

PEA법에 의한 캐패시터내 전하분포 측정

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Charge Distribution in a capacitor observed by PEA Method

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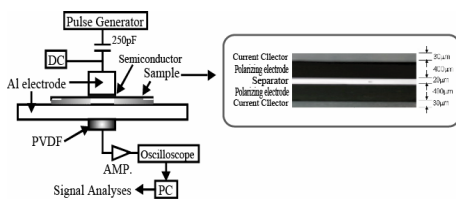
Abstract - The use of the pulsed electro acoustic (PEA) method allowed us to perform the direct observations of spatio-temporal charge distributions in Electric double layer capacitors (EDLCs) based on polarizable nanoporous carbonaceous electrode. The negative charge density became the maximum, about 205 C/m³ 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/m³ at the region where it was located around the cathode layer. The PEA measurement used here is a very useful method to quantitatively investigates the spatio-temporal charge distribution in EDLCs.

1. INTRODUCTION

Electric double layer capacitors (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. The pulsed electro acoustic (PEA) method[2-6] 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

2.1 Preparation of EDLCs



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

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 μ m thick nanoporous

carbonaceous electrodes mixed dielectric (polytetrafluoroethene, PTFE) and carbon black (Stream Chemicals Co.). A 20 μ m thick cellulose separator was used between the two carbonaceous electrodes, which were set in a hermetic Al container (30 μ m thick). The total thickness of EDLCs samples, which were composed of 5-layers, was 880 μ m.

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.

<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

2.2 Measured by Pulsed Electro Acoustic 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. 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 0~2.5V 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 400Hz 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 μ m-thick Lithium Niobate (LiNbO) was used as the piezoelectric transducer. In this work, we measured the charge distributions in EDLCs under various conditions of the charging/discharging time (t_c/t_d) of 020 sec and the applied DC voltage (V_{DC}) of 0.5~2.5 V. The sample 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.

3. RESULT AND DISCUSSION

The charge distributions in EDLCs (sample) 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 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 $t_c = 20$ 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 ($L=520\mu m$) 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 ($L=1400\mu m$) in EDLCs. Thus, it is understood that the polarized charge accumulation occurs intensively in the narrow region around porous carbon layer ($L=520\sim 1400\mu m$) 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, $t_d = 5, 10$ 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, $t_d = 5, 10$ and 20 sec, were about $-130, -36.0$ and -0.025 C/m^3 , respectively. For case $t_d = 20$ sec, there were few charges still left in EDLCs. The remaining negative charges near the cathode 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} s 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[1,2,4].

For case sample, 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

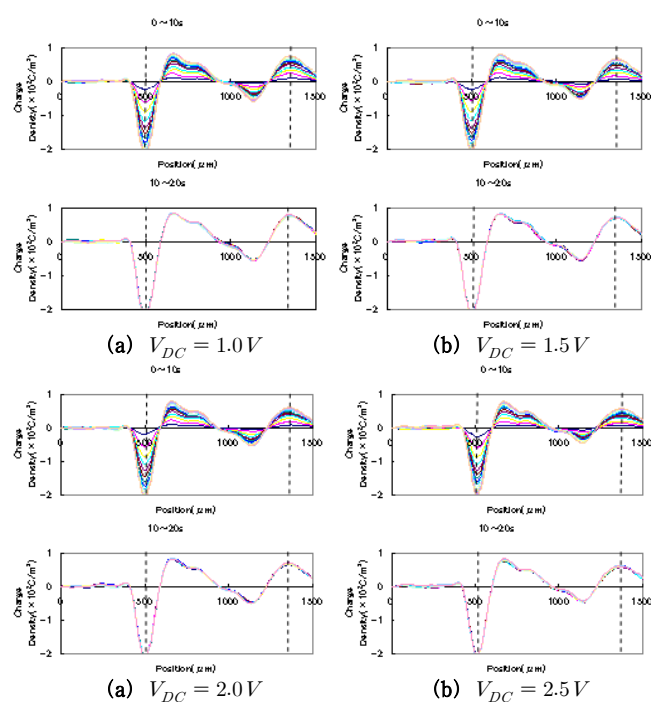


Fig. 2 Charge distributions in EDLCs (sample A) with the applied dc voltage (V_{DC}) obtained from the PEA measurement. Each profile represents the spatial charge distribution in EDLCs for each charging/discharging time (t_d/t_c) under the given V_{DC} .

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 is shown in Fig. 3. 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 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.

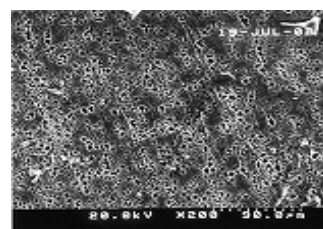


Fig. 3 SEM photograph of the carbonaceous electrode surface of EDLCs

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. an essential role in the improvement of the charge density in EDLCs, and it effectively promotes the wettability of the electrodematerial, 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 quantitatively investigates the spatio-temporal charge distribution in EDLCs. Further research for cell application using the EDLCs is in progress.

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