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# A study of 3D-printed carbon electrodes for the manufacture of electric double-layer capacitors

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***Abstract*****—** Screen printing, inkjet printing, doctor blade coating and dip coating are among the most common methods that have been developed and researched for the manufacture of supercapacitors. A more recent method to emerge in this field is 3D printing. This research investigates the most effective concentration of carbon conductive paint (CCP) for 3D printing electrodes and current collectors for small cuboidal electric double layer capacitors (EDLCs). The precise CCP used for experiments was Bare Conductive Electric Paint. CCP is designed to create custom conductive surfaces and is compatible with 3D printing. The EDLC samples were produced using a combination of two well-established 3D printing techniques. Several 1.0 mm thick EDLC samples were produced with varying concentrations of CCP to compare electrical performance and printing feasibility. Electrical performance and printability was found to be impacted by the carbon concentration of the CCP. Lower carbon concentrations limited the conductivity of the components printed, while higher concentrations were too viscous to be printed. A ratio of 0.3:3.0 parts CCP to distilled water (specifically 3.0 g CCP and 3 g distilled water) was found to optimize electrical performance of samples that could feasibly be 3D-printed.

***Keywords—Carbon Conductive Paint, Fused Deposition Modelling, Paste Extrusion System, Electrical Performance, Energy Storage Devices***

## I. Introduction

Supercapacitors or electrochemical double-layer capacitors (EDLCs) are capacitors that use electrode materials with high surface area to provide higher capacitance. Thus, supercapacitors are considered promising in the field of energy storage. In EDLCs, the two electrodes are generally placed on metal current collectors, such as copper and aluminium. EDLC devices require the current collectors to be highly conductive because the conductivity of the electrode material is generally inadequate. The material used as current collectors in EDLCs must be electrically conductive and resistant to chemical weathering caused by the electrolyte solution. Based on these requirements, the standard materials used for current collectors are aluminium, steel, and iron [1-4]. Various means of improving the performance of supercapacitor current collectors have been studied previously [5-15]. A coating method was used to manufacture graphite foil or carbon nanotube current collectors in the majority of these prior investigations. For example, super-aligned carbon nanotubes were used by Zhou et al [9] as nanoporous current collectors. These carbon nanotubes were produced to exploit the advantages of both carbon nanotubes and metal oxide nanoparticles. A combination of the materials was applied to the current collector in the form a thin film. A similar experiment was undertaken by Dyatkin et al [10] using materials with a smaller environmental footprint. Graphite-foil sheets, carbon fibre and carbon nanotubes were tested as current collector materials, and, of those, graphite-foil sheets were found to be most suitable.

The purpose of this paper is to investigate, experimentally, the performance of the designed 3D-printed supercapacitor when using carbon conductive paint to construct the current collectors and electrodes. The process of combining paste extrusion and FDM 3D printing technologies to produce 3D-printed supercapacitors has been developed in preceding work. The frame of the supercapacitors was printed by an FDM 3D printer, whereas paste extrusion was employed to deposit the electrolyte-soaked separator, the current collector layer and the electrode layer. Furthermore, to avoid the use of metals, carbon conductive paint (CCP) was selected for producing the electrodes and current collectors. This was done to reduce production and environmental costs, and enhance corrosion resistance. This paper describes a novel method and a new material for use in the fabrication of 3D-printed supercapacitors. The efficacy of varied concentrations of CCP is evaluated, as well as the overall electrical performance of the resulting 3D-printed supercapacitors.

## II. Experiment

### A. Printers and Materials

In this experiment, the primary 3D printer used was an FDM printing machine (Ultimaker3®), which was integrated with a paste extrusion system. The FDM method (main extrusion) was used in this work was to create the packaging frame for the supercapacitors. Figure 1 shows the schematic techniques applied in this study, i.e. a paste extrusion system (Discov3ry® extruder) attached to an FDM printing machine (Ultimaker3®).

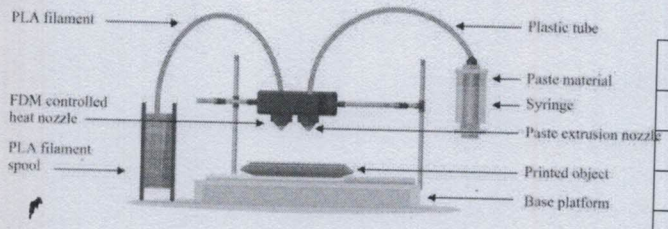


Fig. 1 Schematic of a combination of two 3D printing techniques.

The frames for the supercapacitor samples were built using polylactic acid (PLA) filaments with a diameter of 2.89 mm. obtained from 3DGBIRE Ltd. Bare Conductive Electric Paint, obtained from RS Components, was the carbon conductive paint (CCP) used to produce the current collectors and electrodes in this experiment. This CCP is designed for the purpose of applying conductive areas onto surfaces and is compatible with 3D printing. The substance is solvent-free, non-toxic, organic, and water-based. It can be applied in a variety of settings, such as stencil and screen printing, however it is only suitable for low-current circuits. The electrolyte in this study consists of ($H_3PO_4$) and polyvinyl alcohol, PVA (MW 146,000-186,000, > 99% hydrolyzed) were also obtained from Sigma-Aldrich and used as gel electrolyte. The gel electrolyte was made by dissolving 0.9 mL $H_3PO_4$ and 1.0 g PVA in 10 mL deionized water. Postlip filter paper (d= 127 mm, the thickness is 130 $\pm$ 1µm), manufactured by Evans Adlard & Company ltd., was used as the separator. All the materials above were used without further purification.

### B. *Design and manufacturing of 3D – printed EDLCs*

*1) Preparation of the activated carbon (AC) slurries for current collectors and electrodes*

In this study, the current collectors and electrodes of the 3D printed supercapacitor were printed using carbon conductive paint diluted in distilled water. As displayed in Table 1, four alternative concentrations of slurry were prepared. The various AC slurries were made by mixing carbon conductive paint of mass 0.1, 0.2, 0.3 and 0.4 g with 3 g of distilled water respectively. These were then stirred for two hours to produce a uniform mixture. The paste extruder is only able to deposit mixtures that are not too viscous, such that they will flow easily through the extrusion tube. The thickest slurry tested (0.4 g of carbon paint) proved to be too viscous to be deposited, so a supercapacitor sample for this concentration could not be produced.

TABLE I. List of carbon conductive paint mixtures tested

| AC slurry | Carbon Conductive paint, CPP | Distilled Water |
|---|---|---|
| no: 1 | 0.1 g | 3 g |
| no: 2 | 0.2 g | 3 g |
| no: 3 | 0.3 g | 3 g |
| no: 4 | 0.4 g | 3 g |

*2) Design and printing of the PLA frame with FDM*

The manufacturing process was designed such that the supercapacitor could be produced in a single event and to minimize assembly. The structure of the supercapacitor was designed based on the working mechanism of a capacitor. Each individual supercapacitor consists of three layers (frame base, current collector layer and electrode layer) on each side with an electrolyte layer in between the two layers, as shown in Figure 2. The packaging frame of the supercapacitor was similar to a hinge, with dimensions of 4 x 4 cm. The thickness of both current collector and electrode was 1 mm. The design of the structure and all layers of the supercapacitor was created using Solidworks®. The printing speed was set to 50 mm/sec. 60°C was the controlled temperature of the printer bed, and 220°C was the temperature of the FDM printing nozzle. Dimensional accuracy of the packaging frames represents the degree of agreement between the manufactured dimension and its designed specification, with mean differences of $\pm$ 1.0 mm.

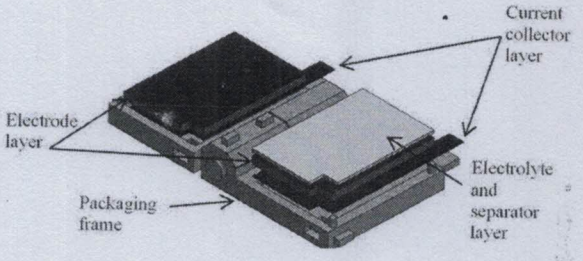


Fig. 2 Schematic of the structure of the 3D printed supercapacitor.

*3) Printing the current collector, electrode and separator with electrolyte using paste extrusion system*

For this study, three different carbon paint slurry concentrations were deposited using the paste extrusion system. This paste extrusion system was selected for this work because it provides a simple fabrication method for paste and paint materials, and can be used to deposit several materials for different purposes. A CCP slurry was prepared as previously described and administered through the 3D printer to create both electrodes and current collectors. Firstly, the current collector layer was built onto the surface of the packaging frame with size of 3.2 x 3.2 cm. Secondly, the electrode material was deposit

directly onto the current collector layer with a size of 3.0 x 3.0 cm. The slurry was printed twice to achieve the required thickness, and dried at room temperature (approximately 22-24°c).

The PVA gel electrolyte separator was then also printed on top using the paste extruder. Finally, filter paper is manually placed on top of the electrolyte on one side of the supercapacitor sample, then the two sides are folded together to form a fully assembled electrochemical supercapacitor as shown in Figure 3.

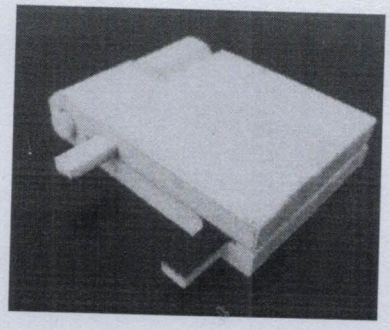

Fig. 3 A complete 3D printed supercapacitor.

*4) Characterisation of the electrochemical properties*

If electric potential is applied an EDLC's electrodes, opposing ion charges gather on the respective electrode surfaces. A non-conductive separator is placed between the two electrodes to prevent short-circuiting. This creates an electric field between the two electrodes which can be used to store energy. It is possible to test the EDLCs capacity to store energy using cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests. A Versa-STAT3 electrochemical workstation was used to do this in this research.

The CV tests involves using a potentiostat to linearly sweep potential between the working and the reference electrode. A charging (positive) sweep is applied within a specific voltage range, and then a discharging (reversing) sweep immediately after the preset voltage limit is reached. The electrochemical behaviour of the supercapacitor can be measured based on the current response against the applied voltage. The following equation (1) is used to calculate the capacitance ($C_1$) of the EDLC:

$$C_1 = \frac{Q_{total}}{2\Delta V} \tag{1}$$

Where $Q_{total}$ is the supercapacitor's charge in coulombs. This value is measured from the CV response curve. $\Delta V$ is the voltage change between the device's terminals in volts (V).

The specific capacitance can be calculated using the equation (2):

$$Cs_1 = \frac{C}{m} \tag{2}$$

Where, $Cs_1$ is the specific capacitance, C is the capacitance formulated from equation (1), and $m$ is the total mass of active materials in the two electrodes (g).

Another method used to determine the performance supercapacitors is the Galvanostatic charge/discharge (GCD) test. This is the most common DC (direct current) test. This test involves first applying a constant current to charge the supercapacitor, then discharging the supercapcitor in a set voltage range or charge/discharge time. The following equation (3) is used to calculate the capacitance ($C_2$):

$$C_2 = \frac{i \times \Delta t}{\Delta v} \tag{3}$$

Where, $i$ is the discharge current in amperes (A), $\Delta t$ is the discharge time in seconds (s) and $\Delta V$ is the discharge voltage in volts (V), excluding the iR drop.

Likewise, specific capacitance ($Cs_2$) can be calculated with the following equation:

$$Cs_2 = \frac{i \times \Delta t}{m \times \Delta v} \tag{4}$$

Where, $i$ is current in amperes (A), $\Delta t$ is the discharge time in seconds (s), m is the mass of active materials of two electrodes in grams (g), and $\Delta V$ is the voltage of the discharge in volts (V).

## III. Results and Dicussion

*1) Impact of carbon conductive paint concentration on performance*

In this study, three EDLC samples (no 1, 2 and 3) with 1 mm thickness were fabricated with different concentrations of AC slurry. The electrical performance evaluations of the samples were conducted using CV and GCD tests. For the CV test, all the CV curves were recorded using a two-electrode system with a voltage window from 0 to 0.8 V and a scan rate of 20 $mVs^{-1}$. For the GCD test, the charge current was set at 15 mA and the potential window was 0.8 V. Figure 4 and 5 show the measured CV and GCD curves for all samples and the capacitances and specific capacitances calculated from CV and GCD measurement are shown in Table 2. It can be seen that the two tests were fairly consistent, albeit capacitances measured using the GCD test were higher as is generally the case. Sample no 3 obtained the highest capacitance (241.92

mF) of the samples tested. The CV curve of sample no 3 presents the largest area and its GCD curve shows the smallest iR drop.

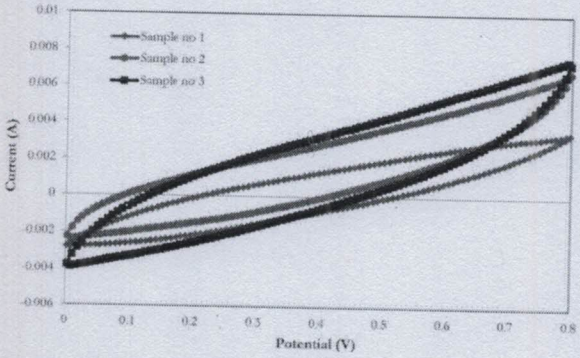


Fig. 4 The CV curves for the three samples with alternative concentrations of AC slurry.

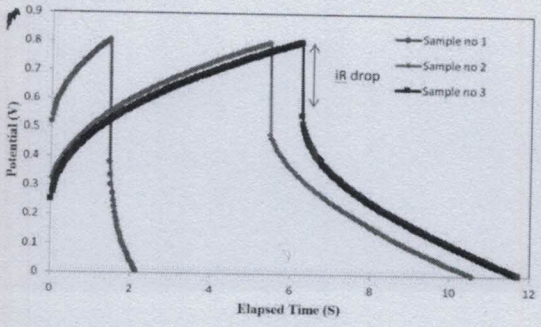


Fig. 5 Galvanostatic charge/discharge curves for the three samples with alternative concentrations of AC slurry.

TABLE II Capacitance and specific capacitance of the samples as calculated by CV and GCD tests

| Sample | $C_1$ (mF) | $Cs_1$ (mF/g) | $C_2$ (mF) | $Cs_2$ (mF/g) |
|---|---|---|---|---|
| No 1 | 81.96 | 97.45 | 122.48 | 145.64 |
| No 2 | 120.07 | 142.77 | 160.64 | 191.01 |
| No 3 | 163.34 | 194.22 | 203.45 | 241.92 |

From the results, it can be implied that the CCP is a viable option for fabricating current collectors and electrodes in supercapacitors. The concentration of AC slurry directly affected the capacitance and specific capacitance of the samples. The capacitance of samples was improved by intensifying the concentration of CCP in the AC slurry. Since the AC content of the slurry was derived from the CCP content, capacitance also increased with increasing AC concentration. Increasing the concentration of AC in the slurry may have increased the conductivity of the sample, which in turn improved the capacitance. It should be noted, however. increasing the concentration further appears to be limited by the increased viscosity preventing printing by the paste extruder.

## IV. Conclusion and Future Work

This study combined two 3D printing processes to produce three metal-free supercapacitors varying only in the concentration of carbon paint (CCP) used to print the current collector and electrodes. The electrical performance of these samples was then characterized and compared. The objective was to discover which concentration could produce the sample with the highest capacitance. First it was discovered that the slurry with 0.4 g of CCP to 3 g of distilled water was too viscous and thus not suitable for 3D printing. Of the 3 slurries which could be used, the slurry with the highest concentration of CCP (0.3 g CCP to 3 g of water) produced the sample with the most capacitance, 203.45 mF. Since the three samples had near identical active material mass, this sample also had the highest specific capacitance, 241.92 m F.

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