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Technical Paper

A study of 3D printed active carbon electrode for the manufacture of electric double-layer capacitors

Milad Areir*, Yanmeng Xu, Ruirong Zhang*, David Harrison, John Fyson, Eujin Pei

Cleaner Electronics Group, College of Engineering, Design and Physical Sciences, Brunel University London, Uxbridge, UB83PH, UK

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ABSTRACT

This paper reports an experimental investigation of the potential for printing selected commercially available activated carbon (AC) onto a flexible fabric. A dual nozzle deposition system was used based on fused deposition modelling (FDM) solid-based process. This is capable of extruding an AC slurry for making Electric Double-Layer Capacitors (EDLCs). We used an adaptive slicing approach which allows us to modify the layer thickness and deposit a controlled amount of AC materials with an accurate orientation to form predetermined tracks. Several forms of AC slurry were difficult to deposit because of the carbon particle size and acid concentration. This work discusses how the supercapacitor behaves in relation to the printed AC layers. The effects of the fabrication processes on the AC electrodes were further investigated. FDM/Paste material deposition could provide a method for making several functional elements in one process, for example printing piezoelectric materials and energy storage for smart products. The major contribution of this work is an approach for printing multilayer AC as electrodes by using 3D printing technology. The 3D printing technology allows the manufacture of complex internal patterns accurately, and provides the ability to build various thicknesses of layers in a fast and smooth operation.

1. Introduction

The rapid development of wearable electronic devices has increased the requirement for flexible energy storage devices [1–6]. Electrochemical energy storage devices EDLCs also named supercapacitors are designed to be promising challengers for power devices. EDLCs contain AC with a high surface area as two porous electrodes with a current collector on each electrode separated by a gel electrolyte. AC is a crude form of graphite and has holes encompassed by carbon atoms. It is made from naturally occurring organic material usually coals or charcoal and is activated by acid treatment or thermal activation using water vapour under pressure. The ACs are conductive and have an excellent range of surface areas and therefore have been used as electrode material to store energy. Their surface area is based on the size, volume of the pores [6] and distribution [7]. Several carbon materials have been used to create supercapacitors especially in EDLCs. The specific capacitance varies with carbons of differing morphology. AC in the form of porous carbon including carbon black, carbon fibre cloth, carbon aerogel and graphene [1] have been selected due to their large specific surface areas. Standard Oil of Ohio Company SOHIO and Donald L. Boos [8] developed successful flexible electrolytic carbon paste electrodes by mixing finely divided carbon particles with an electrolyte to produced EDLCs by compressing the paste to 20,000 psi to form the electrodes.

Many researchers have concentrated on improving the properties of electrode materials to enhance energy storage performance. The electrochemical performance of carbon materials on different substrates have been investigated based on the electric double-layer mechanism and reported in the literature including graphene/AC composite [9], single walled carbon nanotubes SWNTs electrodes [10], AC nanowhiskers [11], AC microporous [12], AC fibres with a mesoporous structure [13] and AC slurry by Zhang et al. [2,14]. Other researchers have focused on the electrode fabrication technique investigating the effect of build time, surface finish and capacitance behaviour. Different fabrication techniques the effect of transfer of electrodes onto EDLCs substrates and may influence the electrochemical performance. There are many fabrication techniques used to create electrodes for instance, dip coating [3], doctor blade coating [15], screen printing [16], masking [17], spraying [10], roll-to-roll printing [5], selective laser melting technology [18] and 3D fused filament fabrication [19]. These techniques may include pre-treatment to ensure more efficient penetration of AC patterns onto the substrate. All the fab-

* Corresponding authors.
E-mail addresses: milad.areir@brunel.ac.uk, meladarir@hotmail.com (M. Areir), ruirong.zhang@brunel.ac.uk (R. Zhang).

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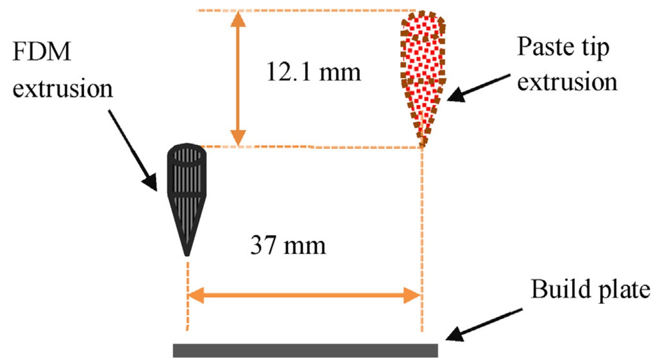

Fig. 1. Illustration showing the modification of a part.

rication methods such as conventional lithographic techniques or those that utilize masks for the definitions of patterns on substrates are inconvenient for building cost-effective devices for commercial applications [4]. It is a challenge to develop EDLCs using a convenient fabrication method. The major contribution of this work is developing an approach for printing multilayer AC as electrodes by using 3D printing technology. This paper demonstrates the novel use of a 3D dual nozzle deposition system. The system developed uses a conventional fused deposition head to deposit composite flexible filament, combined with a nozzle tip fed by a syringe tool which was capable of extruding AC slurry, and gel electrolytes. This dual nozzle system was used to manufacture 3D supercapacitors for future energy storage.

2. Experimental

2.1. Materials

Silver conductive paint with the volume resistivity of 0.001 Ω cm was purchased from RS® Components Ltd. and was used due to its strong adhesion onto flexible composite substrates and its ability to provide high conductivity when fully hardened. Flexible LAYWOO-FLEX 3 mm diameter filament created by Kai Parthy was used. Double face tape was purchased from 3 M®. All other materials including AC powder, sodium carboxymethyl cellulose (CMC, MW 250,000), polyvinyl alcohol (PVA, MW 146,000 ~ 186,000, 99+% hydrolysed), sulfuric acid (H_2SO_4, 98.08 g mol^{-1}), phosphoric acid (H_3PO_4, 98.00 g mol^{-1}) were supplied by Sigma Aldrich.

2.2. Machine process

To extrude several forms of material, the machine was changed from only one extrusion to dual extrusion. The FDM system by the 3D printer Ultimaker® was used with a 0.4 mm nozzle able to produce layer heights of 0.02 mm [20–23]. A single syringe tool (called Discov3ry®), driven by a linear stepper motor, was installed in the printer firmware and controlled by simplify3D software. The double head calibration was setup using simplify3D software for a tool head offset. To set up the modified fixture, the nozzle tip had to be zeroed to the same tip dot and therefore the offset was measured manually for the nozzle tips of both heads for FDM and Discov3ry. They were approximately 37 mm away from each other and this dimension was applied as an Y-axis offset to the simplify3D software. (As shown in Fig. 1, the X-axis offset was set at 12.1 mm, and Y-axis was set at 37 mm).

The Discov3ry extrusion takes time for building up enough pressure to achieve a steady-state of extrusion for printing; the retraction will take a similar time to propagate through the length of tubing. Marlin G codes are preparatory functions which set the mode for the rest of the commands. M codes are machine specific miscellaneous functions [24]. Once a syringe has been filled the G-code commands are sent to the Ultimaker® machine as shown in Table 1.

Table 1
List of G-code commands.

Command	Description
M302 S190	set safe Ultimaker extrude to 190°
M92 E282	change steps per mm to default if using Ultimaker extruder
M92 E700	change steps per mm to high if using Discov3ry extruder
M302	set safe Discov3ry extrude to 0°

2.3. Fabrication technique

Designs were first drawn using Solid Works software. The electrodes were then fabricated using a paste extrusion Discover3y syringe tool with an open source 3D printer Ultimaker. The FDM 3D printer uses a spool of filament drawn through a 0.4 mm heated nozzle. The materials were deposited by the FDM process using a layer by layer technique. The EDLC was printed using a flexible composite material, LAYWOO-FLEX. This flexible composite material was created by Kai Parthy with 65% co-polyesters and 35% recycled wood and has a comparatively lower tensile strength and high degree elasticity with no warping. Filament deposition of this material with a 0.4 mm nozzle was found to be possible using high temperatures, based on experimental work. Table 2 shows the process parameters used for this work. The fill density was set at 20%, wall line width was set at 0.6 mm, the travel speed was 150 mm s^{-1} and the build plate was cooled to 10 °C. The layer height was initially set at 0.4 mm for the first layer and double face tape 3 M® was used on the build plate to help the object stick. The samples were printed on flexible composite substrates with the same size of electrodes for three capacitors with the length of 40 mm, the width of 2 mm, and same thickness sizes. During these tests, there were no issues with clogged nozzles or material jams. To successfully print 2 mm thickness of AC layers and with geometries, the height of the attached Discove3ry nozzle was set at 1 mm using a 0.6 mm diameter smooth flow tapered tip. The primary layer height was set at 0.6 mm for the first layer in rectilinear infill pattern, and extrusion multiplier was fixed at 30. During this test there were no issues with clogged nozzles or air bubbles.

2.4. Preparations of 3D AC electrode

Table 3 shows different kinds of AC slurries. To provide a printable slurry matrix for the EDLCs, the AC slurry 2 is made as following method: 2 g of PVA were dissolved in 40 mL distilled water at 50 °C with 1 h stirring, and then this PVA solution was mixed with 2 g AC powder that had been already pre-heated to 100 °C for 1 h, all the mixing materials were kept stirring overnight to make a homogenous slurry. AC 2 has been selected as electrode paste because of its optimum viscosity. Table 3 summarizes the differences between each slurry formulation. The viscosity of the AC slurry must be suitable to allow deposition under the optimum feed-rate while considering the filament shape. It can be seen from the table that the AC slurry 1 does not contain electrolyte acid and needs an increased pre-treatment temperature and process time for the PVA binder. It displayed a wrinkled morphology especially when air was entrained during the syringe filling procedure leading to a variation in viscosity. AC slurry viscosity is a property arising from collisions between particles. When the AC slurry does not mix well with the acid and is then forced through a tube, the PVA liquid which com-