Studies of Electric Double Layer Capacitors Used For a Storage Battery of Dye Sensitized Solar Cell Energy

Hee-Je Kim† , Jin-An Jeon*, Youl-Moon Sung, Mun-Soo Yun*** and Jin-Young Choi***

Abstract - To design the effective usage of electric double layer capacitors (EDLCs) used for a storage device of dye sensitized solar cell (DSC) energy, we first investigated the accumulation state of electrical charges and the charge behavior in the EDLCs. Based on the results, the voltage characteristics of EDLCs connected to DSC energy were evaluated. The results showed that the charge accumulation region concentrated on the central part of the carbonaceous electrode in EDLCs and the required times for charging and discharging were almost the same.

Keywords: Carbon Charge behavior, Dye sensitized solar cell (DSC), Electric double layer capacitors (EDLC)

1. Introduction

Photovoltaic power generation [1] is a useful technique for the prevention of global warning and energy problems. However, the generation of power is strongly influenced by the weather, and therefore the stable supply of electric power is difficult. To use DSC energy efficiently, a storage battery that can deliver the stable electric power to the load is required. One of the widely accepted storage batteries is the sealed lead-acid cell, which has some superior properties such as a long life cycle and superiority in terms of 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] have attracted much attention and demonstrated a good power capability; nevertheless the response to the instanttaneous power is relatively poor. Therefore, we examined the use of electric double layer capacitors (EDLCs) [3~7] operating as a storage device for some DSC energy.

EDLCs, in which the double-layer is formed at the interface between nanoporous carbonaceous electrode and nonaqueous electrolyte solution, have attracted special interest recently because of their superior properties such as high power density, good cycle-ability and 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 the DSCs, 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, which was useful 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. At the development stage of the PEA method, the 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 DSCs were examined.

2. Experiments and methods

Fig. 1 shows the schematic drawing of the EDLC sample, which comprises two 400- m-thick nanoporous carbonaceous electrodes mixed with dielectric (polytetrafluoroethene; PTFE) and carbon black. Carbon black and PTFE were mixed in a mass ratio of 17:1:2. 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. A 20- m-thick cellulose separator was used between the two carbonaceous

† Corresponding Author: Department of Electrical Engineering, Pusan National University, Korea. (heeje@pusan.ac.kr)
* Department of Electrical Engineering, Pusan National University, Korea.
** Department of Electrical Electronic Engineering, Kyungsung University, Korea. (sung@cc.miyazaki-u.ac.jp)
***Korea Electrotechnology Research Institute, Korea. (msyun@keri.re.kr)
Received October 8, 2005 ; Accepted February 16, 2006

electrodes. The carbonaceous electrodes operating as the polarized electrodes and the separator were arranged in a hermetic Al container (30 m in thickness) operating as a current collector. Then, the total thickness of the EDLC sample, which was composed of 5-layers, was 880 m. 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 2004m^2/g, 1.24m^3/g and 2.72 nm, respectively.

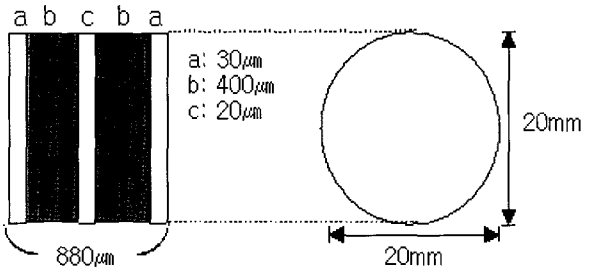


Fig. 1 Schematic drawing of EDLC sample which comprises two 400- m thick nanoporous carbonaceous electrodes mixed dielectric PTFE and carbon black

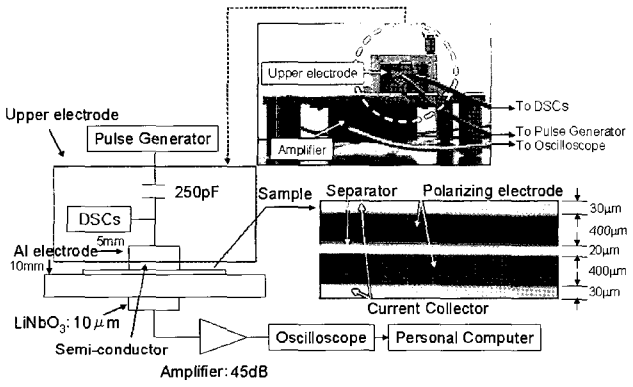


Fig. 2 Experimental arrangement for measurements of charge distributions using the PEA system

The experimental arrangement for measurements of the charge distributions using a PEA system is shown in Fig. 2. The principle of the PEA method is briefly outlined as follows: an electric pulse voltage together with a high DC voltage is added to the EDLC sample sandwiched between an upper and a lower electrode. Hence, acoustic waves are generated by the charges on the electrode and in the EDLC 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 voltage (V_{DC}) of 2.5 V from a 1 DSC panel was added to the EDLC 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 a frequency of 400 Hz. Here, it is noted that a semiconductor layer was formed between the upper Al electrode and the EDLC sample. The semiconductor layer adjusted the acoustic impedance on the interface between the EDLC 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 times (t_c) of 0 - 20 s and discharging times (t_d) of 0 - 20 s.

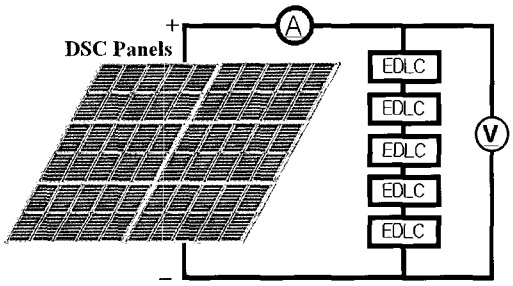


Fig. 3 Charging circuit of EDLC connected to 10 modules × 6 panels DSCs.

Fig. 3 shows the charging circuit of EDLCs connected to DSCs. The number of EDLCs connected in series was 5, and their total capacitance was 500 F. They were connected to 10 modules × 6 panels of DSCs with the output voltage of 12.5 V and the output power of 20 W. Fig. 4 shows an appearance of DSC with photoelectric efficiency of 4% under solar-light source (AM1.5, 100mW/cm^2). 1 DSC panel was fabricated by using 10 DSCs parallel modules with similar performance. In the same way, five more panels were connected in parallel. In DSC panels connected in series and parallel, the output voltage of 12.5 V and the output current of about 1.6 A was obtained. Just after electrification, the discharge characteristic of the EDLCs was examined by connecting a 20 W lump to the EDLCs.

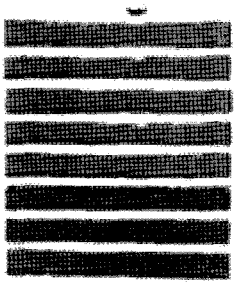


Fig. 4 Appearance of DSC with photoelectric efficiency of 4% under solar light source of AM1.5, 100mW/cm^2

3. Results and discussions

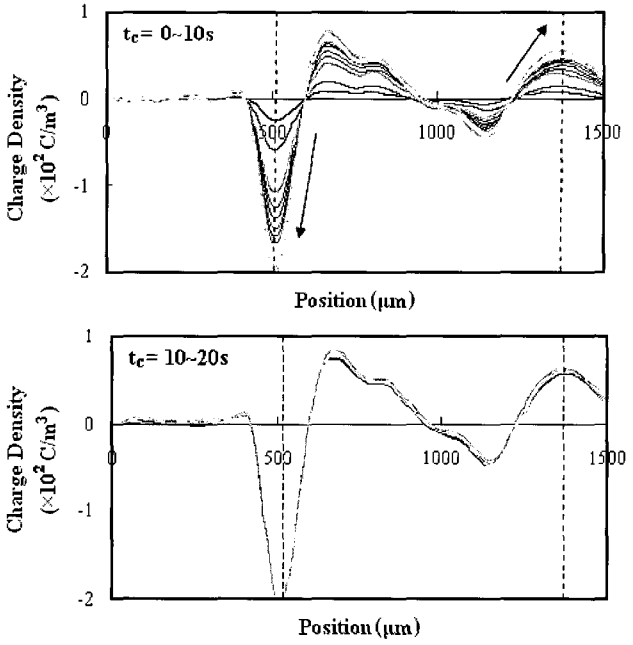


Fig. 5 Charge distributions obtained during charging

The charge distributions in EDLCs, obtained during charging are presented 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 the EDLC 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 m) while the positive charge density had a maximum value of about 61.1 C/m^3 around the cathode layer (at L = 1400 m). It is also noted that the polarized charge accumulation intensively occurred in the narrow region around the porous carbon layer (at L = 520 - 1400 m).

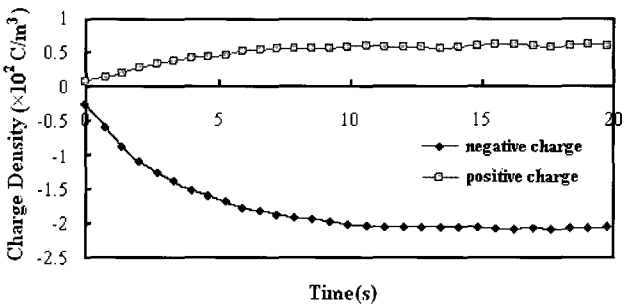


Fig. 6 Temporal variation of negative and positive charge densities with t_c.

The temporal variation of negative and positive charge densities with t_c is shown in Fig. 6. Each plot denotes the absolute peak value of negative and positive peaks in the charge distribution and is the average of five measurements It seems that the charge density increases as t_c increases and saturates at t_c>10 s.

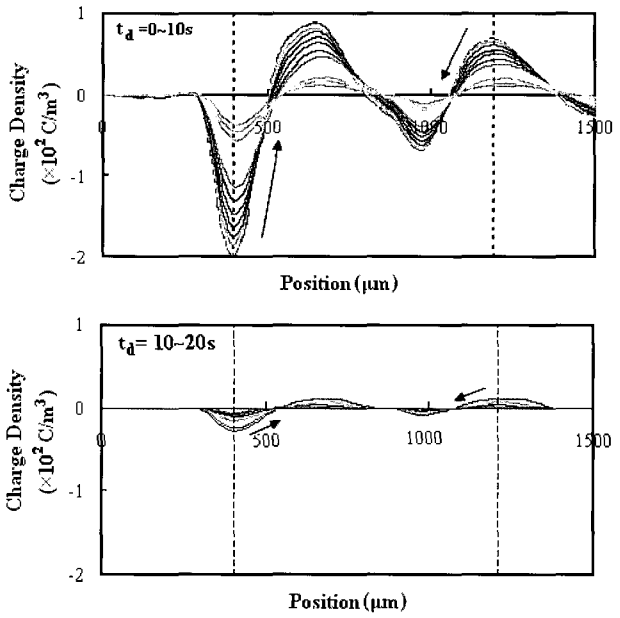


Fig. 7 Charge distributions obtained during discharging

The charge distributions in EDLCs, obtained during discharging, are shown in Fig. 7. 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 7 suggest that the charge distribution in the 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 the discharge voltage obtained from the EDLC sample is indicated in Fig. 8. The DSC with voltage of 2.5 V and the current density of 5 mA/cm^2 was carried out in this experiment.

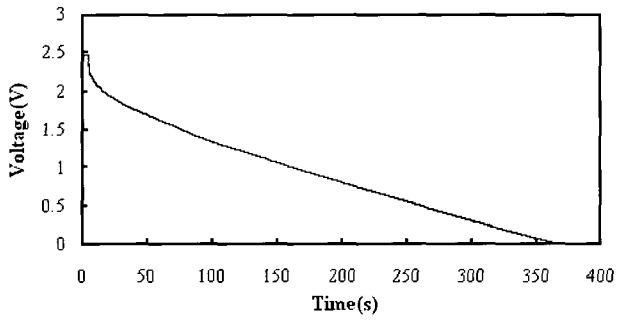


Fig. 8 Example of oscilloscope trace of the discharge voltage obtained from EDLC sample. The DSC with voltage of 2.5 V and the current density of 5 mA/cm^2 was carried out in this experiment.

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 the 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 the EDLC. The capacitance (C_1) per sheet of carbonaceous electrode can be described as follows, using ΔV_{cap} during the discharge.

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

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. 8, 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 m, the area charge density could be obtained. In the case of Fig. 5, the whole area charge density was calculated as 8.92 $\times 10^3$ C/m^2. The entire amount of electrical charges was obtained by multiplying the area charge density by the complete surface area of the carbonaceous electrodes. C_s could be estimated by dividing V_{DC} into the whole amount of the 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 showed good agreement, differing only by about 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 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 the experimentally obtained results shown in Figs. 5 and 7.

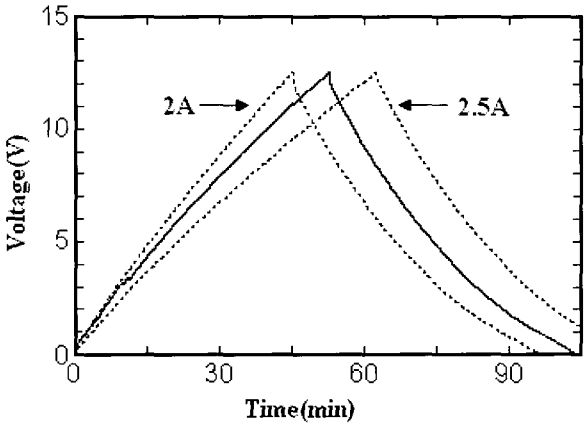


Fig. 9 Voltage characteristics of EDLC connected to DSCs. The dotted lines denote the voltage change obtained using DSCs whose total currents were set to 2 and 2.5 A.

Fig. 9 shows the voltage characteristics of the EDLCs connected to the DSCs. The quantity of solar radiation was 100mW/cm^2. The dotted lines denote the voltage change obtained using DSCs whose total 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 Fig, the required time for charging is almost the 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%.

5. Conclusion

We first investigated the charge distributions in EDLCs in order to design the effective usage of the EDLCs used for a storage device of DSC energy. 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 the EDLCs connected to the DSCs were consistent with the result obtained through measurements of charge distributions and the required time for charging was almost the same as that for full discharging

Acknowledgements

This work is partly supported by KOSEF (the Korea Science and Engineering Foundation) of Korea, grant No. R01-2004-000-10318-0.

References

[1] Louis Rosenblum, William J. Bifano, Gerald F. Hein and Anthony F. Ratajczak, "Photovoltaic power systems for rural areas of developing countries", *Solar Cells* , vol. 1, no. 1, pp. 65-79, *Nov. 1979.*

[2] Ross A. Lemons, "Fuel cells for transportation ", *Journal of Power Sources*, vol. 29, no. 1-2, pp. 251-264, *Jan. 1990.*

[3] Brian. E. Conway, *Electrochemical Supercapacitors*, NTS, 2001.

[4] M. Takeuchi, T. Maruyama, K. Koike, A. Mogami, T. Oyama and H. Kobayashi, Electro-chemistry, vol. 69, pp. 487, 2001.

[5] M. Okamura, H. Hasuike, M. Yamagishi and S. Araki, Electro-chemistry, vol. 69, pp. 414, 2001.

[6] Yukari Kibi, Takashi Saito, Mitsuyoshi Kurata, Junji Tabuchi and Atsushi Ochi, "Fabrication of high-power electric double-layer capacitors ", *Journal of Power Sources,* vol. 60, no. 2, pp. 219-224, June 1996.

[7] Enn Lust, Alar Jänes, Mati Arulepp, "Influence of electrolyte characteristics on the electrochemical parameters of electrical double layer capacitors", *J. Solid State Electrochem.*, vol. 8, no. 7, pp. 488-496, 2004.

[8] Chao Zhang, Teruyoshi Mizutani, Kazue Kaneko, Tatsuo Mori and Mitsugu Ishioka, "Space charge behaviors of low-density polyethylene blended with polypropylene copolymer " *Polymer*, vol. 43, no. 8, pp. 2261-2266, Apr. 2002.

[9] Yoon-Hyeok Kwon, Seung Hwangbo, June-Ho Lee, Dong-Young Yi and Min-Koo Han, "The Space Charge Effect on the Discharge Current in Cross-Linked Polyethylene under High AC Voltages", *Jpn. J. Appl. Phys.*, vol. 42, pp. 7576-7579, 2003.

[10] Weichuan Du, Wei Zhong, Yijian Lin, Liang Shen and Qiangguo Du, "Space charge distribution and crystalline structure in polyethylene blended with EVOH", *European Polymer Journal*, vol. 40, no. 8, pp. 1987-1995, Aug. 2004.

[11] D. Tashima, Y. Hirata, M. Otsubo, Y. M. Sung, C. Honda, *Institute of Electrostatics Japan,* vol. 29, pp. 244, 2005.

Hee-Je Kim

He received his B.S. and M.S. degrees in electrical engineering from Pusan National University, Korea in 1980 and 1982, respectively. He joined the Plasma & Laser Lab of the Korea Electro-Technology Institute in 1983 as a Research Engineer and went to Kyushu University, Hukuoka, Japan in 1985 where he received his Ph.D. degree from Kyushu University, Hukuoka, Japan in 1990. From 1995 to the present he has been a Professor at the school of electrical engineering, Pusan National University.

Jin-An Jeon

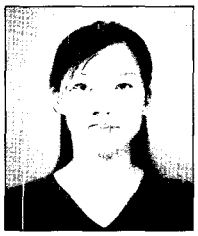
He received his B.S. degree in Management Information Systems from Tongmyong University in 2000. He received a M.S. degree in 2002 and currently is working towards a Ph.D. in Electrical Engineering at Pusan National University.

Youl-Moon Sung

He graduated from Pusan National University in 1992, Korea. He obtained his M.S. and Ph.D. from the same university in 1994 and 1996 respectively. He undertook a postdoc from 1997 to 1998 in Kyushu University, Japan. He became a Research Associate in Kyushu University and the University of Miyazaki in 1999 and 2000, respectively. Presently, he is an Associate Professor at the School of Electrical Electronic Engineering, Kyungsung University. His research interests include plasma applications and energy technologies

Mun-Soo Yun

He received his B.S. and M.S. degrees in Physics at Kyungpook National University in 1973 and 1977, and his Ph.D. degree in Electric Engineering at Osaka University in 1985. From 1986, he has been working as a Researcher at the Korea Electrotechnology Research Institute (KERI), Changwon, Korea. His research fields are focused on the R&D of Electrical Materials including Secondary Batteries, Superconductors and Polymer Insulators.



Jin-Young Choi

She received her B.S. degree in Electrical Engineering from Silla University in 2002. She received a M.S. degree in 2004 and is currently working towards a Ph.D. degree in Electrical Engineering at Pusan National University.