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Supercapacitor Consisting of a Form Core Sandwich with Woven Carbon Fiber Skin

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Abstract

Structural capacitors are composite structures that function as energy storage capacitors. Parallel plate-type capacitors have the advantage of high voltage resistance, but are limited by low capacitance. An electric double-layer capacitor with a composite structure using a solid polymer electrolyte matrix with a glass fiber fabric separator has recently been developed. However, the solid polymer electrolyte caused the capacitor to possess high internal resistance. In the present study, a new design of supercapacitor using a form core sandwich with high water retention is proposed and experimentally investigated. Activated carbon sheets are used as electrodes on the form core sandwich to make a supercapacitor. Woven carbon fabric is used as lead wires of the supercapacitor. The resulting supercapacitor displays a low surface resistance of 810 Ωcm^2 and high areal capacitance of 520 mF/cm².

1. Introduction

Multifunctional composites have been developed to integrate the function of one structure with that of another for applications such as energy storage, antennas and sensors. Multifunctional composites make it possible to reduce the number of parts and required space of a system [1]. Structural capacitors are composite structures that behave as energy storage capacitors. Luo and Chung [2] fabricated structural capacitors using a paper interlayer that exhibited an areal capacitance of 12 nF/cm². Meanwhile, Lin and Sodano [3] made a cylindrical capacitor composed of piezoelectric material $BaTiO_3$, which can be used to reinforce composites. Carlson et al. [4] [5] used a paper and polymer sheet as a dielectric separator in a capacitor, and obtained an areal capacitance of 25

nF/cm^2. O'Brien and colleagues also developed a parallel plate-type structural capacitor [6], which exhibited high voltage resistance but low capacitance.

Shirshova *et al*. [7] [8] developed an electric double-layer capacitor (EDLC) or supercapacitor with a composite structure consisting of a solid polymer electrolyte matrix and glass fiber fabric separator. The areal capacitance of this supercapacitor was approximately 8.9 mF/cm^2. Qian *et al*. [9] improved the supercapacitor using a carbon aerogel, obtaining an areal capacitance of 640 mF/cm^2. Although the modified supercapacitor exhibited a higher areal capacitance by around the order of 1 F/cm^2 than that without the carbon aerogel, its voltage resistance was smaller than that of a film capacitor. The voltage resistance of a supercapacitor is approximately 1 V, while that of a film capacitor is approximately 10 kV. The extremely high voltage charged to a capacitor is not safe for regeneration capacitors in automobiles during service because it may easily cause an electrical short if damaged. Therefore, a supercapacitor is preferable over a film capacitor for regenerated energy storage in automobiles.

In the structural supercapacitor developed by Shirshova *et al*. [7] [8], the solid polymer electrolyte caused the capacitor to possess high internal resistance and thus low power density. A new method to produce a supercapacitor with lower internal resistance is desired. One method to achieve this is to use liquid electrolyte solution instead of a solid polymer electrolyte. However, using a liquid electrolyte solution is a considerable drawback from the structural viewpoint because it decreases the stiffness and strength of the structure. Recent development of supercapacitors is reviewed in the reference [10].

In the present study, a new structure consisting of a form core sandwich with high water retention is proposed and the possibility of a supercapacitor with such a structure is experimentally investigated. Because activated carbon sheets are used as electrodes in the supercapacitor, the present approach is not strictly speaking a structural capacitor. Woven carbon fabric is used simply as lead wires of the supercapacitor with a form core sandwich structure. This new structure is expected to have low internal resistance and high capacitance. We examine the electric properties of the supercapacitor composed of a form core sandwich composite; its mechanical properties will be evaluated elsewhere.

2. Concept of a Capacitor Composed of a Form Core Sandwich Composite

The concept of the form core sandwich capacitor is depicted schematically in **Figure 1**. The skin of the sandwich structure was a woven fabric of carbon fiber-reinforced polymer (CFRP). The woven CFRP sheets act as structural support and lead wires, as well as protecting the supercapacitor. The woven CFRP fabric was infused with epoxy resin. After curing, part of the CFRP surface was polished with sand paper to make an electric contact with the electrode.
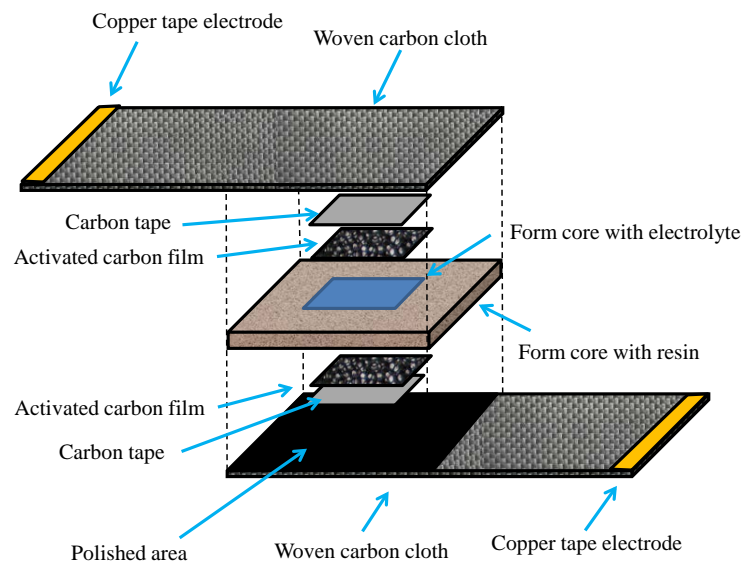

Figure 1. Schematic representation of a form-core capacitor for woven carbon skin composites.

The electrodes of the supercapacitor must have a large surface area to realize large capacitance. Usually, electrodes are composed of materials like activated carbon or carbon nanotubes to realize large surface area. In the present research, activated carbon sheets were used as electrodes to minimize cost. To form an electrical contact with the woven CFRP fabric, double-sided carbon adhesive tape was used, as shown in **Figure 1**. The central square area of the thin form core was immersed in liquid electrolyte solution. This immersed region was used as the supercapacitor.

Because the liquid electrolyte solution and activated carbon electrodes are separated from the structural woven CFRP fabric, this new supercapacitor system does not have problems from a structural point of view. In addition, because this system uses liquid electrolyte solution, the internal resistance of the capacitor is lower than that of a system using an electrolyte polymer matrix. This supercapacitor system should also have high capacitance without the drawback of structural degradation that affects film capacitors.

The main design challenges facing this new supercapacitor system are to find an appropriate form core to retain the liquid electrolyte solution, determine how to seal up the capacitor in the form core sandwich structure, and establish how to include the liquid electrolyte solution in the form core sandwich after it is made. The capacitance of the new supercapacitor system is experimentally measured in the present study.

3. Fabrication of the Form Core Sandwich Composite

3.1. Selection of a Form Core

The new system needs to include an optimum form core that has the ability to hold electrolyte solution while retaining ion conductivity in the through-thickness direction of the form. Three types of form core materials were experimentally investigated, as shown in **Figure 2**.

The first form core was composed of polyvinyl chloride (Divinycell H80, BASF Japan Ltd, Tokyo, Japan) with a thickness of 4 mm (**Figure 2(a)**). The second form core was made of polymethacrylimide (Rohacell, IG51, Dicel-Evonik Ltd, Tokyo, Japan) with a thickness of 1 mm (**Figure 2(b)**). The third form core was composed of polystyrene (moisture absorption type, Sekisui Plastic Co. Ltd, Osaka, Japan) with a thickness of 0.4 mm (**Figure 2(c)**). Both Divinycell and Rohacell are typically used in lightweight sandwich structures for aircraft. Both have high compressive strength and are commercially available in many countries as typical form core sandwich materials. The water-absorbent polystyrene form core is specially designed to keep water inside the form, and is typically used in trays to keep food warm in Japan. The commercially available polystyrene form had open cells on the top surface, while the bottom surface was closed to prevent leakage of water. In the present study, the solid polystyrene bottom surface was mechanically removed to obtain a water-permeable form core.

To investigate the ability of the form cores to keep electrolyte solution inside them while retaining ion conductivity in the through-thickness direction, water colored with red ink was added dropwise on the surface of each form core. A uniform surface area with dimensions of 20 × 20 mm was first prepared using masking tape,
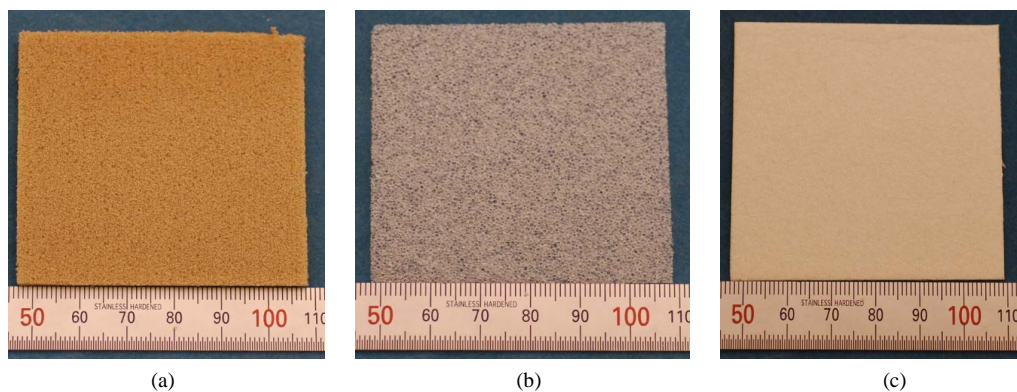

(a) (b) (c)

Figure 2. Three types of form used in the present study. (a) Polyvinyl chloride (Divinicell) form (4 mm thickness); (b) Polymethacrylimide (Rohacell) form (1 mm thickness); (c) Polystyrene (moisture absorption type) form (0.4 mm thickness).

as illustrated in **Figure 3**. The surface of each form core after the addition of red ink is also displayed in **Figure 3**. The Divinycell had residual red ink on its top surface (**Figure 3(a)**), as did the Rohacell (**Figure 3(b)**). In contrast, the polystyrene form absorbed all of the red ink, as shown in **Figure 3(c)**.

Figure 4 shows the ink leaked from the back surface of each form core onto a sheet of paper placed there. The Divinycell form core had some water permeability (**Figure 4(a)**), while the Rohacell was not water permeable because the paper was completely dry (**Figure 4(b)**). These indicate that these form cores are not appropriate because the paths for ions are small number or there is no path. Meanwhile, **Figure 4(c)** reveals that the polystyrene form core was completely water permeable. These results show that the polystyrene form core is appropriate for keeping liquid electrolyte solution inside it when both surfaces are completely sealed. Moreover, the polystyrene form is very thin (0.4 mm thick), so we can make a thin sandwich panel using this polystyrene form core. Therefore, we used the polystyrene form core to construct the sandwich structure in the present study.

3.2. Woven CFRP Cloth with an Electrically Conductive Surface

In the supercapacitor developed in the present paper, a single ply woven CFRP cloth is used as lead wires. Because the electrodes in the supercapacitor are activated carbon sheets, the woven CFRP cloth needs to exhibit electrical conductivity. To realize electrical contact to the carbon fibers, the surface resin of the woven CFRP composite must be removed. We polished the CFRP cloth with sandpaper to make electrodes as reported previously [11].

The woven CFRP composite cloth plate with an area of 250 mm^2 was made by resin infusion molding. The woven CFRP cloth (SA-3102, 13 μm thickness, Sakai Ovex Co. Ltd., Fukui, Japan) had a thickness of 0.013 mm. The epoxy resin (Z2/H02, GH Craft Ltd., Gotenba, Japan) was cured at room temperature.

After curing, samples of the woven CFRP plate that were 100 mm long and 50 mm wide were made. Half of each sample (50 × 50 mm) was polished using sandpaper to remove the surface resin. The removal of resin in
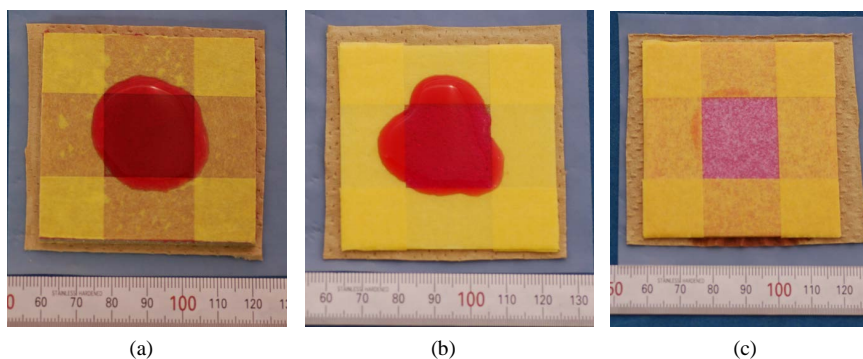

(a)   (b)   (c)

Figure 3. Water-holding capability test results (a drop of red ink is placed on the surface of three types of form). (a) Polyvinyl chloride (Divinicell) form (4 mm thickness); (b) Polymethacrylimide (Rohacell) form (1 mm thickness); (c) Polystyrene (moisture absorption type) form (0.4 mm thickness).
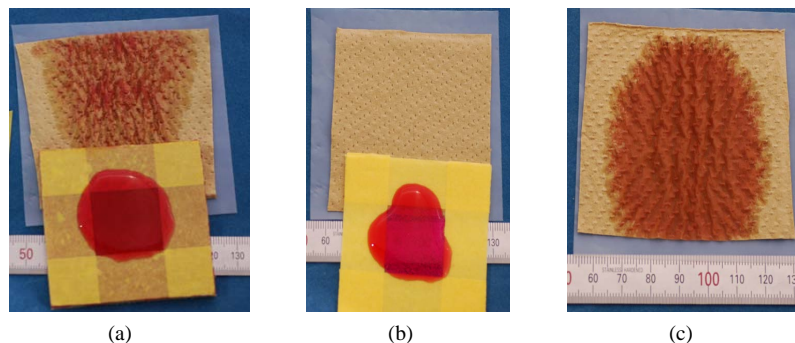

(a)   (b)   (c)

Figure 4. Permeated water results of the three types of form core. (a) Polyvinyl chloride (Divinicell) form (4 mm thickness); (b) Polymethacrylimide (Rohacell) form (1 mm thickness); (c) Polystyrene (moisture absorption type) form (0.4 mm thickness).

the polished area of the plate was confirmed using a digital microscope (KH-1300, HiroxInc, Tokyo Japan) as shown in **Figure 5**. In **Figure 5**, the right side is the unpolished area and the left side has been polished. The conductivity of the polished area was confirmed using a LCR meter (3522, Hioki Co. Ltd., Japan). The other end of the woven CFRP plate was also polished and used as an electrode. Using copper tape, an electrode was made at the end of the woven CFRP plate. As shown in **Figure 1**, double-sided carbon adhesive tape with a thickness of 0.16 mm was attached onto the surface of the polished woven CFRP plate. The other side of the carbon adhesive tape was attached to an activated carbon sheet ($40 \times 40 \times 0.15$ mm, Nippon Valqua Industries Ltd., Tokyo Japan), as illustrated in **Figure 1.**

3.3. Fabrication of the Supercapacitor Containing a Form Core Sandwich Composite

A square polystyrene form core with sides of 60 mm was prepared. The polystyrene form core was 10 mm wider than the width of the woven CFRP plate. This was to prevent unexpected electrical shorting between the top and bottom woven CFRP plates. This extra width can be removed after fabrication of the supercapacitor.

The center area of the polystyrene form core (40×40 mm) was left vacant to fill with liquid electrolyte solution after making the sandwich structure. To prevent leakage of the liquid electrolyte solution from the four sides of the form core, the surrounding polystyrene form core was infused with epoxy resin ($Z2/HO_2$). The central vacant square of the polystyrene form core was aligned with the activated carbon sheet attached to the woven CFRP plate, and the woven CFRP plate was bonded with epoxy resin, as shown in **Figure 6**. As the woven 0/90 fabric cloth has isotropic electric conductance, fiber direction is not important for the electrical point of view. In the present study, the fiber direction is aligned to the specimen longitudinal direction and transverse direction as shown in **Figure 6**. The dimension of the vacant area of the foam core should be optimized with considering mechanical properties. That is our future work.

Another woven CFRP plate was similarly bonded to the other side of the polystyrene form core except for an opening left to fill the central vacant area of the polystyrene form core with liquid electrolyte solution. A sheet of polytetrafluoroethylene was used to make this opening, as depicted in **Figure 7**. The sample was sandwiched between aluminum plates and held using vices during curing.
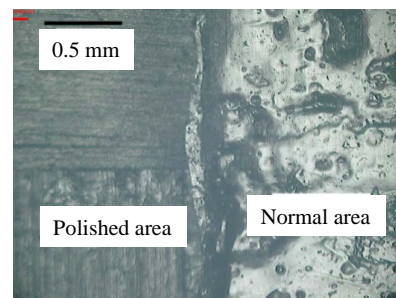

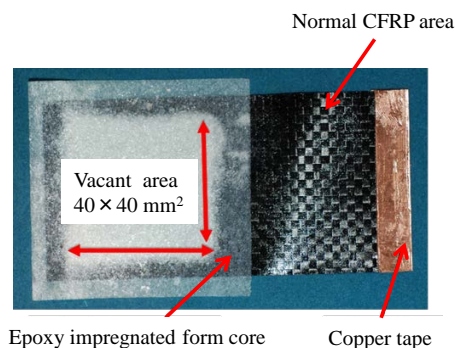**Figure 5.** Surface observation of the polished area made to realize electric contact.

Figure 6. Configuration of form core pre-preprocess to make a form-core capacitor.

Polytetrafluoroethylene sheet
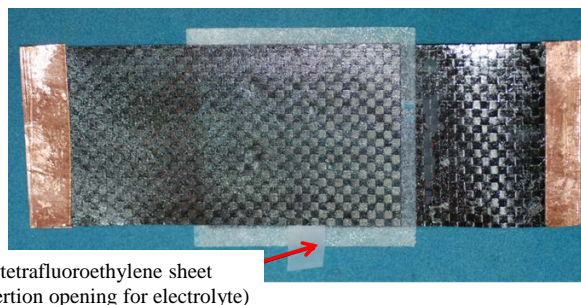(insertion opening for electrolyte)

Figure 7. Process to make insertion opening for electrolyte.

There are several kinds of liquid electrolyte solution available to use in supercapacitors. Liquid organic electrolyte solutions possess higher voltage strength than liquid inorganic electrolyte solutions. This means that the total stored energy of the supercapacitor using an organic electrolyte solution is higher than that using an inorganic electrolyte solution. However, organic electrolyte solutions are easily degraded by moisture. In the present study, a 10 wt% solution of copper sulfate was used as the electrolyte to allow easy handling during the fabrication process. The solution of copper sulfate (approximately 640 mm^3) was injected into the opening of the sample, and then the opening was closed using epoxy resin (Z2/HO$_2$).

4. Measurement of the Capacitance of the Supercapacitor with a Form Core Sandwich Structure

4.1. Measurement Methods

Two methods were used to measure the capacitance of the supercapacitor with a form core sandwich structure in the present study. The first was cyclic voltammetry, and the second was chronoamperometry. Cyclic voltammetry uses constant rate voltage increases and decreases to determine capacitance by measuring the current during the voltage sweeps. The capacitance $C(t)$ at time (t) can be calculated as follows,

$$C(t) = \frac{\int_0^t I(t)\,\mathrm{d}t}{V(t)} \tag{1}$$

where $V(t)$ is the voltage at t, and $I(t)$ is the electric current at t.

Chronoamperometry uses a constant voltage and measures changes in electric current. This method requires a circuit model to identify parameters such as capacitance and internal resistance. In the present study, a circuit model including a capacitor and two resistors was used, as shown in **Figure 8**. Non-linear parameter fitting was performed and the two resistors and capacitor were identified. The electric current of the circuit in **Figure 8** can be calculated as follows [8],

$$I(t) = \frac{V_a}{R_s}\mathrm{e}^{-t/\tau} + \frac{V_a}{R_s + R_p}\left(1 - \mathrm{e}^{-\frac{t}{\tau}}\right) \tag{2}$$

$$\tau = \frac{R_s R_p}{R_s + R_p}C \tag{3}$$

where R_s is the resistor connected in series and R_p is the resistor connected in parallel in **Figure 8**, and C is the capacitor. Cyclic voltammetry gives reliable capacitance measurements, while chronoamperometry allows internal resistance to be determined.

A potentiostat/galvanostat (Versastat 4, Princeton Applied Research, Oak Ridge USA) was used to measure the capacitance of the sample. In the present study, because the electrolyte was a solution of copper sulfate, the maximum voltage was set to 0.5 V to prevent insulation breakdown of the EDLC.

4.2. Results and Discussion

Figure 9 shows the results obtained by cyclic voltammetry. The abscissa is the charged voltage and the ordinate
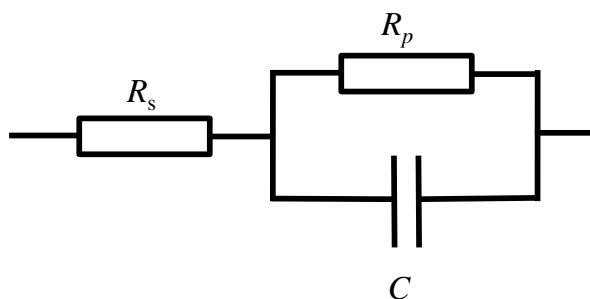
Figure 8. Circuit model to measure capacitance and resistances for the chrono amperometry.
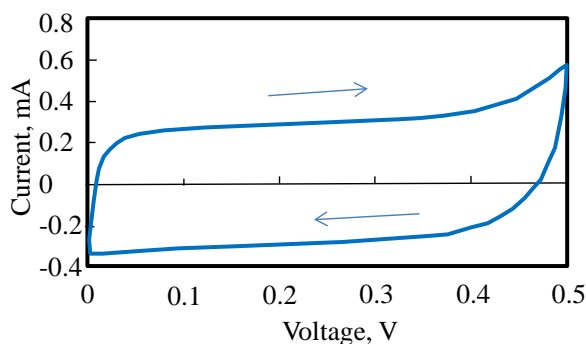

Figure 9. Measured results using the cyclic voltammetry.

is the measured current. The voltage change rate was 0.1 mV/s, and three cycles were performed. The electric current-voltage curve is almost rectangular in shape. Let us consider the capacitance:

$$Q = CV \tag{4}$$

$$I = \frac{\mathrm{d}Q}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t} \tag{5}$$

where Q is electrical charge, V is voltage, C is capacitance, and I is electric current. Equation (5) shows that capacitance can be easily calculated when the voltage change ratio is constant. In the present study, the capacitance was calculated using an increasing time period of voltage. The measured capacitance was 3.1 mF. Because the area of the sample was 40×40 mm = 16 cm^2, the areal capacitance is 520 mF/cm^2, which is approximately 106 times higher than that of a film capacitor. This indicates that an EDLC has successfully been fabricated, although the capacitance is a little bit smaller than that achieved by Qian and co-workers [9]. The maximum capacitance of this structure can be improved using electrodes that have a larger surface area such as carbon nanotubes [12] [13]. The advantages of this new system are easy handling during the fabrication process and its light weight because of the form core.

Figure 10 displays the results of chronoamperometry measurements. The abscissa shows time and the ordinate is measured electric current. In chronoamperometry measurements, a step voltage of 0.5 V was applied for 3600 s. The blue curve is the measured results and the red curve shows the results of curve fitting using Microsoft Excel to Equation (2). R_s is 50.7 Ω, and R_p is 490 Ω. The measured capacitance is 3.6 mF, which is consistent with the value of 3.1 mF measured by cyclic voltammetry. Because the curve fitting is poor at short t, the capacitance determined by chronoamperometry is not accurate. However, chronoamperometry gives relatively accurate resistances when the curve fitting is performed using a long t.

Table 1 presents the energy density and power density of the supercapacitor with a form core sandwich structure. Because copper sulfate solution undergoes voltage strength around 1 V, the voltage limit was set to 0.8 V. The energy and power densities in **Table 1** are the converted values to 0.8 V. The electrode area is only 16 cm^2, so the extremely high capacitance obtained indicates that the developed form core sandwich structure behaves as an EDLC. We intend to report the mechanical properties of this new system soon.
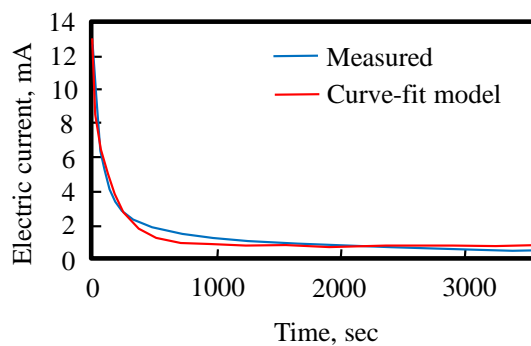
Figure 10. Measured results using the chronoamperometry to measure capacitance.

Table 1. Measured results of form-core supercapacitor composites (converted to 0.8 V).

Areal capacitance [mF/cm^2]	520
Specific capacitance [mF/g]	845
Surface resistance [Ω/cm^2]	810
Energy density [mWh/kg]	57.1
Peak power density [mW/kg]	563

5. Conclusions

In the present study, a supercapacitor with a new form core sandwich composite structure is proposed. Because this method uses liquid electrolyte solution to make the EDLC, the internal resistance is small, and extremely high capacitance is obtained. The results are summarized as follows.

1) A water-absorbent polystyrene form core with a thickness of 0.4 mm is appropriate for keeping liquid electrolyte solution in the sandwich structure.

2) The developed supercapacitor exhibits high capacitance compared with that of film-type structural capacitors, and realizes EDLC with small internal resistances. High areal capacitance of 520 mF/cm^2 and low surface resistance of 810 Ωcm^2 were obtained.

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