



# Rate and cycle performances of supercapacitors with different electrode thickness using non-aqueous electrolyte



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## ABSTRACT

Activated carbons (AC) powder was coated onto Al current collectors with different thickness ( $\sim 30$  and  $\sim 80 \mu\text{m}$ ) for use as electrodes of supercapacitors. The relationship between the electrode thickness and the specific capacitance of the supercapacitor cells using a non-aqueous electrolyte was investigated under different charge–discharge current density and for charge–discharge cycling at constant current density. Two types of microporous AC powders of which specific surface areas were  $1454$  and  $2587 \text{ m}^2/\text{g}$  were deposited using a binary binder composed of styrene-butadiene rubber and sodium carboxymethyl cellulose. The rate stability of the specific capacitance was shown to be independent of the electrode thickness, and thinner electrodes could maintain higher specific capacitance regardless of the AC type. Thicker electrodes allowed a larger increase in equivalent series resistance with cycling, decreasing the voltage allocated to the formation of the electrical double-layer and thus reducing the specific capacitance. Microscopic surface observation showed that the thicker electrodes exhibited voids resulting from reduced adhesion among AC particles. The reduced adhesion and the electrolyte decomposition in the thicker electrodes were likely to be connected to their performance deterioration.

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## 1. Introduction

An interface between an electrically conductive solid and an electrolyte across which voltage is applied produces two layers of polarized ions in the electrolyte. The electrical double-layer consists of the Helmholtz layer, which is responsible for the physical adsorption of ions on the solid surface, and the diffusion layer, related to the concentration gradient of ions. An external energizer connected to two conductive solids, the positive and negative electrodes, forms two electrical double layers on the respective electrodes, realizing a repetition of charge accumulation and release. Supercapacitors are energy storage devices based on the above mechanism. Physical adsorption-desorption of ions at the interface between the electrode material and the electrolyte, without an involvement of faradaic reactions, provides the supercapacitor outstanding high power density ( $5\text{--}10 \text{ kW/kg}$ ) and long cycle life ( $>5 \times 10^5$  cycles) [1], promoting their application for areas such as renewable power generation systems and next-generation vehicles.

Higher capacitance of supercapacitors is obtainable by increasing the area of the double-layer formation. Hence, activated carbon (AC) is widely used as the active material owing to the large specific surface area (approximately,  $1000\text{--}3000 \text{ m}^2/\text{g}$ ), low cost, and high chemical stability. Commercial electrodes of supercapacitors are generally fabricated by coating powdered active material onto an Al current collector, which provides better conductivity by minimizing the charge path length in the AC [2]. A binder and a conductive agent are incorporated in the electrode to enhance the adhesion to the current collector and among AC particles, and to increase the electrode conductivity (or to reduce the internal resistance), respectively [3]. Most commercial electrodes are fabricated using slurry composed of AC, a binder, a conductive agent and a solvent. The slurry is applied onto the current collector at a controlled thickness and dried [4]. The electrolytes used in commercial supercapacitors can be divided aqueous and non-aqueous types. Aqueous electrolytes, e.g.,  $\text{H}_2\text{SO}_4$  and  $\text{KOH}$  solution, are low cost, have good safety implications, long cycle life, and low internal resistance [5]. However, non-aqueous electrolytes enable a high withstanding voltage of  $>2.5 \text{ V}$ , leading to higher energy density than aqueous electrolytes. Typical non-aqueous electrolyte formulations used in supercapacitors are quaternary ammonium salts dispersed in a solvent with high permittivity. Tetraethyl ammonium tetrafluoroborate/acetonitrile or propylene carbonate

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(TEA·BF<sub>4</sub>/AN or PC) and triethylmethyl ammonium tetrafluoroborate/acetone nitrile or propylene carbonate (TEMA·BF<sub>4</sub>/AN or PC) are typical mixtures for commercial supercapacitors [6]. In spite of their high internal resistance resulting from high viscosity and low conductivity, flammability, and high cost, non-aqueous electrolytes are now becoming a mainstream of commercial supercapacitors because they allow higher energy density.

The roles of type and level of binders [3,7–12] and conductive agents [12–16] in the electrochemical performance of AC-based electrodes have been intensively studied. Tsay et al. has investigated the effect of the electrode thickness on its specific capacitance in the aqueous electrolyte: 0.5 mol/L (M) Na<sub>2</sub>SO<sub>4</sub> [12]. Using a polytetrafluoroethylene (PTFE) binder, AC powder of unknown textural structure was molded into 2 cm × 2 cm electrode sheets, with thickness range 50–300 μm. Sheets with thickness 100–200 μm showed higher specific capacitance of ~85 F/g (half-cell value) in cyclic voltammetry (CV) and a galvanostatic charge–discharge test using two-electrode cells. However, a relationship between the thickness of electrode and its rate and cycle stabilities was not investigated [12]. Furthermore, the cell system employed was quite different from recent commercial supercapacitors using non-aqueous electrolytes and AC-coated Al foil electrodes produced through aqueous processing.

A thicker electrode is capable of realizing higher energy density supercapacitors. However, thicker coatings may also increase the internal resistance [17]. Depending on whether a supercapacitor is constructed to optimize energy density or power density, electrode thickness of commercial cells ranges from approximately 10 μm (high power density) to several hundred μm (high energy density) [18]. Fluorinated thermoplastic binders such as PTFE and polyvinylidene difluoride (PVDF) have been used for the commercial electrodes. While PTFE can be dispersed in water and thus enables aqueous processing, it prohibits direct casting onto a metal current collector and requires pressing to achieve good adhesion to the current collector [10]. On the other hand, PVDF can be dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent and mixed with AC and a conductive agent [12]. The slurry is coated onto the metallic current collector and dried, producing a stable electrode layer on the current collector. However, PTFE and PVDF binders can be a source of fluorine pollution and are rather expensive (15 euro/kg) [3]. The use of NMP solvent further increases the cost of using PVDF and its toxicity is harmful to human health and the environment. A binary binder system composed of styrene-butadiene rubber (SBR) and carboxymethyl cellulose (CMC), enabling aqueous processing, has been used for negative graphite and Si-based electrodes in lithium ion batteries [19–22]. The SBR/CMC system provides advantages of aqueous processing and stable adhesion to the current collector [11]. However, water-solubility of CMC restricts its use with aqueous electrolytes.

The present study provides new insight regarding the rate and cycle performances of supercapacitors compatible with modern fabrication methods. Two types of commercial ACs intended for supercapacitor applications and a typical non-aqueous electrolyte, 1 M TEA·BF<sub>4</sub>/PC, were used. The specific capacitance of AC electrodes with coating thickness ~30 and ~80 μm, using the SBR/CMC binder system, was evaluated under different charge–

discharge current density (0.01–10 mA/cm<sup>2</sup>) and for charge–discharge cycling at constant current density (10 mA/cm<sup>2</sup>, 50000 cycles). The electrodes before and after the charge–discharge testing were microscopically observed to probe their changes in electrochemical performance. Combining these outcomes, the roles of electrode thickness in the rate and cycle stabilities of supercapacitors were deduced.

## 2. Experimental

### 2.1. Sample ACs and electrode preparation

Two types of AC powders (AP15, AT Electrode Co., Ltd., Japan; and RP25, Kuraray Chemical Co., Ltd., Japan), both made from a phenolic resin and with a microporous structure, were coated on an Al foil current collector. The Brunauer–Emmett–Teller (BET) specific surface areas of AP15 and RP25 were measured as 1454 and 2587 m<sup>2</sup>/g, respectively, using the nitrogen adsorption–desorption isotherm obtained by a gas adsorption analyzer (Autosorb-iQ, Quantachrome Instruments Inc., USA). The mean pore widths of AP15 and RP25 were also measured as 2.0 and 2.1 nm, respectively, based on the above isotherms. The median diameters of AP15 and RP25 powders were 4 and 5 μm, respectively, evaluated using a laser diffraction particle size analyzer (SALD-300 V, Shimadzu Corp., Japan).

The binder was a binary system composed of SBR (TRD2001, JSR Corp., Japan) and sodium carboxymethyl cellulose (Na-CMC; Cellogen 7A, DKS Co. Ltd., Japan). Acetylene black (AB; Denka Black, Denki Kagaku Kogyo Kabushikikaisya, Japan) was used for the conductive agent. The mixture of AC, SBR (5 mass%), Na-CMC (5 mass%), and AB (10 mass%) was dispersed in distilled water. The water-based slurry, produced using a rotary kneader (AR-100, Thinky Corp., Japan), was coated on the Al foil (t20 μm) using a baker-type applicator, and then dried at 100 °C for more than 6 h. The electrode thickness was varied by changing the slit width of the applicator.

### 2.2. Cell assembly

The assembled electrode sheets were punched into φ15 mm discs and degassed at 140 °C for more than 6 h. The mass and the thickness of the positive and negative electrodes were chosen to be similar from among the discs produced. The coating thickness was measured using a micrometer (293–821, Mitutoyo Corp., Japan). Table 1 shows the sample identification of the AC-coated electrodes. A denser structure was produced for electrodes using AP15, which had lower porosity than those using RP25.

The positive electrode, a piece of cellulose-type separator (φ 23 mm, t55 μm; TF4050, Nippon Kodoshi Corp., Japan) which was degassed at 120 °C for more than 6 h, and the negative electrode were sealed with the electrolyte (1.0 mL) in the two-electrode Al cell system (HS cell, Hohsen Corp., Japan). The 1 M TEA·BF<sub>4</sub>/PC (Ube Industries, Ltd., Japan) electrolyte was used without further purification.

All processes for cell assembly were performed in an argon-filled glove box.

**Table 1**  
Identification and properties of the φ15 mm electrode samples.

ID	AP15t34	AP15t86	RP25t26	RP25t78
Type of AC	AP15	AP15	RP25	RP25
Thickness (μm)	34	86	26	78
Total mass of AC in positive and negative electrode (mg)	5.48	14.76	3.18	9.97
Bulk density of AC in positive and negative electrode (g/cm <sup>3</sup> )	0.91	0.97	0.69	0.72

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