

# Thin Film Energy Storage Device with Spray-Coated Silver Paste Current Collector

Seong Man Yoon, Yunseok Jang, Jeongdai Jo, and Jeung Sang Go

**This paper challenges the fabrication of a thin film energy storage device on a flexible polymer substrate specifically by replacing most commonly used metal foil current collectors with coated current collectors. Mass-manufacturable spray-coating technology enables the fabrication of two different half-cell electric double layer capacitors (EDLC) with a spray-coated silver paste current collector and a Ni foil current collector. The larger specific capacitances of the half-cell EDLC with the spray-coated silver current collector are obtained as 103.86 F/g and 76.8 F/g for scan rates of 10 mV/s and 500 mV/s, respectively. Further, even though the half-cell EDLC with the spray-coated current collector is heavier than that with the Ni foil current collector, smaller Warburg impedance and contact resistance are characterized from Nyquist plots. For the applied voltages ranging from  $-0.5$  V to  $0.5$  V, the spray-coated thin film energy storage device exhibits a better performance.**

**Keywords:** Current collector, Electric double layer capacitor, Energy storage, Spray coating.

## I. Introduction

Recent demands on electric energy storage devices for portable and flexible electronic systems are centered towards characteristics such as compactness, light weight, cost effectiveness, and flexibility. Further, these devices require a thin-film fabrication process, high capacitance, improved safety, and higher yield of mass manufacturing. Conventional charge storage devices such as batteries do not meet these demands because they are heavy and bulky [1]. Electrochemical double layer capacitors (EDLCs), known as super-capacitors, are best suited for these requirements and are complementary to batteries because of their large energy storage capacity and printability on a flexible polymer film.

EDLCs generally comprise two pairs of carbon-based electrodes and current collectors on a polymer film with double-layers of charge at an electrolyte interface. A variety of materials and fabrication processes have been developed to construct the EDLCs. Carbon-based materials such as carbon nanotubes (CNT) [2]–[4], graphene [5], and activated carbon [6]–[10] have been studied for electrode fabrication. Activated carbon-based super-capacitors have been most developed because of their low fabrication cost, large capacitance, and long cycle time [11]. Further, electrolytes have been exploited to improve electrochemical properties [8]–[19]. For the current collector, thin metal foils of nickel, copper, and titanium have been commonly used.

However, using a metal foil as the current collector on a flexible polyethylene terephthalate (PET) substrate causes problematic deformation resulting from the mismatch between the metal foil and the PET substrate during fabrication and this results in wrinkles and warpage. Thus, instead of using thin metal foils, coating single-walled carbon nanotubes (SWCNTs) was reported [1]. The

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SWCNT thin films can be easily deposited on the PET substrate by spray coating or other coating methods. However, an additional process should be developed to obtain better adhesion and electrical conductivity because there is weak adhesion between the SWCNTs film and the PET substrate.

All solution-based EDLC fabrication enables solving the deformation of the metal foil and the weak adhesion of the SWCNTs. Material properties such as rheological properties, dispersion stability, and surface characteristics have a significant impact on the performance of the EDLC, and they also depend on the fabrication method for high-quality printability [20].

Various printing methods such as gravure, offset, and screen printing have been studied for mass manufacturing; however, spray coating to print EDLCs has not been reported because of the requirement of masks [21]. However, by adapting the roll-to-roll process with multiple nozzles, spray coating can be used for mass manufacture. In this study, two different EDLCs with the spray-coated silver current collector and with the Ni foil were fabricated on the flexible polyimide (PI) film instead of the PET film. The electrochemical performances of the two half cells of EDLCs were compared.

## II. Preparation of Materials

A printable silver paste (ES ink, NPK) was prepared for the current collector and its specification is summarized in Table 1. In order to apply it for the spray coating process, the rheological properties of the silver paste were manipulated by adding ethylene glycol. The solid content decreased to 66% after adding ethylene glycol. Figure 1 shows that the designed silver paste behaves like Newtonian fluid. The viscosity of the silver paste was almost constant and the shear stress increased linearly with the increased shear strain rate.

In the experiment, two different current collectors of the Ni foil (LS388465 VCS, Goodfellow Cambridge Limited) and the spray-coated silver paste (ES ink, NPK) were fabricated and compared. Activated carbon (US Research Nanomaterials Inc.) with a diameter of < 100 nm, specific

Table 1. Specification of the silver paste.

Solid content (wt%)	Particle size (nm)	Viscosity (mPa·s)	Specific resistance ( $\Omega\cdot\text{cm}$ )	Drying temperature ( $^{\circ}\text{C}$ )/time (min)
86.7	40–100	5,000–10,000	$2.0 \times 10^{-5}$	145/2

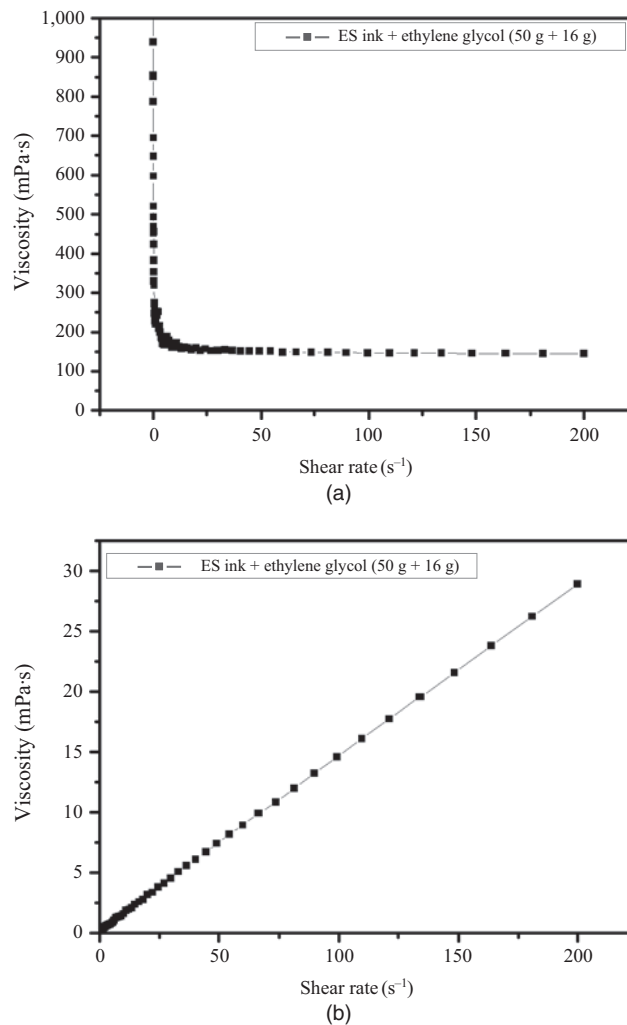


Fig. 1. Rheological characteristics of silver paste: (a) viscosity versus shear rate and (b) shear stress versus shear rate.

surface area of  $1,300 \text{ m}^2/\text{g}$ , and coconut shell as a raw material was used to make electrode ink. Polyvinylphenol and poly (melamine-co-formaldehyde) were used as a polymeric matrix and a cross-linking agent, respectively. Then, they were dissolved in propylene glycol methyl ether acetate [22]. The solid content of the electrode ink was 1.5 wt%.

The silver paste was coated on the heat resistant flexible PI film (U-pilex 75S, Ube industries, Ltd.) by using spray coating and patterned with  $5 \text{ cm} \times 5 \text{ cm}$  mask. The spray-coated silver current collector was dried at  $200 \text{ }^{\circ}\text{C}$  on a hot plate for 30 min. Figure 2 shows the measured thickness of the spray-coated silver current collector. The thickness was measured using a confocal microscope (C-130, OPTELICS) and it is  $\sim 82 \text{ }\mu\text{m}$  including the thickness of the PI film.

During the fabrication process, the weight of the PI film changed after the drying process. It is important to

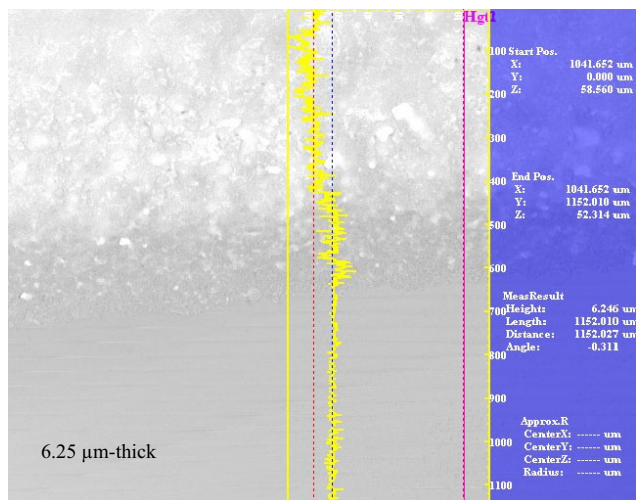


Fig. 2. Thickness measurement result of the coated silver current collector.

measure the mass of the activated carbon to measure the specific capacitance. However, it cannot be measured accurately after completing the fabrication of the electrode. Thus, the mass change of the PI film was examined with respect to time. It was preheated at 250 °C on the hot plate. The change of the weight of the PI film was measured as shown in Fig. 3. It did not change after 10 min of heating because it was preheated at a temperature of 250 °C.

Then, the activated carbon electrode was coated by spray coating on the spray-coated silver current collector and the Ni foil current collector. They were cured at 200 °C for 30 min on the hot plate. The mass of the spray-coated activated carbon electrode on the patterned silver current collector was measured to be 1.15 mg and that on the Ni foil was 1.19 mg. The sheet resistances of the spray-coated silver current collector and the Ni foil

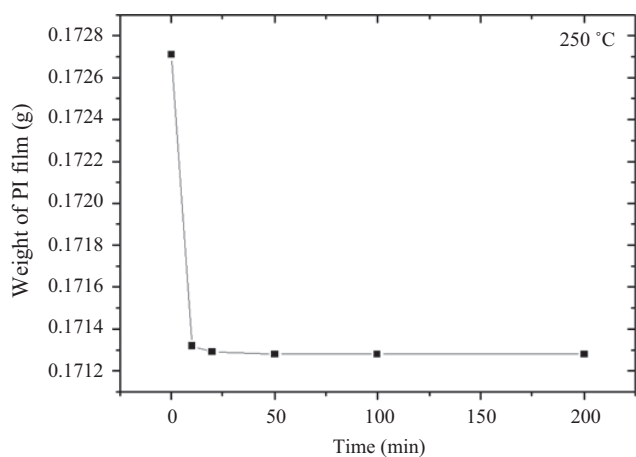


Fig. 3. Change in the PI film weight with heating time.

were between 1.6 mΩ/□ to 3 mΩ/□ and 0.9 mΩ/□ to 1.1 mΩ/□, respectively.

### III. Results and Discussions

The electrochemical properties of the half cells of the EDLC were evaluated by using cyclic voltammetry (CV) for the application of input voltages ranging from -0.5 V to 0.4 V for the spray-coated silver current collector and -0.5 V to 0.5 V for the Ni foil current collector.

The CV measurement was conducted using an electrolyte of 1 M Na<sub>2</sub>SO<sub>4</sub> with scan rates ranging from 10 mV/s to 500 mV/s. In order to prevent the chemical reaction between the acid-based electrolyte and silver, a nonelectrolyte was used in the experiment.

Figure 4 shows the CV results of the two half cells of the EDLC with the spray-coated silver current collector and with the Ni foil current collector. The CV response shows good agreement with the characteristic behavior of

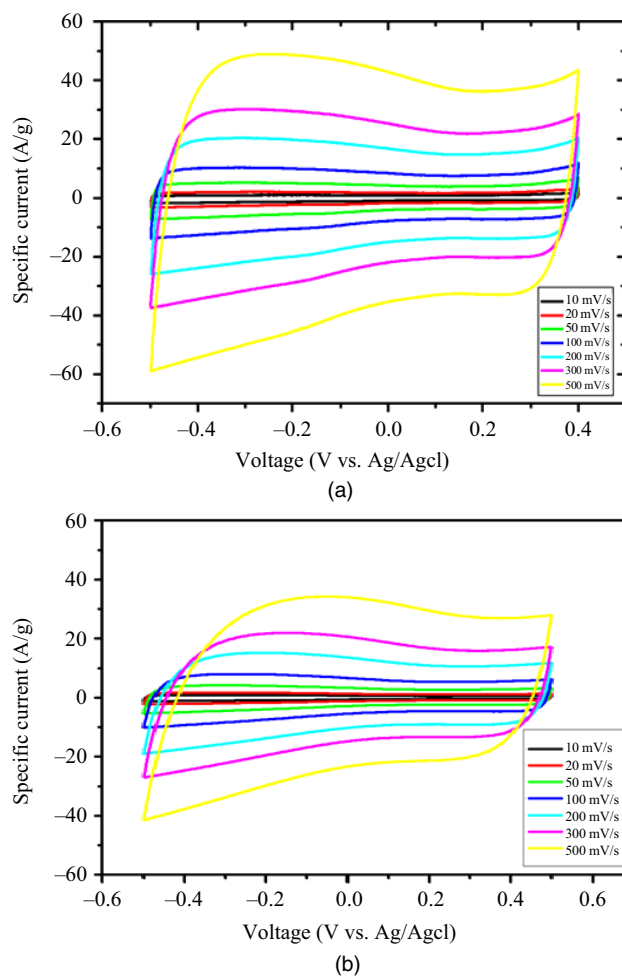


Fig. 4. Cyclic voltammogram: (a) spray-coated silver current collector and (b) Ni foil current collector.

the general EDLC. As the scan rate increased to 500 mV/s, the cyclic voltammogram of the EDLC showed stable performance for the applied voltage ranges.

Specific capacitance was calculated by using the equation  $(q_a + q_c)/(2m\Delta V)$ . Here,  $q_a + q_c$  denotes the electric charge of oxidation and reduction, defined by dividing the area of the cyclic voltammogram by scan rate. Mass  $m$  is the mass of the activated carbon and is obtained from the mass difference between the current collector/PI film and the activated carbon/the current collector/PI film.  $\Delta V$  is the magnitude of potential window [21]. As shown in Fig. 5, the specific capacitances of the half cell with the spray-coated silver current collector were obtained as 103.86 F/g and 76.8 F/g for scan rates of 10 mV/s and 500 mV/s, respectively, while those of the half cell with the Ni foil current collector were 69.74 F/g and 48.31 F/g,

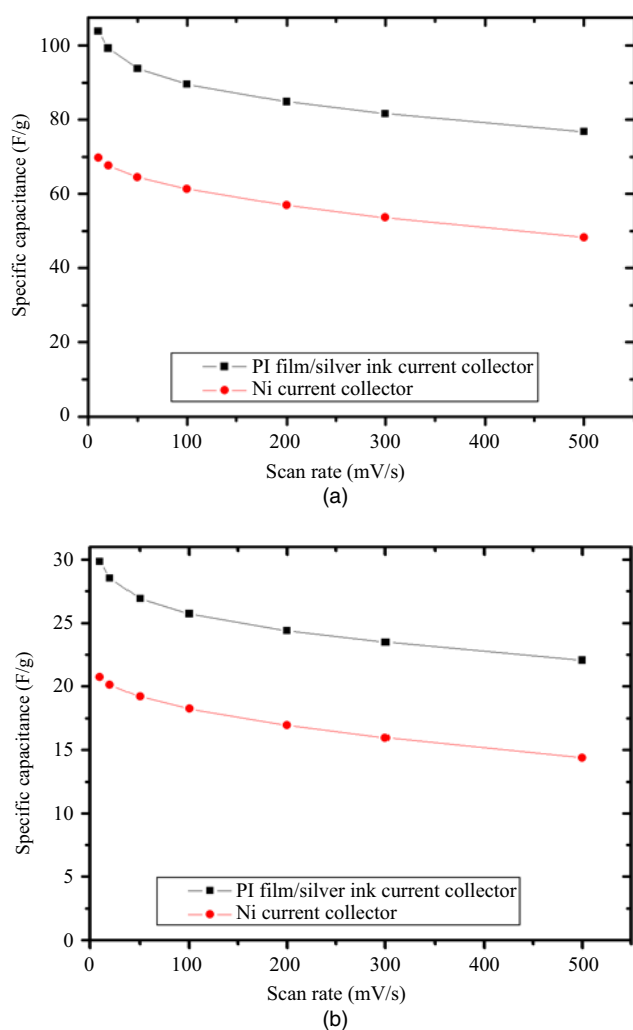


Fig. 5. Calculated specific capacitances versus scan rate: (a) specific capacitances based on the weight of electrode and (b) specific capacitances based on the area of electrode.

respectively. The half cell with the spray-coated silver current collector showed larger specific capacitances with an advantage of being light weight.

Further, to investigate the larger specific capacitance of the half cell with the spray-coated silver current collector, electrochemical impedance spectroscopy was performed. Figure 6 shows the Nyquist impedance plot of the same activated carbon electrode. In general, the appearance and the size of a semicircle in the plot indicate the magnitude of the contact resistance between the electrode and the current collector. A distorted and large semicircle was observed in the Ni foil current collector in the high-frequency region, while in the spray-coated silver current collector, the semicircle was not distinct. This indicates that the spray-coated silver current collector can provide better electrical contact, compared with the Ni foil current collector. In addition, with an increase in frequency, the equivalent series resistance (ESR) of the spray-coated silver current collector moved to the left, compared to that of the Ni foil current collector.

The Bode plot of the fabricated EDLC electrode used to analyze Warburg impedance is shown in Fig. 7. Warburg impedance is a function of frequency, and is related to the diffusion mass transfer of the electrolyte. In the Bode plot, the Warburg impedance can be calculated at the frequency of a  $45^\circ$  phase angle. The Warburg impedance is expressed as

$$Z_W = \frac{\sigma}{\omega^{1/2}} + \frac{1}{\sigma\omega^{1/2}}, \quad (1)$$

where  $\sigma$  is the parameter related with the mass transfer. The Warburg impedance decreases as frequency increases. The frequency of the spray-coated silver current collector was larger than that of the Ni foil current collector at the  $45^\circ$  phase angle. This also means that the Warburg

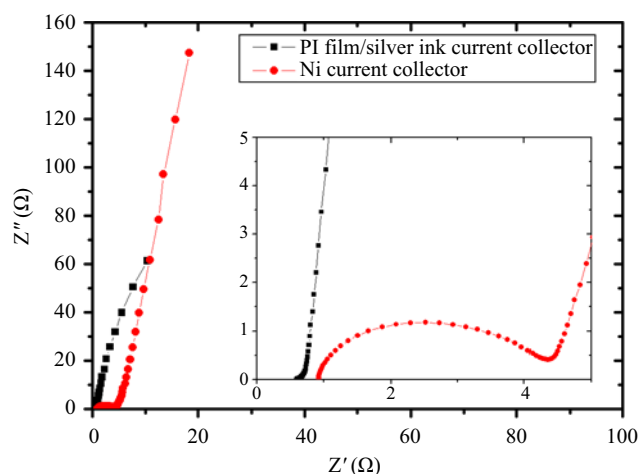


Fig. 6. Nyquist plot of the fabricated electrodes.

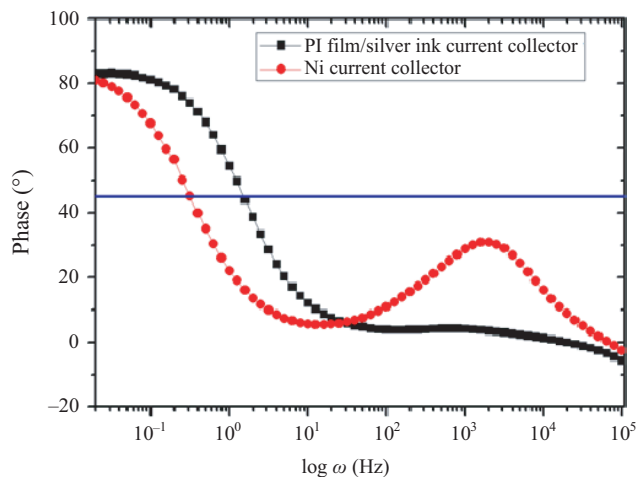


Fig. 7. Bode plot of the fabricated electrodes.

impedance of the spray-coated EDLC with the silver current collector was smaller than that with the Ni foil current collector.

#### IV. Conclusions

The spray-coated thin film EDLC consisted of activated carbon; the silver current collector on the flexible PI substrate was successfully fabricated; and the larger specific capacitance was measured. The calculated specific capacitances of the half cell of EDLC with the spray-coated silver current collector were 103.86 F/g and 76.8 F/g under scan rates of 10 mV/s and 500 mV/s, while those of the half cell of EDLC with the Ni foil current collector were 69.74 F/g and 48.31 F/g. In the Nyquist plot, the larger semi-circle was observed in the cell with the Ni foil current collector, while it was not distinguished in the cell with the spray-coated silver current collector. The electrochemical performances indicate that the spray-coated silver current collector has lower contact resistance between the current collector and the electrode. Further, the ESR and Warburg impedance for the spray-coated silver current collector showed lower value than those for the Ni foil current collector.

By replacing the metal foil current collector with the spray-coated silver current collector, the thin film energy storage device with an EDLC can be fabricated with light weight and high performance. In addition, the measured specific capacitances of the EDLC with the spray-coated current collector can be improved by optimizing the electrode material, thickness, and electrolyte for wearable and portable electronic device applications. For future study, the thermal treatment of the current collector,

electrolyte, electrode material, and process optimization will be examined for performance improvement.

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