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Characteristics of Electrode for Electric Double Layer Capacitor Made of Carbonized and Activated Cotton Cloth

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Abstract

The electric double layer capacitor (EDLC) electrode is made of carbonized and activated organic materials. In this study, material surface and electrical characteristics of carbon materials produced from low cost organic materials were examined. First, a cotton cloth has been carbonized and activated, and optimal times and temperatures of carbonization and activation processing were examined. And, surface area, pore volume and pore size distributions were analyzed. Second, activated carbons were applied to the electrodes of EDLC. Two kinds of EDLC cell, which were small area cell (2cm×2cm) and large area cell (15cm×10cm), were assembled. The capacitances and internal resistances of the assembled EDLC cell were evaluated by charge and discharge circuit using constant voltage source. And, the charge and discharge cycle test was performed on these assembled EDLC cells. As a result, specific surface area of the activated carbon processed for 0.5-1 hour at 450-600°C in the carbonization and 1-2 hour at 700-1000°C in the activation was the largest in prepared conditions. Therefore, EDLC cells using the activated carbon with large surface area of 1300m^2/g have shown the high density of capacitance 1F/cm^2. The internal resistances of both cells were less than 1Ω. It is also found that the activated carbon shows almost the same density of capacitance, internal resistance and no deterioration in the charge and discharge cycle test. It was clearly understood that the activated carbon made of cotton cloth has a large surface area and a low internal resistance which contribute to the low cost electrode of an EDLC.

INTRODUCTION

In recent years, studies on the use of EDLC as energy storage devices in place of secondary battery such as lead batteries are underway in many countries and regions [1]. EDLC utilizes a double layer formed at the interface between the nonporous carbonaceous electrode and the electrolyte solution. EDLC has advantages such as rapid charge and rapid discharge. In addition, EDLC is a physical battery without redox reaction. Therefore, there is little deterioration in the electrode. However, the serious disadvantage of this EDLC is its cost and/or low energy density; hence, research on the development of a new electrolyte solution [2] and a new carbon electrode material [3] and studies of the low cost electrode materials are underway. A principal material in the EDLC is porous activated carbons because of their relatively low cost and very high specific surface area.

Especially, the cost performance is very important for the development of EDLC. The purpose of this study is to solve these problems producing carbon materials for EDLC with low cost and large capacitance, using the low cost and safe materials. The large surface area is effective for increasing the capacitance of EDLC. In particular, the capacitance can be increased effectively by increasing the percentage of the micro meso pore (pore diameter: 1 to 4 nm) distribution. In recent years, the activated carbon from cotton cloth was made and investigated on the basic electrode properties of application EDLC; it was made certain that pore sizes of these activated carbons were effective for increasing the capacitance. In this paper, EDLC cells were made of carbonized and activated carbons made of the cotton cloth, of which capacitance, internal resistance and degradation of reputation test of charge and discharge were examined.

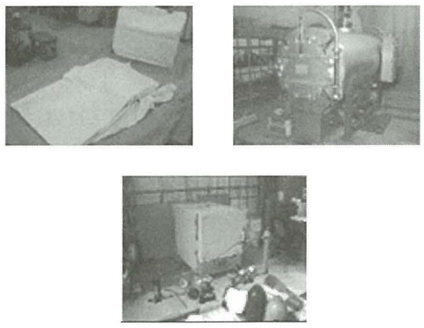
PRODUCING ACTIVATED CARBON

(a) Cotton cloth activated carbon

The large specific surface area and high conductivity are required for electrode of EDLC. As an industrial requirement, low cost, safety and high reliability are also required as well as the properties. Conventional activated carbon electrodes for EDLC are separated into two types, which are powder and fiber active carbon. The fiber active carbon has some advantages for manufacturing EDLC in the industrial requirement [2]. However, an activated carbon made of cotton cloth has never been investigated though it is one of the materials of fiber active carbon of low cost and of safe materials which are close to us.

(b) Manufacturing method of the activated carbon

Figure 1 shows a manufacturing process of active carbon of cotton cloth. The electric heating furnace is used for carbonization in cotton cloth as shown in Fig. 1(b). The cotton cloth was carbonized for 0.5-1 hour at 450-600°C in N_2 gas atmosphere. After, the carbonized cotton cloth was activated for 1-2 hour in 700-1000°C in CO_2 and N_2 mixed gas by using another electric heating furnace. Figure 2 shows a SEM image of carbonized and activated cotton cloth, which has very porous surface.



(a) Cotton cloth　(b) Carbonize (450-600°C)
(c) Activation (700-1000°C)
Fig.1 Manufacturing process in activation carbon made of cotton cloth

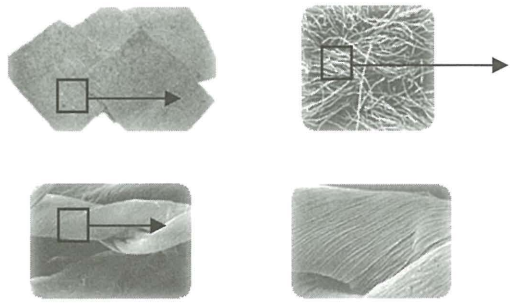


Fig.2 SEM images in carbonized and activated cotton cloth

(c) Pore size analysis and specific surface area of the activated carbon

After activation process for 1-2 hour at 700-1000°C in CO_2 and N_2 mixed gas, the specific surface area is measured by using Brunauer-Emmentt-Teller (BET) method [4]. Table 1 shows BET surface area and pore volume distribution. The typical specific surface area is 1350m^2/g in activated carbon of cotton cloth. The specific surface area of commercial activated carbon of power type is more than 1500-3000m^2/g. The specific surface area of cotton cloth is close to one of commercial activated carbon. The micro and meso volume of cotton carbon is also smaller than one of commercial activated carbon; however the pores volume distribution is as same as one of the commercial activated carbon. It shows that the pore size is same, and the density of pores and the specific surface area are small in comparison with the commercial activated carbon.

Table 1 BET surface area and pore volume distribution

Sample Activated Carbone	BET Surface Area [m^2/g]	Pore Volume micro < 2nm [cm^3/g]	Pore Volume meso < 2~50nm [cm^3/g]
Activated towel (after washing with distilled water)	1353	0.777	0.696
Commercial activated carbon (powder type)	2414	1.572	1.532

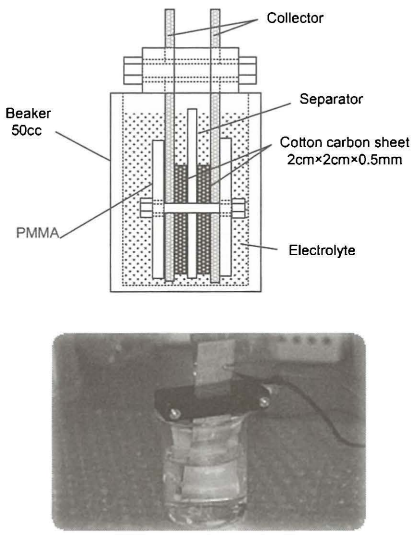
EXPERIMANTAL

ASSEMBLE OF TEST CELL

The activated carbons of cotton cloth were applied to the polarized electrodes of EDLC. Two kinds of EDLC cell were assembled by using different sizes of cotton carbon sheets.

(a) Beaker cell

Figure 3 shows the beaker cell which consists of 50cc beaker, two collectors (7cm×3cm), separator (4cm × 4cm), electrolyte solution, two cotton activated carbon sheets(2cm × 2cm×0.5mmt) and some plastic (PMMA) suspensions. The hermetically seal beaker cell to exclude any external air is also made to exam stability of capacitance.



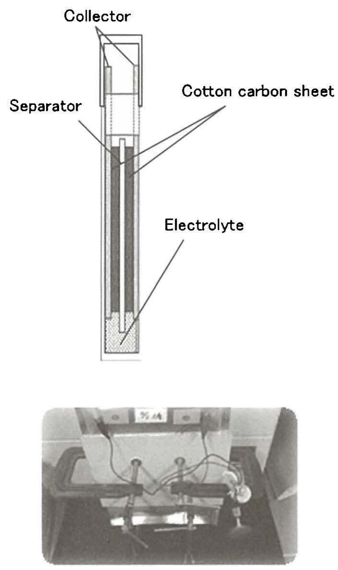
(a)

(b)

Fig.3 Beaker cell
[(a)structure of sample, the cotton carbon 2cm×2cm × 2 pieces, (b)photogragh]

(b) Package cell

In order to examine the dependence of carbon sheet size, the package cell has been assembled as shown in Fig. 4. The cell consists of two cotton carbon sheets (15cm×10cm×0.5mmt), separator (21cm × 20cm), collector (24cm × 20cm), electrolyte solution, gas barrier pack(A4 size), two collectors (21cm × 20cm × 3mmt) and same suspensions. The cotton sheet size is 37.5 times larger than one of the beaker cell.



(a)

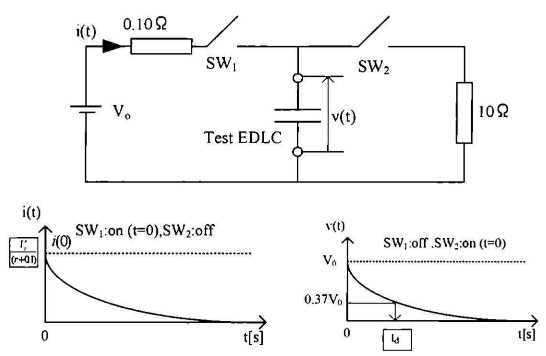
(b)

Fig. 4 Package cell
[(a)structure of sample, the cotton cloth 15cm×10cm × 2 pieces,(b) photograph]

(c) Test circuit for charge and discharge

The properties of test cell are measured by simple circuit which is charge and discharge circuit using a constant voltage source. Figure 5(a) and (b) show the circuit and wave forms in charging and discharging, respectively. The internal resistance r of test cell is determined by charging current $i(t)$. The capacitance C of test cell is determined by wave form of discharging voltage $v(t)$. The r and C are calculated by equation (1) and (2). The t_d is time until voltage decreases to V_0/e. The constants 0.1 and 10 are resistance in the test circuit.

$$r = \frac{V_0}{i(0)} - 0.1 \ [\Omega] \quad (1) \qquad C = \frac{t_d}{10} \ [F] \quad (2)$$



(a) Test circuit
(b) Charging current　(c) Discharging voltage
Fig.5 Measurement of capacitance and internal resistance using constant voltage source

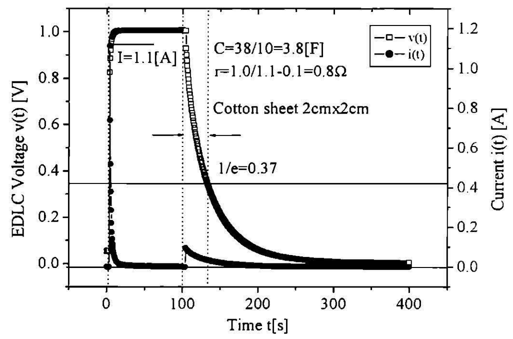


Fig. 6 Typical wave form in charging and discharging in beaker cell

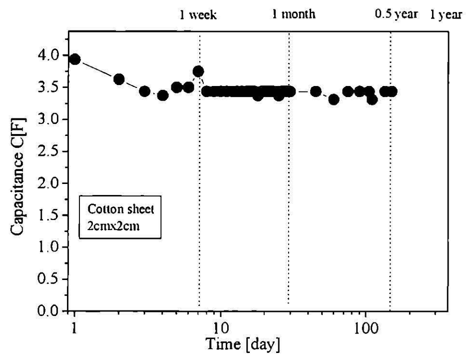


Fig.7 Change of capacitance in beaker cell

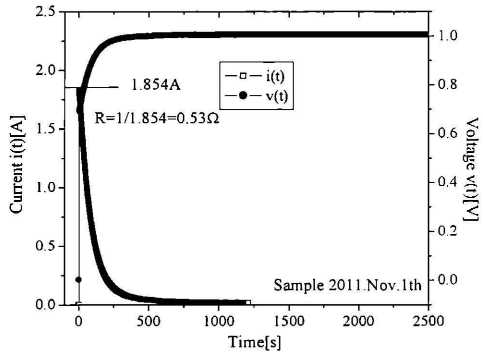
RESULTS

(a) Beaker cell

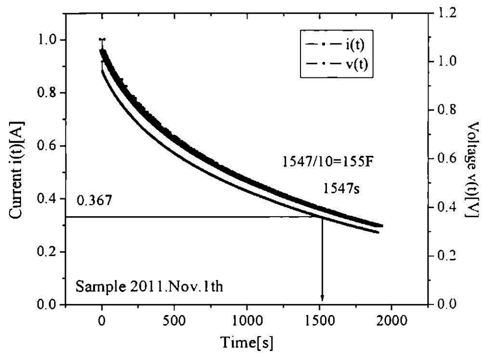
Figure 6 shows typical wave forms in charging and discharging from which capacitance C and internal resistance r were measured in beaker cell. The *C* and *r* are 3.8F and 0.8Ω, respectively. The density of capacitance is approximately 1F/cm^2, which is 60% of capacitance of the commercial active carbon which was introduced in the literature [4]. The *r* is slightly higher than one of commercial EDLC. Figure 7 shows change of *C* during half year when the hermetically seal beaker cell was used. The results show that the *C* of beaker cell is very stable. The obtained results show that the capacitance is very stable in the charge and discharge cycle test during a half year.

(b) Package cell

When EDLC is used as energy storage devices, the huge area active carbon electrode is necessary; the capacitance of the active carbon should be proportional to the area of active carbon sheet. The large size cell was assembled to confirm the viewpoint. The package cell which has two 15cm×10cm size carbon sheets was assembled and *C* and *r* were measured in the same manner as the beaker cell. Figure 7 (a) and (b) show typical wave forms in charge and discharge in the package cell. The *r* was measured from current wave form in charging process, and the *r* is 0.53Ω. The *r* is less than one of the beaker cell; it shows that the internal resistance is independent from the area of active carbon sheet in the one layer cell. The *C* was measured from voltage wave form in discharging process. The *C* of package cell was 155F. The density of capacitance is approximately 1F/cm^2; the density of capacitance is almost the same as the one of the beaker cell. It is confirmed that the capacitance of active carbon sheet made of cotton cloth is in proportion to the area of active carbon. It is important for making large capacity EDLC. Figure 8 shows results of repetition test of charge and discharge in the package cell. The degradation of capacitance due to charging and discharging was not measured in the reputation test up to 3000 times.



(a) Charge



(b) Discharge

Fig. 7 Typical wave form in charge and discharge in package cell

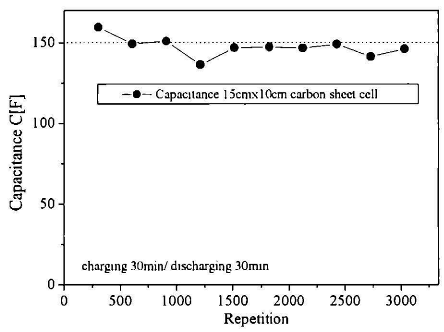


Fig. 8 Repetition test in package cell

CONCLUSION

A Cotton cloth has been carbonized and activated, and optimal times and temperatures of the carbonization and activation processing were examined and surface area, pore volume and pore size distributions were analyzed. The activated carbon sheets were applied to the EDLC electrodes. Two kinds of EDLC test cell, which are small and large area cell, were assembled. The capacitance and internal resistance of the assembled EDLC cell were measured. The internal resistance is less than 1Ω in the both kinds of EDLC cell. It shows that the internal resistance is independent from the area of active carbon sheet in the one layer cell. The density of capacitance is approximately $1F/cm^2$ in the both cells. It is confirmed that the capacitance of active carbon sheet made of cotton cloth is in proportion to the area of active carbon. The deterioration of EDLC cell is not observed over 3000 times in repetition tests. From the obtained results, there is a possibility of the practical use of EDLC which is made of the carbonized and activated cotton cloth in low cost.

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