as active oxidized hydrogen observed by NMR, and of the elimination method for the residual active oxidized hydrogen by heat treatment in H₂ atmosphere, as well as the preparation method for source carbon.

Key Words : Non-porous Carbon, Solvent Co-intercalation, Solvent Molecular Volume

1 Introduction

As one of the provisional storage means for electric energy, the electric double layer capacitor(EDLC) has been developed for higher density of capacitance and higher working voltage.¹⁻³⁾ So far, most of the materials used for the polarized electrodes of the EDLC have been activated carbon with a large specific surface area such as 1,000~2,000 m²/g(BET).^{4, 5)} On the other hand, carbon with an apparently very small specific surface area—less than 350 m²/g, which has a inter-layer distance, d_{002} , larger than 0.36 nm, was reported to show a larger capacitance and a higher working voltage.⁶⁾ Such carbon was prepared by the KOH heat treatment of the graphitizable carbon, which was petroleum coke or pitch calcined at 700~850°C.⁶⁾

The behavior of the carbon under charge-discharge process has been investigated by X-ray diffraction(XRD) and ¹⁹F nuclear magnetic resonance(NMR) observations of several states during electrode charging and discharging, and by the observation of expansion pressure under volume restriction in the direction of the applied electric field. Thus, the phenomenon observed on the carbon electrode has been explained by the mechanism called as "solvent co-intercalation of ions"⁷⁾ by electro-chemical force.⁶⁾

We have studied the phenomenon from the viewpoints of the dependence on the inter-layer distance, d_{002} , of activated carbon and on the molecular volume of solvents

for (C₂H₅)₄NBF₄ as electrolyte. A spin-echo NMR observation revealed that the KOH activated carbon dried by heating at 250°C in a pressure of about 5×10⁻³ Pa still keeps residual active oxidized hydrogen. When the carbon was heated in H₂ atmosphere, a considerable amount of such active oxidized hydrogen could be eliminated, though complete elimination could be attainable only in the extreme case. The carbon treated by heating in H₂ showed a specific surface area less than 100 m²/g without any loss of the attainable performance characteristics.

2 Experimental

2. 1 Preparation of carbon electrodes and their assembly for EDLC

2. 1. 1 Source material, pre-treatment and activation Petroleum needle coke, S-JA(r) (Koa Oil Co., Ltd.) was crushed by Wonder Blender (Osaka Chemicals Ltd.) into fine particles with size less than 210 μm, and the powdered carbon was calcined at 750°C for 4 hours in a stream of N₂. The calcined carbon crushed easily was mixed with 2-fold weight of small tablets of KOH in a melting pot made of alumina with a high purity, 99.98%. Then, the calcined carbon containing KOH was heated at 800°C for 2~4 hours in N₂ for activation. After cooling down, the alkali rich residual carbon was washed with hot water until the outlet water reached pH = 7. After that the carbon was dried by heating in a vacuum.

2. 1. 2 Post-treatment The activated carbon pro-

duced by the above procedure was not so porous with specific surface area of 150~500 m²/g(BET), and contained some amounts of active oxidized hydrogen. For eliminating active oxidized hydrogen, the activated carbon was heated at various temperatures from 500 to 800°C in N₂ and H₂. As described in some monographs,^{3, 8, 9)} eliminated functional groups, such as OH, CHO, COOH and so on, increase with increasing temperature between 400 and 800°C, but hydrogen bonded directly to aromatic ring still remains. As the aromatic hydrogen is inert for EDLC, the elimination of the active oxidized hydrogen is required, even though aromatic hydrogen is increased.

Post heat treatment of the activated carbon in a vacuum or in N₂ brings the active oxidized hydrogen to an elimination state, but active sites (most probably free radicals) may remain, so that, after exposure to air, the active oxidized hydrogen may appear again no matter whether rapidly or slowly, resulting in the decrease in attainable capacitance in some extent. By the heat treatment in H₂ atmosphere, however, the elimination of the active oxidized hydrogen can be done without decrease of attainable capacitances. Even at temperatures lower than 500°C, complete elimination of the active oxidized hydrogen (as far as observed by NMR) was attained with the help of some kind of catalyst.

As the post-treated activated carbon shows so small specific surface area less than 100 m²/g (BET), we call this "non-porous carbon," it shows a smaller inter-layer distance than the value of the activated carbon before the post-treatment.

2. 1. 3 Assembly for EDLC We have made carbon electrode sheets by the ordinary method from powdered carbon.^{5, 6)} The weight ratio of constituent materials was carbon: 10, carbon black: 1, and PTFE binder: 0.5. The test cell is 20 mm in diameter and 0.25~0.4 mm in thickness, and for the separator we used a glass filter GA-100 (Advantec) and a paper CTW57 (NKK Corp.). For the current collector, we used an etched aluminum sheet (KNK Corp.).

The cell was constructed as follows. Two pieces of the carbon electrodes sandwiching the separator, which were immersed in an electrolyte solution in a vacuum, were inserted between the two aluminum current collectors, one for the positive electrode and the other for the negative. Then the assembly was inserted in a poly-bag and sealed with the help of a vacuum. In the case of conventional

three electrode method, a conventional activated porous carbon electrode insulated by a paper separator was added as the third electrode.

2. 1. 4 Preparation of electrolyte solution We have used a ready-made electrolyte solution, 1 mol of (C₂H₅)₄NBF₄ in propylene carbonate(PC) (Mitsubishi Chemical) and some home-made electrolyte solutions, the same electrolyte but in a different solvent such as acetonitrile (ACN), ethylene carbonate(EC), diethyl carbonate (DEC) and gamma butylo lactone(GBL) without further purification. The home-made solution were prepared by dissolving a commercially available reagent, (C₂H₅)₄NBF₄ (Tokyo Kasei) at about 1 mol/L concentration in a neat or a mixture of the solvents (Kanto Kagaku). The solvents, PC and GBL were used as neat state, while ACN, EC and DEC were used as the mixture state (1:1 volume ratio). To eliminate H₂O, the solutions were used after keeping for one day in a bottle including activated alumina powder (LC grade).

The typical characteristics of the solvents used are listed in Table 1.

2. 2 Characterization of materials

2. 2. 1 X-ray diffraction (XRD) The raw coke, the calcined carbon and the KOH activated carbon were investigated in a powdered state with X-ray diffractometer, JDX-3500 with a Cu-K α source (JEOL Ltd.).

2. 2. 2 Pulse NMR (Spin-echo) observation The residual protons in carbon materials can be analyzed by the Pulse NMR, JNM-Mu25 [25 MHz for proton] (JEOL Ltd.). We have tried a quantitative measurement of residual protons in the carbon powder (in some cases, in the state of sheet bound with PTFE) dried by heating at 250°C in a pressure of about 5 $\times$ 10⁻³ Pa. The sample was put into a 10 mm ϕ test tube in a glove box kept at the dryness within 1 ppm (dew point of -80°C), and the capped test tube was packed in a poly-bag and sealed for keeping it dry. Soon after opening the seal, the NMR measurement was performed.

The observable echo spectra from roughly dried powdered carbon usually consist of three components; short relaxation time component, $T_2 = 17 \sim 50$ μ sec, which is assigned to aromatic hydrogen, middle relaxation time component, $T_2 = 60 \sim 400$ μ sec, which corresponds to active oxidized hydrogen, and long relaxation time component, $T_2 = 400$ μ sec ~ several msec, which is due to loosely coupled hydrogen like absorbed water. The well dried powder carbon described above usually shows the

Table 1 Solvent characteristics.¹⁰⁾

Solvent	Symbol	m. w.	s. g.	m. v.	ϵ	η	m. p. °C	b. p. °C	DN	AN
CH ₃ CN	ACN	41.05	0.7822	52.48	37.5	0.375	-43.9	84.6	14.1	18.9
(CH ₂ O) ₂ CO	EC	88.1	1.3383	65.8	43.3	1.92	36.4	238	16.4	
CH ₃ CHOCH ₂ OCO	PC	102.09	1.19	85.8	69.0	1.38	-49	241	15.1	18.3
(C ₂ H ₅ O) ₂ CO	DEC	120.08	0.975	123.2	2.82	0.748	-43	129	16	
CH ₂ CH ₂ CH ₂ COO	GBL	86.1	1.13	76.1	39.1	1.75	-43	202		

m. w.: molecular weight, s. g.: specific gravity, m. v.: molecular volume, ϵ : specific permittivity, η : specific viscosity, m. p.: melting point, b. p.: boiling point, DN: donor number, AN: acceptor number.

Fig. 1 XRD results for carbon samples subjected to different processing. (a) raw needle coke, S-JA(r), (b) calcined carbon at 750°C for 4 hr., S-JA(r)754 and (c) KOH activated carbon at 800°C, 4 hr., S-JA(r)KOH. Inter-layer distance d_{002} (nm) and intensity (k counts) are listed below; (a) 0.348, 471, (b) 0.354, 539, (c) 0.369, 548.

former two components.

2. 3 Charge-discharge test

Charge-discharge test was done by using a 4-channel Test Cell Evaluation System, Model CDT-5R2-4 (Power Systems). A constant current mode of 10 mA was used. When the voltage reached to a specified value, it was kept constant for a given time, and then discharge was done with the constant current of 10 mA (3.2 mA/cm²) until the voltage becomes 0. After a given pause time, charge-discharge process was started again for given cycles. The capacitance was calculated in term of farad per given volume or weight of the electrodes (based on the values measured in a dry state) from the attained discharge energy.

3 Results and Discussion

3. 1 XRD observation

Figure 1 shows the results of XRD measurement for (a) raw coke, S-JA(r), (b) the calcined carbon at 750°C for 4 hours, and (c) the activated carbon at 800°C with KOH. The average values of inter-layer distances, d_{002} and the intensities of crystalline parts are listed in the

caption. As shown in the figure the average inter-layer distances increased in this order. The area intensity of the KOH activated carbon is the largest. A considerable part of amorphous component of raw coke, indicated by broad peak at about $2\theta = 10$ degree, decreased in the calcined carbon and further decreased in the KOH activated carbon. These results suggest the consideration that an amorphous part is attacked by KOH to make porosity when the raw coke is treated by KOH without calcination. It is most probable that the activated carbon with KOH is composed of two parts, one is a rather tight crystalline part with small inter-layer distance as that of the raw coke, and the other is a loose crystalline part with a inter-layer distance larger than the average value, 0.369 nm. The loose crystalline part is ready for accepting to make "solvent co-intercalation of ions" under an electric force.

This may be an answer to the question why BF_4^- (ion radius, $r = 0.218$ nm) or $(\text{C}_2\text{H}_5)_4\text{N}^+$ ($r = 0.342$ nm) ions with the diameters larger than the average inter-layer distance (0.369 nm) can intercalate into the inter-layer of carbon structure even though forced by electric field.

3. 2 Pulse NMR observation

Figure 2 shows the Pulse NMR observation results of powdered carbon, a) raw coke, b) the calcined carbon and c) the KOH-activated carbon. Considering that these three data were obtained at different gains, it is clear that aromatic proton content remarkably decreases from stage b) to c), and this is explained by assuming that KOH attacked the edges of aromatic rings to make them active for intercalation.

Figure 3 shows the pulse NMR spectra of the carbon under post-treatment; a) no post-treatment, b) the post-treatment at 500°C in H_2 without catalyst and c) the post-treatment at 500°C in H_2 with catalyst. As shown in the each figure, the ratio of the components of middle relaxation time against the short relaxation time changed depending on the treatment conditions.

By the way, the fact that the middle relaxation time component corresponds to the active oxidized hydrogen could be confirmed as the following matter. When micro

Fig. 2 ^1H resonance of powdered carbon samples by pulse NMR. (a) raw coke, S-JA(r), (b) calcined carbon, S-JA(r)754, and (c) KOH activated carbon, S-JA(r)KOH. As these are obtained at different gains, the reduced intensities of short relaxation time component at the same gain, are shown below; (a) 18,325, (b) 6,173 and (c) 158.

Fig. 3 ^1H resonance of post-treated carbon samples on different conditions. (a) no post treatment, S-JA(r)KOH, (b) post treatment at 500°C for 4 hr. in H_2 , S-JA(r)KOH + 504 H and (c) same as (b) but in addition with catalyst, S-JA(r)KOH + 504 H^* .

volume of H_2O were added to the dried activated carbon quantitatively, the long relaxation time component which could be shown by H_2O in free state or loosely absorbed, did not appear, but the middle relaxation time component increased in proportion to added amount. This fact may be explained as follows; the active site of carbon reacts with H_2O to produce so called active oxidized hydrogen such as phenolic-OH, CHO, COOH and so on.

Fig. 4 First charging characteristics of non-porous carbon samples. (a) post-treatment at 800°C , 6 hr. in H_2 , S-JA(r)KOH + 806 H, [specific surface area; $67.6 \text{ m}^2/\text{g}(\text{BET})$], (b) post-treatment at 500°C , 4 hr. in H_2 , S-JA(r)KOH + 504 H, and (c) no post-treatment, S-JA(r)KOH, [$262.7 \text{ m}^2/\text{g}(\text{BET})$]. All data are obtained by using $(\text{C}_2\text{H}_5)_3\text{CH}_3\text{NBF}_4$ in PC solution.

Fig. 5 First sequential charge-discharge procedure. Sequential test was done by changing the applied voltage in 0.5 V step and the charging time in 500 sec step, from 0.5 V up to 4.0 V, and down to 0.5 V (or 0.25 V).

3.3 Charge-discharge characteristics

Figure 4 shows three typical charging characteristics of the same carbon but with different post-treatment; a) post-treatment at 800°C for 6 hours in H_2 (specific surface area, $67.6 \text{ m}^2/\text{g}$), b) post-treatment at 500°C , 4 hours in H_2 , and c) without post-treatment ($262.7 \text{ m}^2/\text{g}$). The distinctive voltage of intercalation starting is not clear in c), but in a) and b) they can be clearly read as 3.0 V in a), 2.7 V in b), respectively.

For confirmation of the capacitance formed in carbon electrode under the initial charging state, we tried a charge-discharge cycle test by increasing the voltage from 0.5 V to 3.75 V (or 4.0 V) with 0.5 V (or 0.25 V) step and decreasing the voltage to 0.5 V in the same step, as shown in Fig. 5.

Figure 6 shows the voltage-capacitance characteristics of the non-porous carbon (a) and the conventional porous carbon (b) observed by the above procedure. As shown in the figure, the non-porous carbon shows almost no capacitance at the beginning, indicating that negligible small double layer was formed when dipped into an electrolyte solution. However, once the double layer was

Fig. 6 Plot of capacitance observed above against applied voltage. (a) non-porous carbon with (C₂H₅)₄NBF₄ in ACN/PC and (b) conventional activated porous carbon with (C₂H₅)₄NBF₄ in PC.

produced, it was held in the following process, as can be seen in the large hysteresis curve.

On the contrary, the conventional porous carbon has a capacitance at the beginning and makes no hysteresis curve in the discharge process. The attainable capacitance of the non-porous carbon is more than 2-fold of the conventional porous carbon.

3. 4 Dependence of intercalation starting voltage on d_{002}

Figure 7 shows the correlation between the intercalation starting voltage and the inter-layer distance, d_{002} , of the carbon samples which were prepared by changing the temperatures of the post-treatment on the various carbons from different sources. The observed inter-layer distances were between 0.36 and 0.38 nm. As can be seen in Fig. 7, a clear reversal correlation exists between d_{002} and the intercalation starting voltage.

Fig. 7 Plot of intercalation starting voltage against inter-layer distance. Various carbons with different d_{002} were produced from different carbons mainly by changing post-treatment temperature in H₂. The used electrolyte: (C₂H₅)₄NBF₄ in PC (●) and ACN/PC (■).

Fig. 8 Plot of intercalation starting voltage against the smaller molecular volume of solvents used for the electrolyte solution (ACN/PC, EC/DEC, GBL, PC).

3. 5 Dependence of intercalation starting voltage on molecular volume of solvent

Figure 8 shows the intercalation starting voltage against the molecular volume of solvent used for the electrolyte solution. Here, three carbon samples with different d_{002} values are examined against four different solvents with different molecular volume. The data were obtained from 1 mol solution of (C₂H₅)₄NBF₄ in ACN/PC (1 : 1 volume), EC/PC (1 : 1 volume at 400°C), neat GBL and neat PC, respectively. A linear correlation can be noticed except one data-point for the sample with $d_{002} = 0.362$ nm in PC. The reason for this discrepancy is still unclear.

Intercalation starting voltage is inversely proportional to the inter-layer distance and proportional to the molecular volume of the solvent. This fact leads to the concept that "solvent co-intercalation of ions" is the principal mechanism of the observed phenomenon, which was described already from the study by ¹⁹F NMR based on magic angle spinning of adsorbed BF₄⁻ in porous and non-porous solid carbon samples.⁶⁾ This report provides a strong support to it.

This phenomenon should depend on the size of ions, then we tried some preliminary experiments using (C₄H₉)₄N⁺ ($r = 0.417$ nm) ion as a larger ion instead of (C₂H₅)₄N⁺ ($r = 0.342$ nm), and (C₂H₅)₃CH₃N⁺ ($r = 0.332$ nm) ion as a smaller one, and got poor attainable capacitance on the former and slight improvement on the later.

On the solvent for the electrolyte solution, on the other hand, it is not necessary to use neat solvent for decreasing the intercalation starting voltage as shown above, but a mixture solvent (more than 30 mol% of low molecular volume) may be sufficient enough for the requirement. The actual advantage to use small molecular volume solvent mixing with PC or EC, is making the internal resistance decrease. This may be due to improved mobility of the electrolyte ions.

A cycle test on this non-porous carbon electrode is now under investigation. The preliminary test up to 1,000

Fig. 9 Result of preliminary cycle test. Carbon sample used: S-JA(r)KOH + 806 H, electrolyte: $(C_2H_5)_4NBF_4$ in ACN/PC. The charge-discharge characteristics of 10th and 1,000th cycle are overlaid in the same chart. Charging time of 1,000th cycle is shorter than 10th's. Conventional three-electrodes method is adopted.

cycles with ACN/PC solution at 3 V adapting a conventional three electrode method is shown in Fig. 9. The decrease in the discharged energy observed between the 10th and 1,000th data was less than 22% and accompanied with a small amount of out-gas. There are further items to be improved on the cycle test and the working voltage.

4 Conclusion

Non-porous KOH-activated carbon samples with inter-layer distance $d_{002} = 0.36 \sim 0.38$ nm prepared from calcined cokes were successfully used for the electrodes of EDLC. The non-porous carbon was almost no surface forming double layer in the electrolyte solution at the beginning. Under the applied electric field, intercalation of

cation, $(C_2H_5)_4N^+$, and anion, BF_4^- , with the solvent of smaller molecular volume in the solution into the loosed inter-layer of the carbon, builds double layer to work as capacitor. The intercalation starting voltage is proportional to the molecular volume of the solvent and inversely proportional to the inter-layer distance. These facts provide an additional proof for the idea that the solvent co-intercalation is the principal mechanism of EDLC of the non-porous carbons.

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