CHARACTERISTICS OF ELECTRIC-DOUBLE LAYER CAPACITOR OF THE METAL-POROUS CARBON COMPOSITE FROM ION EXCHANGE RESIN

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Introduction

An electric double layer capacitor (EDLC) has been focused as a new energy storage device. For example, it is expected to be used in a hybrid car. Therefore, the development of high energy density EDLC is conducted actively. Especially, new materials, such as phenol resin[1,2]), activated meso porous carbon fiber[3]), polyvinyliden resin[4]) and so on, have been examined as electrode of EDLC.

The carbon composite material in which the nano-meter scale metallic compounds were highly dispersed could be prepared by a carbothermal reduction of metal ion-exchanged resin[5]) (MIER-CTR). We[6]) found that the nano scale Cu particle and porous carbon composite prepared from the commercial chelate resin had high capacitance (140F/g) for the electrode for an EDLC (30mass% H_2SO_4). In this study, cupper -carbon composites were prepared by the MIER-CTR method. They were characterized as the EDLC electrode. Sawdust immersed in CU^{2+} aq. solution was also examined as precursor of the EDLC electrode.

Experimental

Preparation of carbonaceous samples:
The chemical structures of the ion exchange reins used as a raw material are shon in Fig. I. C467 from Sumitomo Industries Co. Ltd. is a chelate-type-resin, which has both amino- and phosphate groups. CR11 is also a chelate resin with imino diacetate group. PK228L is a strong acid type cation-exchange resin having $-SO^{3-}$ as an ion-exchange group. PA 312 is a strong-anion exchange resin with a quaternary ammonium group. These three resins are commercially manufactured by Mitsubishi Chemicals Co. Ltd. Metal ions were adsorbed in each resin by conventional conditioning. The metal-ion-exchanged resin was carbonized at 800°C in a stream of N_2. The pore structures of the carbonized materials were analyzed by the N_2 adsorption technique with the Dollimore-Heal method[13]) and the t-plot method[14]). The crystalline compounds in the carbon matrix were identified by powder XRD spectroscopy. The metal content in the carbonaceous samples was calculated on the basis of the amount of metal ions eluted by leaching with a concentrated hydrochloric acid solution.

Electrochemical measurement:
The carbonized resin particle were crushed to less than 1.05 x 10^{-4} m diameter. 0.1g of the carbonaceous powder was mixed with 1ml of 30 mass% H_2SO_4. The slurry mixture was placed between two sheets of Pt collector (0.5 cm in diameter). A plastic mesh sheet (0.1 mm in thickness) was inserted between these Pt sheets as a separator. The effective surface area of the single collector unit was 7.07 x 10^{-2} cm^2. Electrochemical measurements were carried out at 30°C with the sandwich-type cell mentioned above. First, the capacitor was charged at 0.9 V for 0.5 h. Then, the capacitor was discharged and charged between 0 and 0.9 V repeatedly at a constant current of 7.1 $mA \cdot cm^{-2}$. The specific electric capacitance (F/g-electrode material) was calculated by the slope of the time vs. voltage curve between 0.45 and 0.55V.

Results and Discussion

The relation between the capacitance and surface area (S_{BET}) is shown in Fig.2. The capacitance of two commercial carbons powders for the EDLC electrode were also measured (X, +). Both capacitance were about 50 F/g. The capacitance and S_{BET} of the samples prepared from metal ion-exchanged resins except for C467-Cu^{2+} were lower than the commercial carbons. However, the Cu - porous carbon composites from C467-Cu^{2+} had greater capacitance than commercial carbons, even through their S_{BET} were not larger than the commercial ones. Especially, the Cu - porous carbon composites washed by conc. Hydrochloric acid showed the highest capacitance (100 F/g). This value was almost twice of the commercial carbons.

The nano - Cu particle in the carbon matrix prepared by carbonizing C467-Cu^{2+} was partially removed by treating with hot conc. hydrochloric acid. The various Cu - content samples (0.005 -0.34 [g-Cu / g-sample]) could be prepared by changing HCI treatment time. The capacitance change with cyclic number of various Cu - content samples are shown in Fig. 3 The capacitance of each sample were almost constant after 2Oth cycle. The capacitance was depended on the Cu - content. When the Cu - content was 0.005 and 0.008, the capacitances were almost the same as the commercial carbons (that is 50 F/g). When the Cu - content was 0.09, the capacitance showed the highest value (140F/g). When the

Cu - content were greater than 0.09, the capacitance became lower. The same tendency was observed when sawdust impregnated Cu^{2+} aq. solution was used as the precursor (below)[7].

The Cu - porous carbon composites were prepared from the sawdust in which $Cu(NO_3)_2$ aqueous solution (0.05-0.40 [mol/L]) was applied[8]. The characterization of the carbonized materials of them is shown in Table I. Here, C1 is the commercial carbon and 81 is not impregnated in $Cu(NO_3)_2$ aq. solution. When concentration of $Cu(NO_3)_2$ solution was higher, the Cu - content also became larger. The capacitance changes with cycle number are shown in Fig.4. The capacitance of the other samples, (S2 - S6), increased. Especially, the capacitance of S4 increased with cycle number over the commercial carbon (C1). These results suggest that the Cu - content is important factor for higher capacitance. The details of the EDLC electrode from sawdust - Cu will be reported at the annual meeting of the electrochemical society (2001) [9].

Conclusion

Various metal-exchanged resins were examined as precursors of carbonaceous material for the EDLC electrode. The Cu - porous carbon composite prepared from C467-Cu^{2+} showed very much higher capacitance. It is suggested the Cu - content is important factor for high capacitance. The sawdust impregnated CU^{2+} aq. solution was found to be the EDLC electrode with high capacitance.

References

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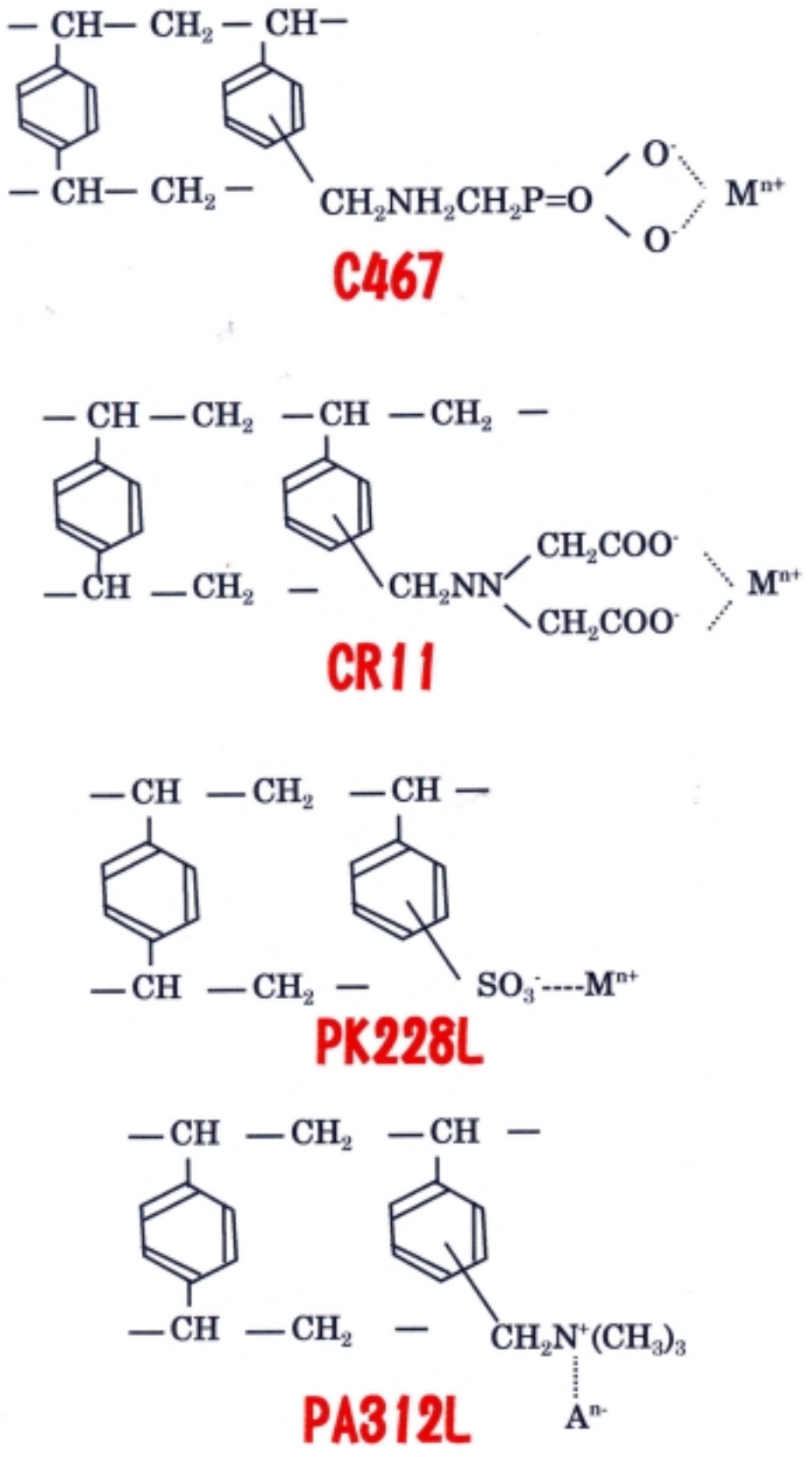

Fig. 1 The chemical structure of the ion exchange resins.

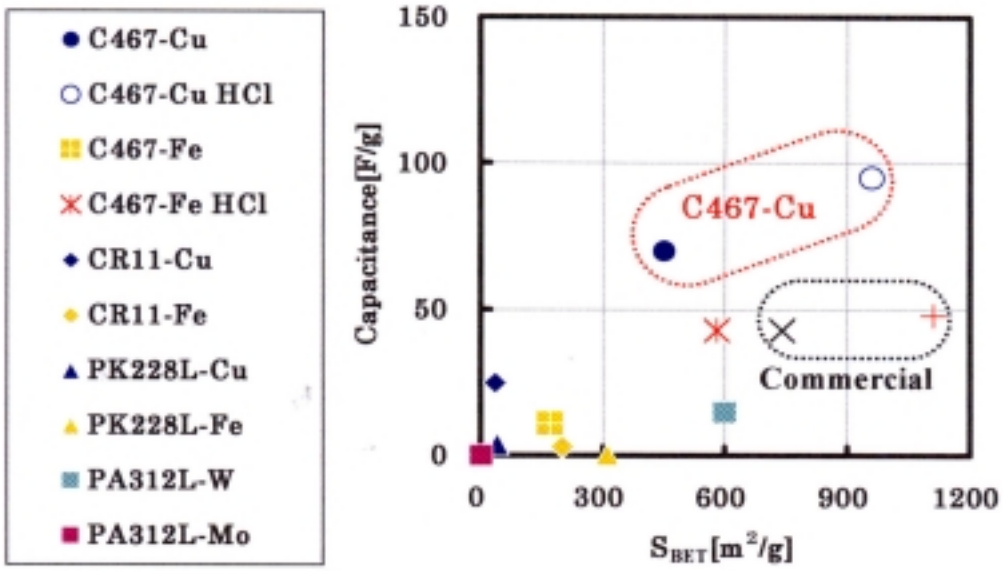

Fig. 2 The relation of the capacitance of EDLC and S_{BET}.

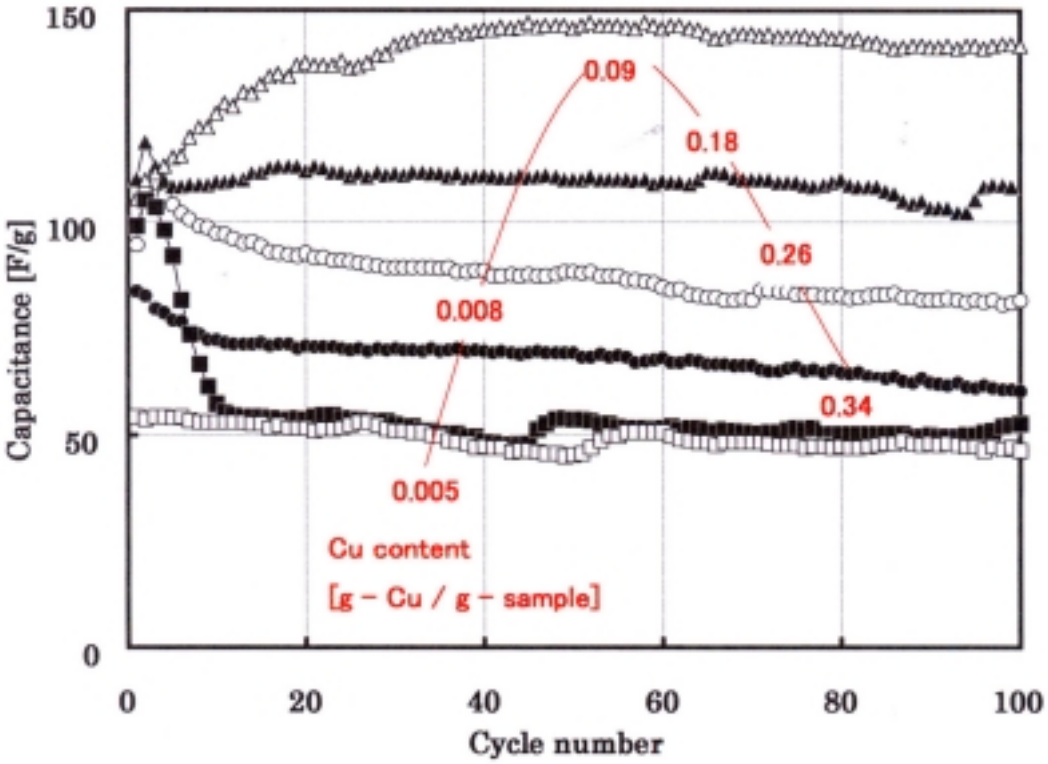

Fig. 3 The capacitance change with cyclic number of various Cu - content carbon electrode prepared by C467-Cu^{2+}.

Table 1 Charactarization of carbonized materials and preparation conditions.

No.	$Cu(NO_3)_2$ [mol/L]	Carbonization temp. [℃]	Cu content [Cu-g/g]	XRD diameter[1](nm)	S_{BET}[2] (m^2/g)	V_P (ml/g) V_{total}[3]	Capacitance4) (F/g)	(F/cm^3)
C1	-	-	0	no peak	1100	0.46	48	29
S1	-	800	0	no peak	170	0.13	5	3
S2	0.05	800	0.041	35 (Cu)	320	0.21	6	3
S3	0.10	800	0.057	21 (Cu)	490	0.25	38	25
S4	0.25	800	0.086	20 (Cu)	550	0.36	71	44
S5	0.30	800	0.094	21 (Cu)	410	0.23	47	34
S6	0.40	800	0.123	21 (Cu)	460	0.25	41	19

I) Calculated by the Sherrer's equation.
2) Calculated by BET method
3) Vtotal = Vmicro + Vmeso, micro pore rp<1 nm, meso pore I <rp<20nm
4) The capacitance of the 1OOth cycle.

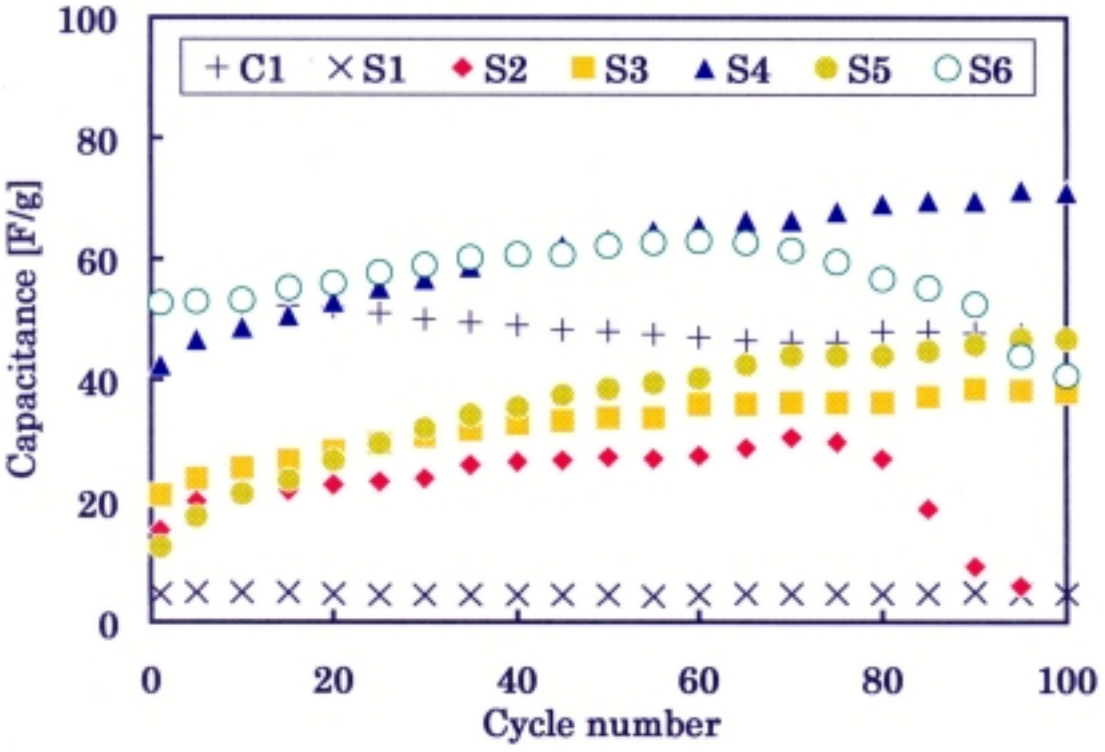

Fig.4 Capacitance of the sawdust - Cu.