Charging and Discharging Characteristics of Electric Double Layer Capacitors used for a Storage Battery of Solar Energy

Youl-Moon Sung[a]
Department of Electrical and Electronic Engineering, Kyungsung University, Daeyeon 3-dong, Nam-gu, Busan 608-736, Korea

[a]E-mail : ymsung@ks.ac.kr

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The charging/discharging characteristics of electric double layer capacitors (EDLCs) for an electric power storage device application were investigated. The specific area of the carbonaceous electrode surface by the BET method was in the range of 1800~2000 m^2/g. The charge distributions during charging and discharging were measured by means of a pulsed-electro-acoustic (PEA) method, and the voltage characteristics of EDLCs connected to solar cells were evaluated. The results showed that the distributions of positive and negative charges were spatially uneven, which was due to the mobility of the positive and negative charges in the carbonaceous electrode surface of the EDLCs. The charge accumulation region concentrated on central part of the carbonaceous electrode and the required times for charging and discharging were almost same.

Keywords : Electric double layer capacitors, Pulsed electro acoustic method, Storage battery, Carbonaceous electrode

1. INTRODUCTION

Photovoltaic power generation[1] is a useful technique for the prevention of global warning and energy problems. However, the generation power is strongly influenced by the weather, and therefore the stable supply of the electric power is difficult. To use solar energy efficiently, a storage battery that can deliver the stable electric power to the load is required. One of the widely accepted storage battery is the sealed lead-acid cell which has some superior properties such as a long life cycle and superiority in good power characteristic to size ratio. However, when the cell is under a remarkably cool condition, the electromotive force rapidly drops and then a higher replenishing voltage is required. In a warmer condition, the risk of overcharge becomes greater. In recent years, the fuel cells[2,3] have attracted much attention and demonstrated a good power capability; nevertheless the response to the instantaneous power is relatively poor. Therefore, we examined to use an electric double layer capacitors (EDLCs)[4-7] operating as a power storage device. EDLCs, in which the double layer is formed at the interface between nanoporous carbonaceous electrode and non-aqueous electrolyte solution, have attracted special interest recently because of their superior properties such as the high power density, the good cycle-ability and the speedy response for load fluctuations. The charge storage process due to the charge behavior influences such properties, i.e., the performance is not dominated by chemical reactions. Therefore, to optimize the EDLCs connected to solar cells, it is necessary to investigate the accumulation state of electrical charges and the charge behavior in the EDLCs. In this article, we first focused on the investigation of the charge distribution in EDLCs to understand the charging and the discharging process. The charge distribution was measured by means of a pulsed-electro-acoustic (PEA) method[8-10]. In this method, a pulsed electric field first applies to a sample, and then the produced elastic waves in proportion to the space charges are detected using a piezoelectric sensor. In early stage, the PEA measurement was performed only in 1-layer dielectric. However, recently, the experimental applications for some layers and their theoretical analyses are expanding rapidly[11]. In this study, measurements of the charge distributions in EDLCs were carried out during charging and discharging. Finally, the voltage characteristics of EDLCs connected to solar cells were examined.

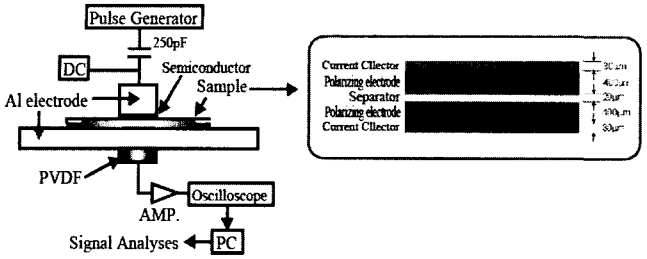

Fig. 1. Experimental arrangement for measurements of charge distributions using the PEA system. EDLC sample which comprises two 400 μm thick nanoporous carbonaceous electrodes mixed dielectric PTFE and carbon black.

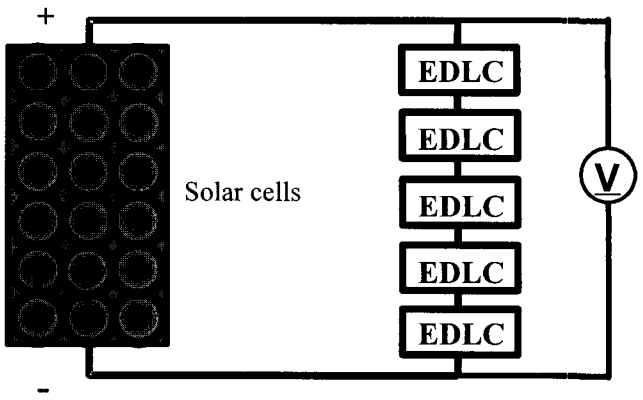

Fig. 2. Charging circuit of EDLC connected to the solar cells.

2. EXPERIMENTS AND METHODS

Figure 1 shows the experimental arrangement for measurements of the charge distributions using a PEA system. The EDLCs sample comprises two 400-μm-thick nanoporous carbonaceous electrodes mixed dielectric (polytetrafluoroethene; PTFE) and carbon black. Carbon, carbon black and PTFE were mixed in a mass ratio of 8.5:0.5:1. The non-aqueous electrolyte was a mixed solution of propylene carbonate (PC) and tetraethylammonium tetrafluoroborate ($(C_2H_5)_4NBF_4$) in a mol ratio of 1:4. A 20-μm-thick cellulose separator was used between the two carbonaceous electrodes. The carbonaceous electrodes operating as the polarized electrodes and the separator were arranged in a hermetic Al container (30 μm in thickness) operating as a current collector. Then, the total thickness of the EDLCs sample, which was composed of 5-layers, was 880 μm. Each component had a sectional area of 314 mm^2. The Al-covered carbon layer was dried at 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 atmospheric pressure. Carbonaceous materials were characterized by applying the method of nitrogen adsorption. The BET (Brunauer, Emmett and Teller) total surface area, the total pore volume and the average pore diameter of the activated carbon were 2004 m^2/g, 1.24 m^3/g and 2.72 nm, respectively. The principle of the PEA method is briefly outlined as follows: an electric pulse voltage together with a high DC voltage is added to EDLCs sample sandwiched between an upper and a lower electrode. Hence, acoustic waves are generated by the charges on the electrode and in the EDLCs sample. The acoustic waves propagate in both upper and lower directions, and they are converted into electric signals by a piezoelectric transducer arranged at the back of the lower electrode. The charge location can be determined by the response time of the electric signal, while the amount of charge is obtained from the magnitude of the signal. The dc voltage (V_{DC}) of 2.5 V, from a DC power supply, was added to EDLCs sample through an upper Al electrode 8 mm in diameter. The pulse voltage from a pulse generator had a maximum value of 600 V and a pulse width of 2.5 ms at frequency of 400 Hz. 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 a piezoelectric transducer. The transformed voltage signal was amplified 45 dB, and sent to a digital oscilloscope connected to a personal computer. 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. We measured the charge distributions in EDLCs under various charging time (t_c) of 0 - 20 s and discharging time (t_d) of 0 - 20 s.

Figure 2 shows the charging circuit of EDLCs connected to the solar cells (GT-133, Sharp Co.). The number of EDLCs connected in series was 5, and their total capacitance was 500 F. They were connected to solar cells with the output voltage of 12.5 V and the output power of 50 W. Just after the electrification, the discharge characteristic of the EDLCs was examined by connecting a 50 W lump to the EDLCs.

3. RESULTS AND DISCUSSION

In order to analyze the specific area and pore size distribution in EDLCs, nitrogen adsorption isotherms were performed at 77 K (Tristar 3000) using the BET method. Also, SEM observation on the carbonaceous electrode surface of EDLCs was performed. Figure 3

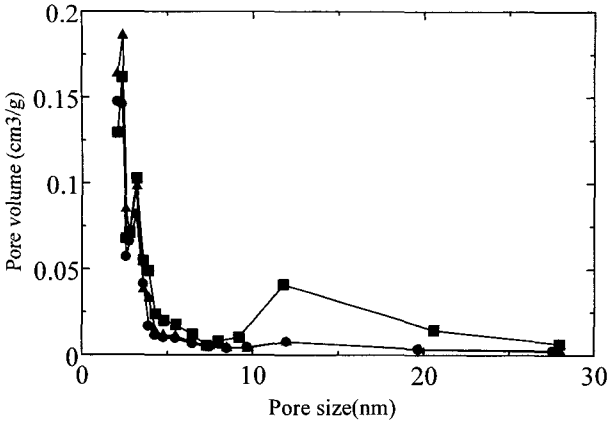

Fig. 3. Pore size distributions for the carbonaceous electrode surface of EDLCs samples obtained by BET method.

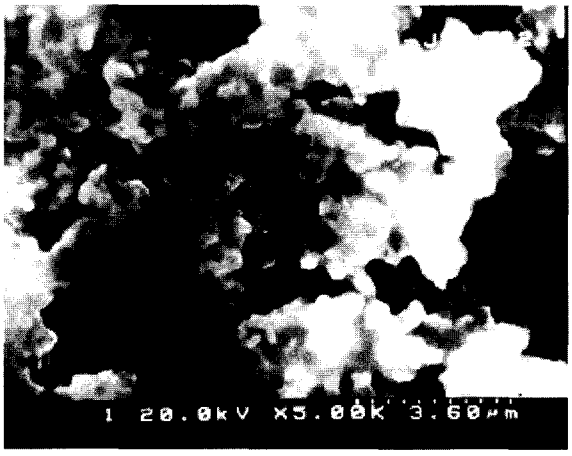

Fig. 4. SEM photograph of the carbonaceous electrode surface of EDLCs.

shows the pore size distributions of the carbonaceous electrode surface of EDLCs samples. The profiles have peaks with diameters in the mesopore range centered at 3 and 12 nm. On the other hand, the other profile was artificially flattened with diameters in the mesopore range centered at ~30 nm. In general, the specific areas of samples obtained by the BET method were in the range of 1800~2000 m^2/g.

Figure 4 shows a SEM photograph of the carbonaceous electrode surface of EDLCs. 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.

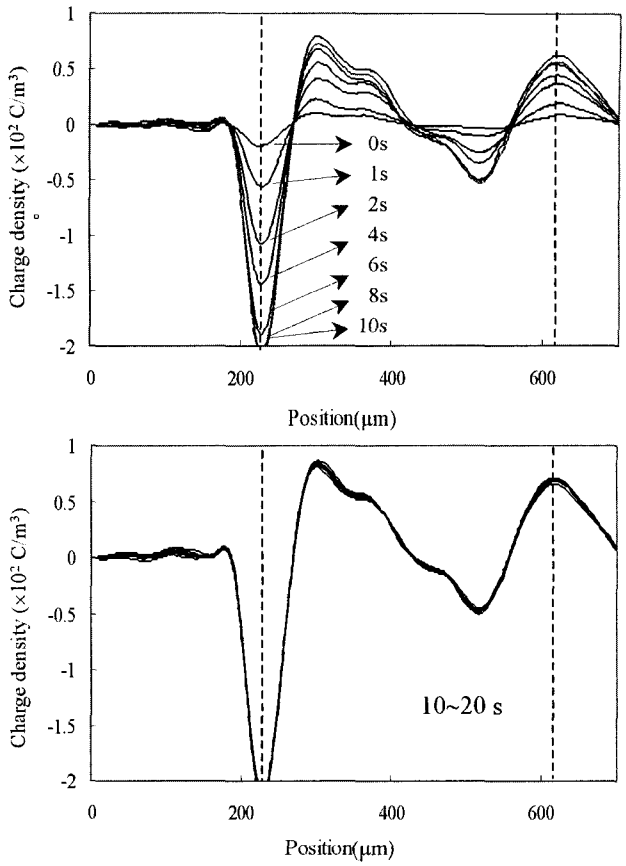

Fig. 5. Charge distributions obtained during charging.

The charge distributions in EDLCs, obtained during charging, are shown in Fig. 5. The transverse axis denotes the vertical distance (L) from the upper Al electrode, i.e., the in-depth variation. The length, which is the distance between two vertical dotted lines, is equivalent to the thickness of EDLCs sample. It can be seen that the negative charge density was larger than the positive density. For example, the negative charge density obtained during charging had a maximum value of about 205 C/m^3 near the collector layer (at L = 520 μm) while the positive charge density had a maximum value of about 61.1 C/m^3 around the cathode layer (at L = 1400 μm). It is also noted that the polarized charge accumulation intensively occurred in the narrow region around porous carbon layer(at L = 520~1400 μm).

The charge distributions in EDLCs, obtained during discharging, are shown in Fig. 6. The remaining charge density gradually decays as t_d increases. The charge densities at t_d= 5, 10 and 20 s are about -130, -36.0 and -0.025 C/m^3, respectively. Thus, the charging and the discharge process for EDLCs are almost achieved until t_c = t_d > 10 s. Incidentally, the charge distributions shown in Figs. 5 and 6 suggest that the charge distribution in

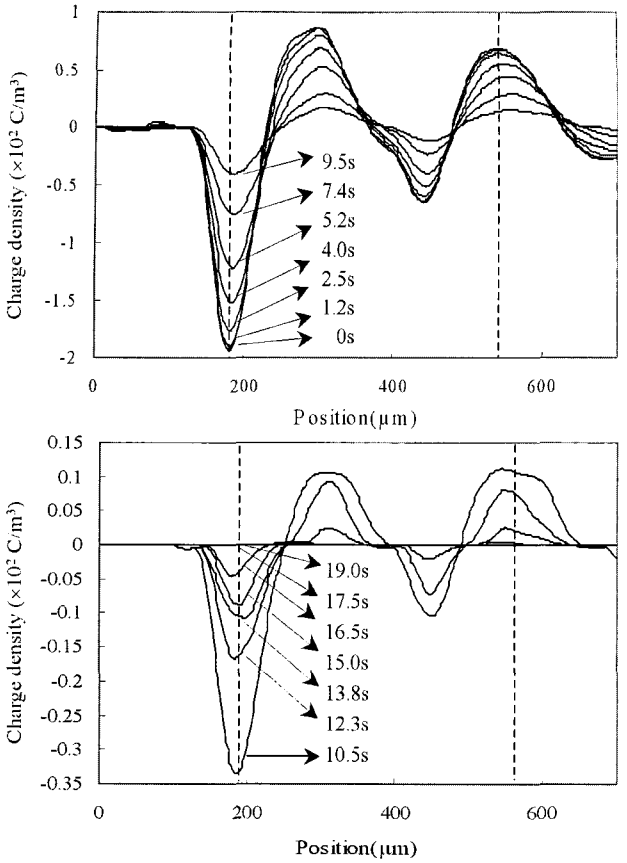

Fig. 6. Charge distributions obtained during discharging.

EDLCs 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 the EDLCs during the charging and the discharge. The charge mobility is closely concerned with the porous structure of the electrode materials, which did not change chemically during the charging and the discharging.

Incidentally, the electrostatic capacity of EDLCs is generally obtained by the energy conversion method. An example of oscilloscope trace of discharge voltage obtained from EDLCs sample is shown in Fig. 7. The applied dc voltage and current density were 2.5 V and 5 mA/cm^2, respectively. It seems that the discharge voltage curve contains two voltage drop components. A sudden voltage drop (ΔV_R), which is associated with the internal resistive component, is seen at the beginning of discharge (~400 ms). ΔV_R was 0.3 V, which was equivalent to the current density of 5 mA/cm^2. The capacitive component (ΔV_{cap}) is related to the voltage variation due to energy change in EDLCs. The capacitance (C_1) per a sheet of carbonaceous electrode can be described as follows, using ΔV_{cap} during the discharge.

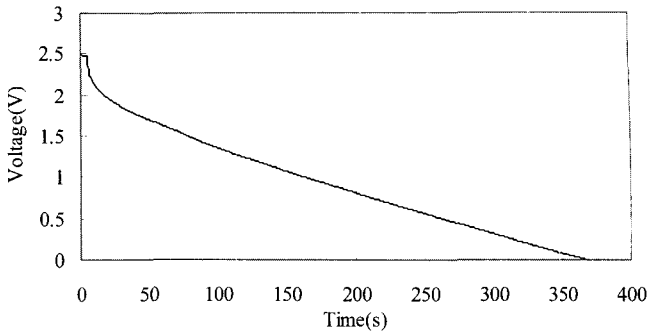

Fig. 7. Example of oscilloscope trace of discharge voltage obtained from EDLC sample. The applied dc voltage and current density were 2.5 V and 5 mA/cm^2.

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

where i_d is the discharge current and m is the mass of the electrode made of activated carbon. The specific total capacitance (Cs) in EDLCs can be calculated as $C_s = 2 \times C_1$ because two carbonaceous electrodes are in series arrangement. In the case of Fig. 7, it was calculated as C_s = 8.7 F/g. C_s can also be estimated by the results of PEA measurements. The whole weight of two sheets of the carbonaceous electrodes was 140 mg, and the specific area of the electrodes was about 1625 m^2/g. Adding up the charge density from L = 520 to 1400 μm, the area charge density could be obtained. In the case of Fig. 5, the whole area charge density was calculated as 8.92 ×10^3 C/m^2. The whole amount of electrical charges was obtained by multiplying the area charge density by the whole surface area of the carbonaceous electrodes. C_s could be estimated by dividing V_{DC} into the whole amount of electrical charges, and its value in the case of Fig. 5 was calculated as C_s = 9.36 F/g. The values of C_s, obtained by two different methods, almost agreed within around 7 %. When the PEA technique is performed on a sample constructed from some layers differing in acoustic characteristics, there is a possibility that the reflected elastic waves from the interfaces influence the interpretation of the experimental results. However, C_s obtained from the PEA method agreed well with that from the energy conversion method although the resulting C_s by the PEA method was estimated through an integration process of each charge distribution. This indicates that the PEA evaluation on C_s was not nearly affected by the component of reflected elastic waves. In our experimental conditions, two collectors were made of Al as with electrodes used in a PEA device. The moving ions in an electrolyte were mainly detected, and there was no metal with the large acoustic impedance in the region bounded by the collectors. Therefore, the influence of the reflected elastic waves

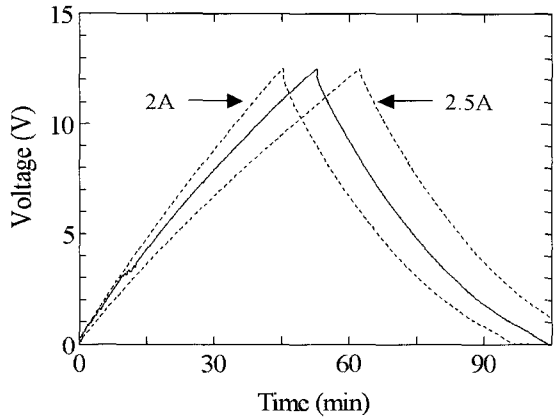

Fig. 8. Voltage characteristics of EDLC connected to solar cells. The dotted lines denote the voltage change obtained using a dc power source whose output currents were set to 2 and 2.5 A.

might be negligible. Even if the charge distributions reported here included some ambiguous factors due to reflected elastic waves, the ambiguity was not as large as that which didn't give physical meanings on the charge distribution. This enabled us to discuss the charge behavior using experimentally obtained results shown in Figs. 5 and 6.

Figure 8 shows the voltage characteristics of EDLCs connected to solar cells. The quantity of solar radiation was 800 W/m^2. The dotted lines denote the voltage change obtained using a dc power source whose output currents were set to 2 and 2.5 A, which are for indicating typical voltage characteristics for a stable power source. As can be seen from this figure, the required time for charging is the almost same as that for full discharging. This is consistent with the result obtained through measurements of charge distributions. Additionally, the efficiency of the output power against the input power was calculated as 98 %. Those results indicate that EDLCs will be an effective storage device for the unstable power source such as solar cells.

4. CONCLUSION

In order to design the effective usage of the EDLCs used for a storage device of solar energy, we investigated the charge distributions in EDLCs. The specific areas of the carbonaceous electrode surface of EDLCs obtained by the BET method were in the range of 1800~2000 m^2/g. The charge distributions during charging and discharging were measured by means of a pulsed-electro-acoustic (PEA) method. The distributions of positive and negative charges were spatially uneven, which was due to the mobility of the positive and negative charges in the carbonaceous electrode surface of the EDLCs. It was also found that the voltage characteristics of EDLCs connected to solar cells was consistent with the result obtained through measurements of charge distributions and the required time for charging was the almost same as that for full discharging.

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