

Short communication

## Electrochemical characteristics of electric double layer capacitor with sheet type polarizable electrode

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### Abstract

This work describes the effect of the number of roll pressings and the composition of carbon black on the electrical and mechanical properties of carbon–PTFE electrodes, in which the composition is MSP 20:carbon black:PTFE = 95 – x:x:5 wt.%. It was found that the best electrical and mechanical properties were obtained in sheet electrodes roll-pressed for about 15 times and in sheet electrode, in which composition is MSP 20:carbon black:PTFE = 80:15:5 wt.%. These results can be explained by the network structure of PTFE fibrils and conducting paths linked with carbon blacks, respectively. On the other hand, a cell capacitor using a sheet electrode with 15 wt.% of carbon black attached to an aluminum current collector with an electric conductive adhesive, and a composition of carbon black:CMC = 70:30 wt.%, exhibited the best rate capability in the current range of 0.5–100 mA cm<sup>-2</sup> and the lowest equivalent series resistance.

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### 1. Introduction

The electrical double layer capacitor (EDLC) has been considered as a promising high power energy source for electrical devices and hybrid electric vehicles [1]. The advantages of EDLC are its better rate capability and longer cycle life as compared to secondary batteries [2,3], and these features are intimately related with the physical interactions between activated carbon and electrolytic solution.

The characteristics of a polarizable electrode for electric double layer capacitor are strongly affected by an electrode configuration consisting of activated carbon, electric conductor and polymeric binder [4,5]. The activated carbon powder must be held together compactly to provide a low resistance and high density electrode. For a compact configuration of the electrode, a polymeric binder, which can maintain particle-to-particle contact, give the electrode mechanical integrity, and allow stable, low resistance bonding to a current collector is needed. Among

the polymeric binders, polytetrafluoroethylene (PTFE) helps the electrode in several ways. Except for its excellent chemical and electrochemical stability, PTFE does not coat more than a small fraction of the surface of the activated carbon, resulting in enhancement of the rate capability of the capacitor. The PTFE is also effective at low concentrations compared to soluble polymeric binder, which allows an increase of capacitance in the capacitor [6,7].

In this study, the electrodes consisting of activated carbon, electric conductors and PTFE were prepared and their electrochemical and mechanical properties in terms of the number of roll pressings, the composition of sheet electrodes, in which the composition was activated carbon:carbon black:PTFE = 95 – x:x:5 wt.%, were examined. The electrochemical performances of cell capacitors using the sheet electrode attached to an aluminum current collector with the electric conductive adhesive were also examined.

### 2. Experimental

MSP 20 activated carbon (2000 m<sup>2</sup> g<sup>-1</sup>, commercially supplied by Kansai Coke & Chemicals Co.) was used as an activated material. An electrical conductor (Super P black, supplied by

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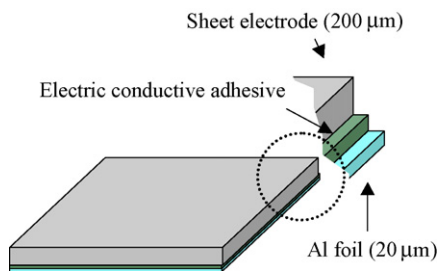


Fig. 1. Schematic structure of the electrode.

MMM Carbon Co.) was added to the activated carbon in order to ensure good electric conductivity. A mixture containing the active material and electric conductor and PTFE with 5 wt.% was mixed with water. In order to make uniform and thin electrode, a paste obtained by drying the mixture was roll-pressed into a form of the sheet type electrode by the rollers. The sheet was folded in half and roll-pressed to make a thinner electrode. The process repeated until obtaining a nearly 200 μm thickness sheet.

On the other hand, a mixture consisting of the carbon black and carboxymethyl cellulose (CMC) was prepared as an electric conductive adhesive. The electric conductive adhesive was prepared by mixing the carbon black and a solution of CMC in water, and spread out on an aluminum current collector. The sheet electrode was attached to the aluminum current collector with the electric conductive adhesive and vacuum dried at 150 °C for 15 h. Fig. 1 shows the schematic structure of the electrode.

The electrical and mechanical properties of the sheet electrodes were measured by the dc 4 point probe method and tensile strength measurement, respectively. The specific resistance of the electrode was calculated from;

$$\rho = R \frac{A}{t} \quad (1)$$

where  $A$  is the area of the electrode,  $t$  the thickness, and  $R$  is the resistivity of the electrode. The specific resistance of the electric conductive adhesive coated on a Polaroid film was also measured by the dc 4 point probe method.

The cell capacitors were constructed with a separator inserted between the electrodes, in which size was 3 cm × 4 cm. These assemblies were housed in aluminum-laminated film cells. After an organic electrolyte solution of 1.2 M tetraethylammoniumtetrafluoroborate in acetonitrile solution was poured, the cell capacitors were sealed taking out the leads. The test cell capacitors were charged and discharged at a constant current from 5 to 100 mA cm<sup>-2</sup> between 0 and 2.5 V with a Maccor test system. The dc capacitance was calculated from;

$$C = i \frac{\Delta t}{\Delta V} \quad (2)$$

where  $\Delta t$  is the time period,  $\Delta V$  the voltage change, and  $I$  is a constant discharge current.

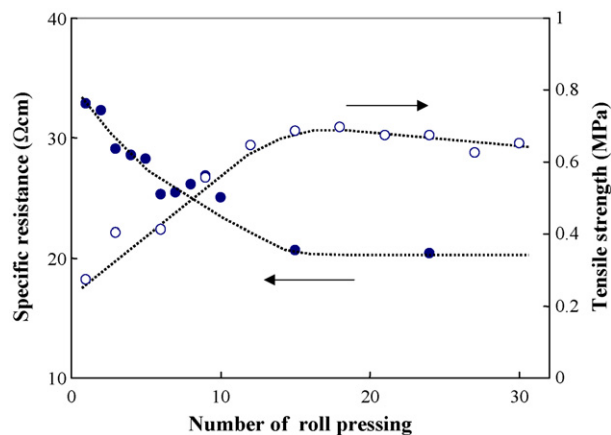


Fig. 2. Variation of the specific resistance and the tensile strength vs. the number of roll pressing for sheet electrode.

### 3. Results and discussion

Fig. 2 shows the variation of the specific resistance and the tensile strength versus the number of roll pressings for sheet electrodes, in which the composition is MSP 20:carbon black:PTFE = 80:15:5 wt.%. It can be seen from the figure that the specific resistance of the sheet electrodes decreased with an increase in the number of roll pressings, and was almost saturated after more than 15 roll pressings.

On the other hand, the tensile strength of the sheet electrodes increased at first and then slightly decreased after 15 roll pressings. These electrical and mechanical properties are intimately correlated with PTFE polymeric binder. When the sheet electrode was roll-pressed repeatedly by the rollers, the PTFE made a well-developed network structure of fibrils. This resulted in a structure with good particle-to-particle contact for low electrical resistance. This compact configuration also enhanced the tensile strength of the sheet electrode. However, excessive roll pressing partially fractures the network structure of fibrils in the sheet electrode, and leads to the decrease of tensile strength.

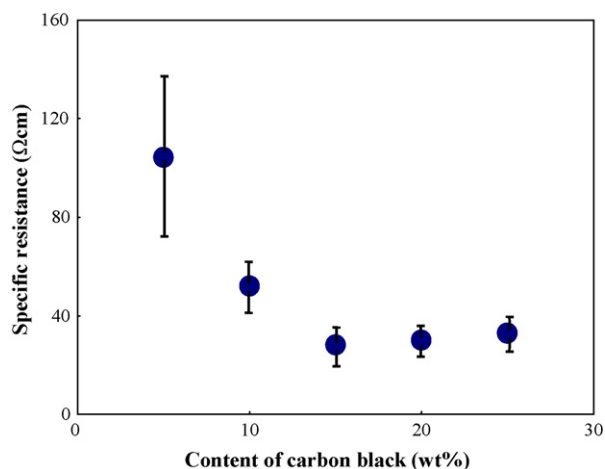


Fig. 3. Variation of the specific resistance vs. the content of carbon black for the sheet electrode, in which composition is MSP 20:carbon black:PTFE = 95 - x:x:5 wt.%.

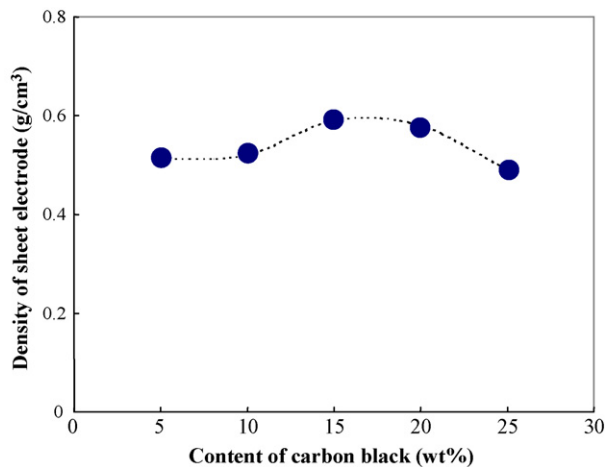


Fig. 4. Variation of the density vs. the content of carbon black for the sheet electrode, in which composition is MSP 20:carbon black:PTFE = 95 – x:x:5 wt.%.

Fig. 3 shows the variation of the specific resistance versus the content of the carbon black in sheet electrodes roll-pressed 15 times. In the figure, the decrease of the specific resistance with the increase of the carbon black can be observed and the sheet electrode with 15 wt.% of the carbon black has a minimum value, 30  $\Omega$  cm. For a higher content of the carbon black, the specific resistance slightly increased.

The densities of sheet electrodes with various amounts of the carbon black are shown in Fig. 4. It can be seen from the figure that the density of the sheet electrodes increased at first and slightly decreased for more than 15 wt.% of the carbon black. When carbon black particles with sub micron size were placed in a void presented between activated carbons with about 8  $\mu$ m size, a dense structure of the sheet electrode was obtained. The increase of the electrical conductivity in the range of 5–15 wt.% of carbon black was caused by the increase of conducting paths linked with carbon blacks, because of their lower intrinsic resistivity compared to activated carbons. For the sheet electrode with more than 15 wt.% of the carbon black, it can be assumed that the decrease of electric conductivity is related to bad particle-to-particle contact caused by the lack of PTFE corresponding to the amount of the carbon black.

On the other hand, to decrease the contact resistivity between the sheet electrode and the current collector, the sheet electrode was attached to an aluminum current collector with an electric conductive adhesive. The required properties of the electric conductive adhesive are an adhesive force between the sheet electrode and current collector and a larger electric conductivity than that of the sheet electrode. The electric conductive adhesives, in this study, composed of carboxymethyl cellulose and carbon black, were tested in terms of the electrical conductivity.

Fig. 5 shows the variation of the specific resistance versus the content of carbon black in the electric conductive adhesive. The specific resistance of the electric conductive adhesive decreased with the increase of the content of the carbon black and increased for more than 70 wt.% of the carbon black. This behavior of the specific resistance is correlated with the condi-

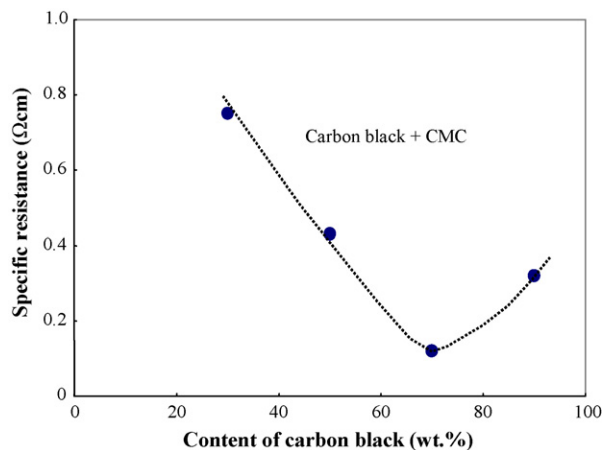


Fig. 5. Variation of the specific resistance vs. the content of carbon black for electric conductive adhesive composed of carbon black and CMC.

tion of particle-to-particle contact. In the range below 70 wt.% of carbon black, the CMC solution can easily coat a very large part of the surface of carbon black. The CMC layers presented between the carbon black particles act as a conducting barrier, resulting in an increase of specific resistance. In this range, although the adherence of the sheet electrode on the current collector is very strong, it is impractical for electrode manufacturing because the electrode attached with a large amount of CMC is rigid and cracks easily during the press and winding process.

On the other hand, for an electric conductive adhesive with 90 wt.% of carbon black, it can be assumed that the decrease of electrical conductivity is related to the bad particle-to-particle contact caused by the lack of CMC corresponding to the amount of the carbon black. The specific resistance of the electric conductive adhesive, in which the composition is carbon black:CMC = 70:30 wt.%, has a minimum value of 0.2  $\Omega$  cm. This value is 100-times smaller than that of the sheet electrode as shown in Fig. 3.

Fig. 6 shows charge–discharge voltage profiles of cell capacitors fabricated with electrodes, in which the composition is MSP 20:carbon black:PTFE = 95 – x:x:5 wt.%, attached with the electric conductive adhesive, in which the composition is carbon black:CMC = 70:30 wt.%. Potential cycling was carried out at current densities of 5 and 100  $\text{mA cm}^{-2}$  in the potential range of 0–2.5 V. When the current density increases from 5 to 100  $\text{mA cm}^{-2}$ , the charge–discharge capacity decreases slightly in the cell capacitor using an electrode with 15 wt.% of carbon black whereas the more rapid decreases are observed in the cell capacitor using an electrode with 5 and 20 wt.% of carbon black. One reason for the better rate capability of a cell capacitor using the electrode with 15 wt.% of carbon black can be found in the charge–discharge profile, where the voltage drop at early period of discharge is visible. The voltage drop is smaller in 15 wt.% of carbon black than in 5 and 20 wt.% of carbon black at high current density. This ohmic voltage drop is caused by the equivalent series resistance (ESR) in these cell capacitors. The cell capacitor using the electrode with 15 wt.% of carbon black has the lowest ESR due to the lowest specific resistance of the sheet

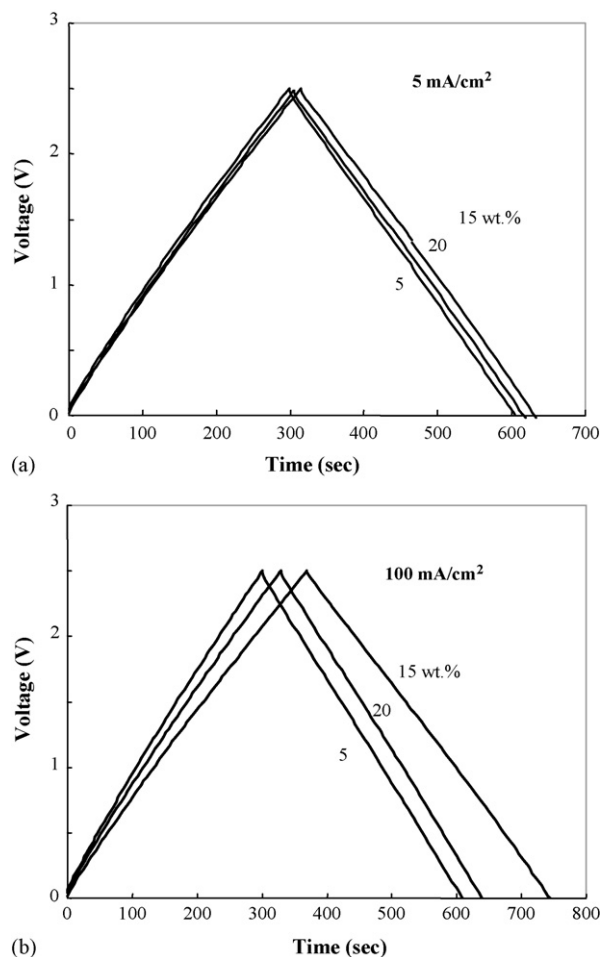


Fig. 6. Charge–discharge voltage profiles at current density of  $5 \text{ mA cm}^{-2}$  (a) and  $100 \text{ mA cm}^{-2}$  (b) for cell capacitors using the electrode with 5, 15, 20 wt.% of carbon black.

electrode shown in Fig. 3. Therefore, this confirms that the better rate capability of cell capacitors results from a lower ESR, which is caused mainly by a lower electric resistance in the sheet electrode.

#### 4. Conclusions

In this study, we have examined the effect of the number of roll pressings and the composition of carbon black on the electrical and mechanical properties of carbon–PTFE electrodes, in which the composition is MSP 20:carbon black:PTFE =  $95 - x$ : $x$ :5 wt.%, and the main results obtained were as follows:

- (1) The sheet electrode, with  $200 \mu\text{m}$  thickness, roll-pressed for about 15 times exhibited the lowest specific resistance and the highest tensile strength.
- (2) The sheet electrode, in which the composition is MSP 20:carbon black:PTFE = 80:15:5 wt.%, exhibited the lowest specific resistance,  $30 \Omega \text{ cm}$ , than with other compositions of carbon black.
- (3) At the composition test of electric conductive adhesives composed of carbon black and CMC, the best electric specific resistance,  $0.2 \Omega \text{ cm}$ , was obtained in composition of carbon black:CMC = 70:30 wt.%.
- (4) The cell capacitor using a sheet electrode with 15 wt.% carbon black attached to aluminum current collector with an electric conductive adhesive, whose composition is carbon black:CMC = 70:30 wt.%, exhibited the best rate capability and the lowest ESR.

#### References

- [1] M.F. Rose, C. Johnson, T. Owen, B. Stephen, J. Power Sources 47 (1994) 303–312.
- [2] B.E. Conway, Electrochemical Supercapacitors, Kluwer Academic Publishers, New York, 1999, p. 12.
- [3] J.R. Miller, Proc. 12th International Seminar on Battery Technology and Applications, Deerfield Beach, FL, 1995.
- [4] A. Yoshida, I. Tanahashi, A. Nishino, Carbon 28 (1990) 611.
- [5] A. Nishino, Proc. Electrochemical Society Meet, Hawaii, HI, USA, 1993.
- [6] L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, A. Dugast, Proc. 38th Power Sources Conferences, Cherry Hill, NJ, 1998.
- [7] L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, J.F. Sarrau, A. Dugast, J. Power Sources 80 (1999) 149–155.