Spatio-temporal Charge Distribution in Electric Double Layer Capacitors observed by pulsed Electro Acoustic Method

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The use of the pulsed electro acoustic (PEA) method allowed us to perform the direct observations of spatio-temporal charge distributions in Electric double layer capacitors (EDLCs) based on polarizable nanoporous carbonaceous electrode. The negative charge density became the maximum, about 205 C/m^3 at the region where was near to collector layer in EDLCs for case V_{DC} = 2.5 V, while the positively charged density became the maximum, about 61.1 C/m^3 at the region where it was located around the cathode layer. The performance of the best sample was found to be better in terms of the charge density (C*s*) and specific energy (E_s) with a maximum value of ~8.4 F/g and 26 Wh/kg. The C_s obtained from the PEA method agreed well with that from the energy conversion method. The PEA measurement used here is a very useful method to quantitively investigates the spatio-temporal charge distribution in EDLCs.

Keywords : Pulsed electro acoustic method, Electric double layer capacitors, Nanoporous carbon, Charge behavior

1. INTRODUCTION

Electric double layer capacitors (EDLCs)[1], a type of physical battery, have attracted much attention from the viewpoint of preventing global warming and energy problems. High power density and very good cyclability make EDLCs useful in power electronic systems and have very promising applications in many other fields of technology[2-5]. EDLCs utilize the double-layer formed at the interface between nanoporous carbonaceous electrode and nonaqueous electrolyte solution. The porous carbons have been used as the material of EDLCs because of their relatively low cost and very high specific area; however, C_s of EDLCs based on carbon materials were lower than anticipated. The lower capacitance is partially attributed to poor wettability of electrode material, which leads to a lower useable specific area for charge storage. The charge storage process in EDLCs, which is not dominated by chemical reactions, is closely related to the charge behavior. Therefore, information on charge behavior during charge and discharge is prerequisite for any rational approach to the understanding of the charge storage process in EDLCs. Until now, measurements of the electrostatic capacity of EDLCs have been chiefly performed using several electrochemical methods[6-9], and no research on direct measurements of the charge distributions in EDLCs was reported. The pulsed electro acoustic (PEA) method[10-14] have been applied for the observation of the charge distributions in EDLCs. The PEA method is an established technique used for measuring directly to determine the charge distributions in solid dielectrics. The measured data are useful for quantitative analyses of the charge accumulation and the charge transport. In this work, we measured the spatio-temporal behavior of positive and negative charges in EDLCs using the PEA method. At the same time, we compared the electrostatic capacity obtained by the PEA method with those obtained by the energy conversion method. Based on the measured electrochemical properties, the relationships between the charge behavior and the performance of EDLCs were discussed.

2. EXPERIMENTAL

The EDLCs sample and experimental arrangement for measurement of the charge distribution using a PEA system are shown in Fig. 1. EDLCs sample was built by assembling two 400-μm thick nanoporous carbonaceous

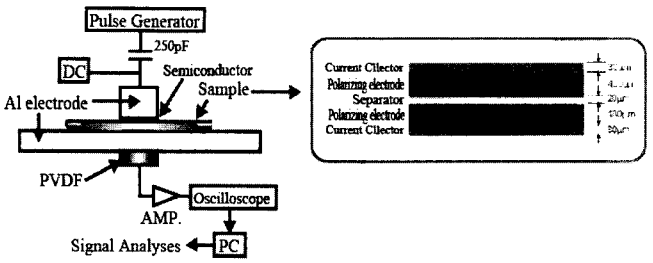

Fig. 1. EDLCs sample and experimental arrangement for measurement of the charge distribution using the PEA system.

electrodes mixed dielectric (polytetrafluoroethene, PTFE) and carbon black (Stream Chemicals Co.). A 20-μm thick cellulose separator was used between the two carbonaceous electrodes, which were set in a hermetic Al container (30-μm thick). The total thickness of EDLCs samples, which were composed of 5-layers, was 880 μm. Each component had a sectional area of 314 mm^2. The active material consisted of nanoporous carbon, the mixture of the PTFE binder (Aldrich, 60 wt% dispersion in H_2O) and carbon black. The carbon black was added to decrease the ohmic resistance of the electroactive material. The preparation of the carbonaceous EDLCs electrodes was as follows: carbon, carbon black and PTFE were mixed in a mass ration of 8.5:0.5:1 and dispersed in deionised water. The slurry was cast onto an Al foil (314 mm^2) with an applicator. The Al-covered carbon layer was then dried under vacuum of 0.1 Torr at 150 °C for 2 h, and was spot-welded in the required size (15 mm in diameter) as electrodes under Ar atmosphere. The nonaqueous electrolyte was a mixed solution of propylene carbonate (PC) and tetraethylammonium tetrafluoroborate ($(C_2H_5)_4NBF_4$) in a mol ratio of 1:4. Table 1 indicates the properties of the carbonaceous electrode materials prepared under various conditions. The specific area and pore-size distribution of these carbonaceous materials were calculated from nitrogen adsorption isotherms at 77 K (Tristar 3000) using the Brunauer, Emmett and Teller (BET) method and Barrett, Joyner and Halenda (BJH) method.

The principle of the PEA method is briefly outlined as follows: an electric pulse voltage together with a high DC voltage is applied to a sample sandwiched between an upper electrode and a lower electrode. Hence, acoustic waves are generated by the charges on the electrode and in the sample. The acoustic waves propagate in both upper and lower directions and are converted into electric signals by a piezoelectric transducer located at the back of the lower electrode. The position of the charge can be determined by the response time of the signal while the amount of charge is obtained from the magnitude of the signal. Therefore, the measurement results using the PEA method allowed us to appreciate quantitatively the charge behavior in EDLCs. In this work, the dc voltage of 0~2.5 V was applied to the EDLCs sample through an upper Al electrode of 8 mm in diameter. The pulse had a maximum value of 600 V and a pulse width of 2.5 ms at 400 Hz of frequency. Here, it is noted that a semiconductor layer was formed between the upper Al electrode and the EDLCs sample. The semiconductor layer adjusted the acoustic impedance on the interface between the EDLCs sample and the upper Al electrode. A 10 μm-thick Lithium Niobate (LiNbO) was used as the piezoelectric transducer. The transformed voltage signal was amplified 45 dB, and sent to a digital oscilloscope and a personal computer. It should be noted that the reflection of elastic waves on interfaces influences the interpretation of results in the case where PEA measurement is carried out on a sample constructed from some kinds of layers differing in acoustic characteristics, which is described in Sec. 3. In this work, we measured the charge distributions in EDLCs under various conditions of the charging/discharging time (t_c/t_d) of 0~20 sec and the applied DC voltage (V_{DC}) of 0.5~2.5 V. Three kinds of ELDCs samples, which have the electrolyte - immersed carbonaceous electrodes with different drying treatments, were prepared for the PEA measurement. The first one was dried under vacuum of 0.1 Torr at 150 °C for 2 hr as the above-mentioned, and the EDLCs sample prepared with this drying treatment was denoted as A. The second one was obtained by carrying out only the vacuum drying treatment without heating it. The resulting sample was denoted as B. The third one, which was non-dried, was denoted as C.

3. RESULTS AND DISCUSSION

The charge distributions in EDLCs (sample A) with the applied dc voltage (V_{DC}) obtained from the PEA measurement are shown in Fig. 2. Each profile represents the spatial charge distribution in EDLCs for each charging/discharging time (t_c/t_d) under the given V_{DC}. The values of V_{DC} in Figs. 2(a), 2(b), 2(c) and 2(d) were 1, 1.5, 2 and 2.5 V, respectively. The measured profiles of spatial charge distribution for each t_d shown in Fig. 2 present the remaining charge behavior after short circuit discharging for 5, 10 and 20 sec. The PEA measurement gives a curve of the charge density versus the vertical distance (depth) from the electrode. The position (L), which is the distance between the two vertical dotted lines, is the depth of samples equal to the distance from anode to cathode. When V_{DC} was set at 1 V, the negative accumulated charge densities in EDLCs at each charging time, t_c=5, 10 and 20 sec, were about -192, -217, and -223 C/m^3, respectively, while positive values were about 63.9, 74.8 and 79.9 C/m^3, respectively (see Fig. 2(a)). When V_{DC} was set at 2.5 V, the negative accumulated charge densities at each charging time, t_c=5, 10 and 20 sec, were

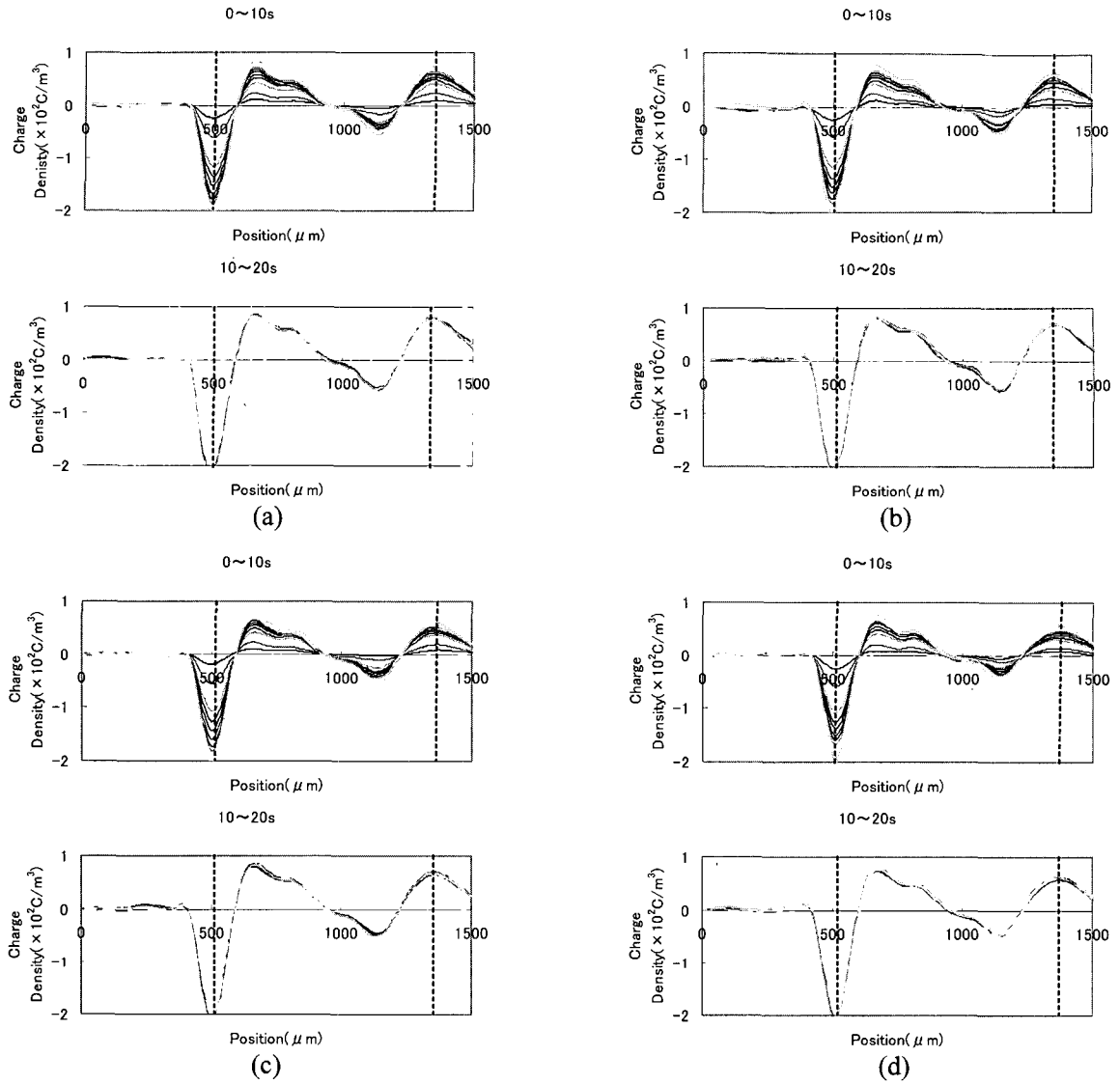

Fig. 2. Charge distributions in EDLCs (sample A) with the applied dc voltage (V_{DC}) obtained from the PEA measurement. Each profile represents the spatial charge distribution in EDLCs for each charging/discharging time (t_c/t_d) under the given V_{DC}.
(a) V_{DC}=1.0 V (b) V_{DC}=1.5 V (c) V_{DC}=2.0 V (d) V_{DC}=2.5 V

about 167, 200 and 205 C/m^3 respectively, while positive values were about 46.2, 57.9 and 61.1 C/m^3, respectively (see Fig. 2(d)). The profiles of accumulated charge density increased with increasing the t_c in the first 20 sec after applying V_{DC}, and showed a tendency to be saturated at $t_c \geq 20$ sec. The amount of negative charge was larger than that of the positive one. The negatively charged density became the maximum, about 205 C/m^3 at the region where it was near the collector layer (L=520 μm) in EDLCs for case V_{DC} = 2.5 V, while the positively charged density became the maximum, about 61.1 C/m^3 at the region where it was located around the cathode layer (L=1400 μm) in EDLCs. Thus, it is understood that the polarized charge accumulation occurs intensively in the narrow region around porous carbon layer (L=520~1400 μm) in EDLCs, and increased remarkably with increasing the V_{DC}. On the other hand, upon removing V_{DC}, the remaining charge density gradually decayed with increasing the t_d after short circuit discharging. When V_{DC} was set at 1.5 V, the charge densities remained in EDLCs after short circuit discharging at each discharge time, t_c=5, 10 and 20 sec, and were about -117, -30.9 and -0.55 C/m^3, respectively. When V_{DC} was set at 2.5 V, the remaining charge densities at each discharging time, t_c=5, 10 and 20 sec, were about -130, -36.0 and -0.025 C/m^3, respectively. For case $t_d \geq 20$ sec, there were few charges still left in EDLCs. The remaining negative charges near the cathode

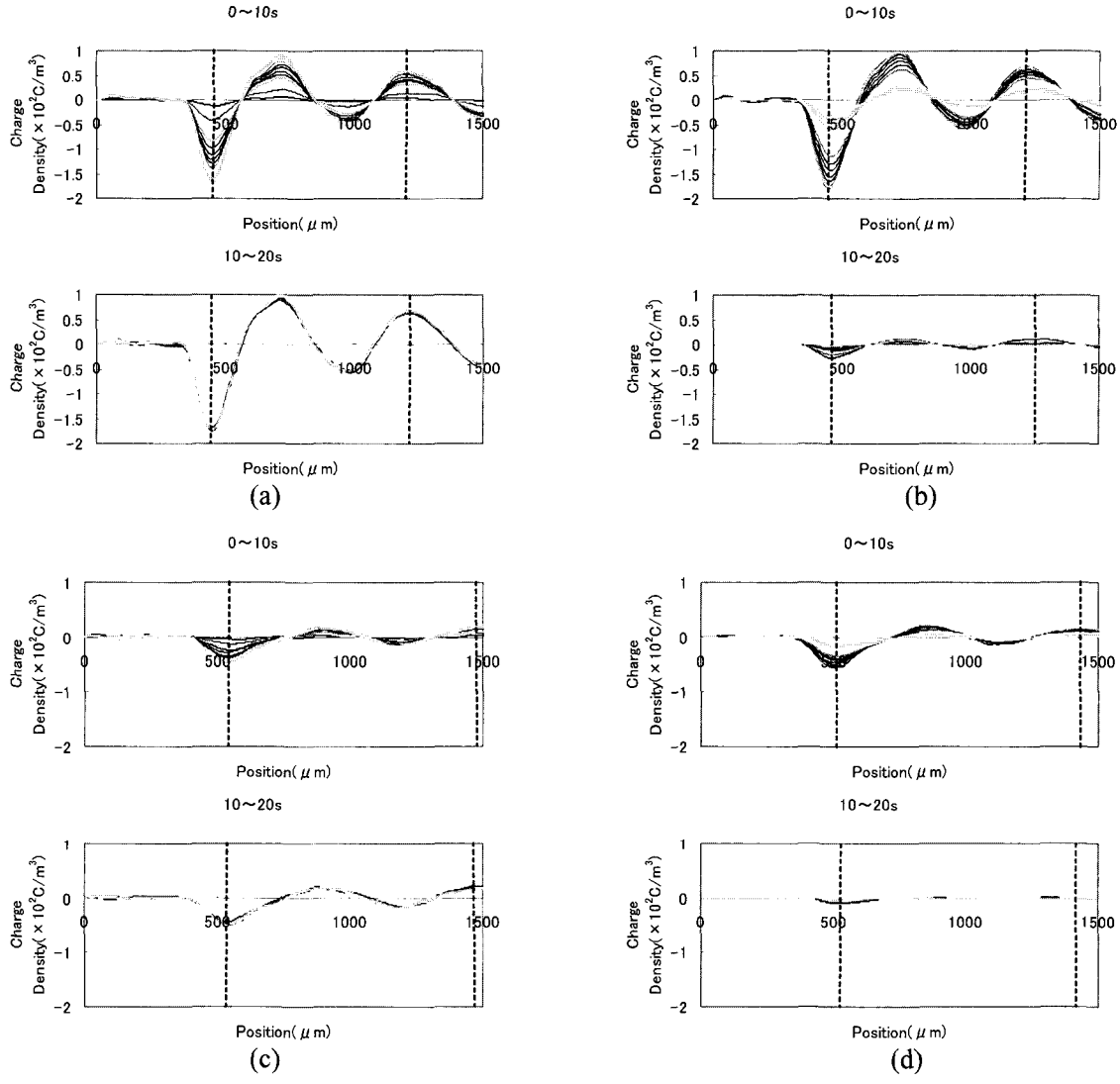

Fig. 3. Charge behaviors in EDLCs under charging/discharging conditions of V_{DC} = 2.5 V for cases of two kinds of sample (B and C) with different drying treatments. The sample B was the only one dried under vacuum of 0.1 Torr for 2 hr. without heating, while the sample C was the non-dried one. (a) Charge of sample B, (b) Discharge of sample B, (c) Charge of sample C, (d) Discharge of sample C.

after discharge is normally considered to be the result of the electrons injected from the cathode and subsequently trapped in the samples under the applied V_{DC}. Upon removing the voltage, the charges will dissipate and return to the electrodes from where they come if there are hopping sites through which charges can migrate. This measure results suggest that the charge distribution in EDLCs under the V_{DC} is spatially uneven, i.e., hetero-charges distribution, which is presumed to be caused by the mobility of the positive and negative charges in the carbonaceous electrode surface of EDLCs during charge and discharge[5,10,12].

The charge behaviors in EDLCs under charging/ discharging conditions of V_{DC} = 2.5 V for cases of two kinds of sample (B and C) with different drying treatments are shown in Fig. 3. The sample B of Figs. 3(a) and 3(b) was the only one dried under vacuum of 0.1 Torr for 2 hr. without heating, while the sample C of Figs. 3(c) and 3(d) was the non-dried one. As shown in Fig. 3(a), the negative accumulated charge densities at each charging time, t_c=5, 10 and 20 sec, were about -137, -167 and -173 C/m^3, respectively, while positive values were about 56.3, 62.8 and 70.7 C/m^3, respectively. For case Fig. 3(b), the negative values of remaining charge density at each t_d were about -114, -31.6 and 0 C/m^3, respectively, while positive values were about 44.3, 12.1 and 0 C/m^3, respectively. For case Fig. 3(c), the negative accumulated charge densities at each t_c were about 36.9, 46.6 and 46.4 C/m^3, respectively, while positive values were about 18.4, 21.4 and 22.0 C/m^3, respectively. For case Fig. 3(d), the negative remaining charge densities at each t_d were about 34.5, 10.3 and 0 C/m^3, respectively,

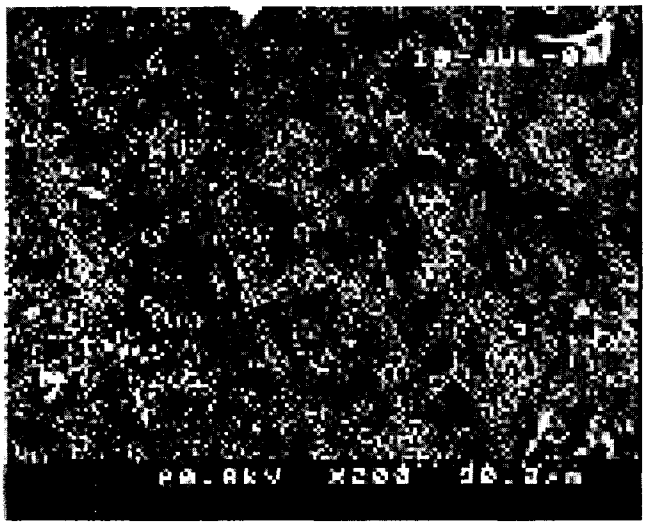

Fig. 4. SEM photograph of the carbonaceous electrode surface of EDLCs (sample A).

while positive values were about 11.5, 1.84 and 0 C/m^3, respectively. It can be seen from the result of Figs. 3(a)~3(d) that the most dominant feature of charge behavior is consistent with Figs. 2(c) and 2(d) under the same V_{DC}, although the amount of charge density is comparatively small. For case B (Figs. 3(a)-3(b)), the charge density was about 3.7 times larger than that of C (Figs. 3(c)-3(d)), while it was less than half that of A (Figs. 2(c)-2(d)). From Fig. 3(d), it is also interesting to note that the decay rate of remaining charge in C was much faster than those of A and B. Within as short as 10 sec., almost no charge remained in C (Fig. 3(d)), while a few positive charges remained in A (Fig. 2(d)). This indicates, we believe, that considerable hopping sites and shallow traps perform on the carbonaceous electrodes of B and C; hence, the charges accumulated under the V_{DC} disappear easily to the collectors during the discharging step. For case A, the charges formed during the charging step may not disappear easily after discharging because of its clear porous structure with many deep traps. It can be also found that the dry treatment plays an essential role in the improvement of the charge density in EDLCs, and it contributes to the rejection of water molecules and impurities existing in the carbonaceous electrodes and can promote effectively the wettability of the electrodes material, which leads to higher useable specific area for the charge storage.

A SEM photograph of the carbonaceous electrode surface of EDLCs (sample A) is shown in Fig. 4. The nano spheres, distributing from 10 to 20 nm in diameter, were interlinked together to form a three-dimensional network in a particle. There were a number of mesopores between the nano carbon spheres. The inter-linked nano units looked like the elements of the puzzle-ball with a smooth surface and no sharp edge. It can be seen that the small mesopores and high BET surface area from A derive

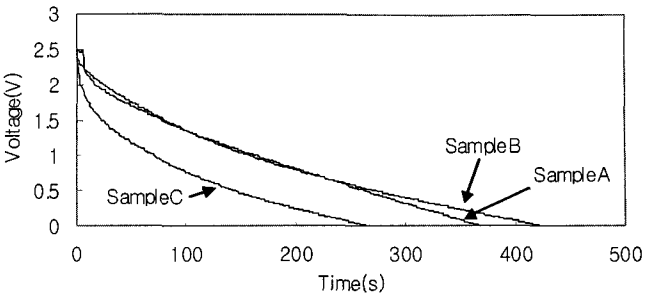

Fig. 5. Example of oscilloscope trace of a discharge voltage of EDLCs. The applied voltage and current density were 2.5 V and 5 mA/cm^2.

from the removal of water molecules and impurities existing in EDLCs by a well-treated drying process, and these factors reflect the charge behavior during charge and discharge.

The electrostatic capacity of EDLCs can be obtained by the energy conversion method. An example of oscilloscope trace of a discharge voltage of EDLCs is shown in Fig. 5. The applied voltage and current density were 2.5 V and 5 mA/cm^2, respectively. As shown in Fig. 5, the discharge voltage curve of EDLCs contains the voltage decrease of two parts. A suddern voltage drop (ΔV_R), which is associated with the internal resistive component, is seen at the beginning of discharge (t_d ~ 400 sec). In this case, the ΔV_R was 0.3 V, corresponding to a current density of 5 mA/cm^2. The capacitive component (ΔV_{cap}) is related to the voltage variation due to change in energy within the EDLCs. From the ΔV_{cap} in the discharge the specific capacitance (C_s) of one sheet carbonaceous electrode was calculated according to the following formula:

$$C_1(F/g) = 2 \cdot \frac{i_d(A) \times \Delta t_d(s)}{m(g) \times \Delta V_{cap}(V)} \quad (1)$$

where i_d is the discharge current, which is chosen as a constant for all the EDLCs samples as t_d is the discharging time, m, the mass of the active carbon material of the electrode, and ΔV_{cap} is the voltage drop during discharge. Therefore, C_s of the EDLCs can be calculated as $C_s = 2 \times C_1$ because both carbonaceous electrodes are in series arrangement within the EDLCs. In the case of Fig. 5, the resulting C_s of EDLCs (corresponding to the A sample) was about 8.0 F/g. Also, C_s can be estimated by the results of PEA measurements. The calculation process in this work is summarized as follows: as shown in Table 1, the whole weight of two sheets of the carbonaceous electrodes was 140 mg. The specific area of the used activated carbon was about 2000 m^2/g; thus, the specific area of the electrodes was estimated

Table 1. Properties of the carbonaceous electrode materials.

Materials	BET surface area(m^2/g)	Total pore volume(m^3/g)	Average pore diameter(nm)
Activated carbon	2004	1.24	2.72
Acetylene black	66	0.14	7.13

as 1625 m^2/g. Adding up the charge density measured by the PEA method under the L = 520~1400 μm, the area charge density could be obtained. In the case of Fig. 2(d) (sample A), the whole area charge density was calculated as 8.92×10^3 C/m^3. The whole amount of electrical charges could be obtained by multiplying the area charge density by the whole surface area of the carbonaceous electrodes of EDLCs. The C_s could be estimated by dividing the V_{DC} of 2.5 V into the whole amount of electrical charges, and its value was calculated as C_s = 7.47 F/g. The values of C_s obtained by two different methods almost agreed within around 7 %. For other EDLC samples (B and C), the values by both methods agreed well within 8 %. The C_s obtained from the PEA method agreed well with that from the energy conversion method, although the resulting C_s in the PEA method was estimated through an integration process of each charge distribution.

4. CONCLUSION

The result showed that the distributions of positive/negative charges were spatially uneven and the charge accumulation region concentrated on central part of the carbonaceous electrode of EDLCs. The negative charge density became the maximum, about 205 C/m^3 at the region where was near to collector layer in EDLCs for case V_{DC} = 2.5 V, while the positively charged density became the maximum, about 61.1 C/m^3 at the region where it was located around the cathode layer. The performance of the best sample was found to be better in terms of the charge density (C*s*) and specific energy (E_s) with a maximum value of ~8.4 F/g and 26 Wh/kg. In addition, it can be found that the dry treatment plays an essential role in the improvement of the charge density in EDLCs, and it effectively promotes the wettability of the electrode material, which leads to a higher useable specific area for the charge storage. Finally, we believe that the PEA measurement used here is a very useful method to quantitively investigates the spatio-temporal charge distribution in EDLCs. Further research for fuel cell application using the EDLSc is in progress.

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