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3D printing of highly flexible supercapacitor designed for wearable energy storage

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ABSTRACT

The rapid development of flexible energy storage devices is crucial for various applications. However, it is still difficult to manufacture functional flexible electrochemical double layer capacitors (EDLCs) in one single process due to many different types of materials being used in EDLCs. This paper presents a novel method of manufacturing highly flexible EDLCs by using an open source 3D printer. The EDLC components were fabricated using a single paste extrusion in a layer wise manner. The detailed fabrication process for a highly flexible EDLCs device has been demonstrated, where acetoxy silicone was used as the flexible substrate. The purpose of this study has been to develop a single continuous manufacturing process for EDLC and to investigate the electrochemical performances of 3D printed flexible supercapacitors. Mechanical bending tests were carried out to prove the stability of the electrochemical performance and flexibility of the 3D printed supercapacitors.

1. Introduction

The development of energy storage devices has faced major technological challenges during the past few decades. Electrical double layer capacitors (EDLCs) are a promising competitor for alternative energy storage because of their low-cost, high power density and long cycle life. Being flexible is one of the critical demands for the recent development of energy storage devices [1–3]. Recently, EDLCs and microsupercapacitors have been studied and manufactured by a number of companies around the world with different novel techniques, such as spray coating, 3D double extrusion, microextrusion, etc [4–25]. The above techniques, however, are often costly or not able to process all the materials necessary for making EDLCs. Thus, a combination of several processes has been required to fabricate a complete and workable EDLC. 3D printers developed for additive manufacture have the ability to create almost any geometrically complex shape and pattern in a wide range of materials and offer highly precise conformal depositions [26–28]. The advantages of additive manufacture have been applied previously in the development of flexible supercapacitors, but it is still a challenge to achieve a good and stable working performance, particularly under mechanical bending conditions [29,30]. Other advantages of this process are that it allows complex shaped supercapacitors to be made, flexibility in packaging due to a variety of 3D shapes, and the manufacturing of 3D electronic structures for consumers. Moreover, compared to other 3D printing methods, 3D paste printing allows a wide selection of composite materials to be deposited by quickly changing syringes. 3D paste printing does not need complicated post-processing such as thermal sintering, a mask to transfer pattern or heat to laminate EDLCs. The use of 3D paste printing is easy, and allows more rapid prototyping of EDLCs for research purposes and achieves end properties of 3D EDLCs.

This study has addressed the above key challenges and developed a novel 3D printing method for manufacturing flexible supercapacitors, by one single continuous process and using low-cost flexible silicone structural materials that are compatible with the electrode, current collector and electrolyte materials.

2. Materials used for EDLCs

2.1. Materials

Dow Corning® acetoxy silicone supplied by Screwfix® was used for substrate and package material. The mixture of silver powder (Ag) purchased from Gwent Group® and zinc metal powder (Zn, MW 65.38) was used for current collector paste. All other materials including the activated carbon particle powder (AC, AR grade, Cat. No. 05105, MW 12.01 g mol^{-1}), sodium carboxymethyl cellulose (CMC, MW 250,000), polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP, MW 400,000–130,000), polyvinyl alcohol (PVA, MW 146,000–186,000, 99+% hydrolysed), 1-methyl-2-pyrrolidinone (NMP, 1.028 g ml^{-1}) and phosphoric acid (H_3PO_4, 6 M) were supplied by Sigma-Aldrich®.

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2.2. Preparation of the activated carbon slurry

In order to reduce the size of the activated carbon (AC) particles and to ensure a uniform deposition of AC slurry through a tiny 0.6 mm tapered nozzle, a ball-milling process was used. 100 g of AC powder was added into 50 mL of carbon-based Chinese ink, and 100 mL of distilled water, and milled for 72 h. The average particle diameter is 0.4 μm. Then 5 g of the milled AC powder was heated at 150 °C in an oven to allow the solvent, mostly water, to evaporate. 2.6 g PVA powder was dissolved in 20 ml distilled water at 50 °C for 1 h under magnetic stirring. The dry AC power was mixed with the PVA gel solution under stirring at room temperature for 24 h. To ensure the homogeneity of the AC slurry 8 mL H_3PO_4 and 1 g of 5% CMC was added.

2.3. Preparation of the gel electrolyte

The PVA gel electrolyte used in this study was an important component for flexible EDLCs and its properties significantly affected the EDLC's electrochemical performance. To prepare an aqueous solution of PVA, 2.5 g PVA powder was mixed with 30 mL distilled water and was stirred at 50 °C for 1 h until fully dissolved. To avoid a rough layer and to get more sticky 1.5 g CMC of 5% was then mixed with the PVA solution followed by 18 mL 6 M H_3PO_4 with magnetic stirring overnight until completely homogeneous.

2.4. Preparation of the current collector paste

It was critical to prepare a conductive paste with a good bonding to the substrate in 3D printing, especially as silicone was used as the substrate material. 1 g PVDF-HFP pellets were dissolved in 15 mL NMP at 40 °C for 1 h first. After that, 4.5 g zinc metal powder was mixed with 5 g silver powder (Ag) and added to the solvent/polymer mixture and kept stirring overnight. PVDF as a type of piezoelectric polymer enhanced the bonding of silver and zinc particles therefore improving the conductivity of the current collector.

3. Manufacturing process and measurement for EDLCs

3.1. Design of the structure of printable wearable EDLC

Fig. 1 shows the schematic diagram of an EDLC designed for this study. Due to the working mechanisms, there are four layers of materials on each side of an EDLC, i.e. silicon substrate, current collector, AC material, and gel electrolyte. This EDLC was also designed as a wearable device, i.e. a bracelet, thus the structure of the supercapacitor designed for this study included a locking mechanism to allow the complete product to be worn around the wrist as a bracelet.

3.2. Manufacturing process

Paste deposition by 3D printing is a promising manufacturing method for controlling the deposition layers, and it can provide accurate and complex structured devices. In this study, a paste extruder (Discov3ry®) was employed to print all the different types of materials for the EDLC. As shown in Fig. 2(a) the paste extruder was attached to, and controlled by, a commercial 3D printer (Ultimaker®). Fig. 2 shows the manufacture processes of a flexible EDLC, and Table 1 lists the manufacturing process parameters. The EDLCs components were deposited in a 100% fill density in grid patterns to make the device robust. Fig. 2(b) depicts the frame part of an EDLC printed by depositing acetoxy silicone material on a build platform covered with Teflon paper, which was used for easy removal when the wet silicone is dried. Subsequently, the frame part printed was left to cure for 2 h. In addition, 5% CMC binder was coated by spreading method on surface of the silicone substrate in order to help the current collector layer stick onto the silicone substrate better. Fig. 2(c) shows the current collector material to be deposited on silicone layer and kept for 2 h to fully cure and adhere to the silicone substrate. Next, the AC electrode layer of 0.6 mm thickness was deposited with a dimension of 163 mm × 5 mm as shown in Fig. 2(d). Following this, the gel electrolyte of PVA/H_3PO_4 was deposited onto the electrodes and they were kept in a vacuum desiccator for an hour to allow the infiltration of the PVA/H_3PO_4 electrolyte into the carbon particle pores fully, as illustrated in Fig. 2(e). The components already built and fully dried were then returned to the platform of the 3D printer to deposit another layer of silicone around the edge to act as a gasket. The other side of the EDLC was printed the same as described above. Finally, the two sides were sealed together as a complete EDLC, as revealed in Fig. 2(f).

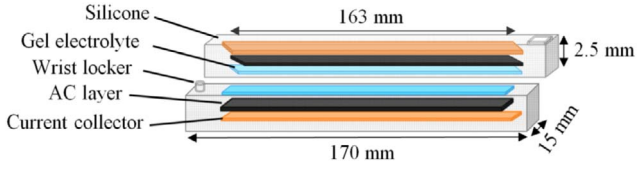

Fig. 1. Schematic of the structure of printable wearable EDLC.

In total four EDLCs (designated as *C1*, *C2*, *C3* and *C4*) have been manufactured under the same conditions in this study to investigate the reproducibility of the manufacturing process and the stability of the electrochemical performance of the EDLCs.

3.3. Measurement of the electrochemical properties

An electrochemical workstation (VersaSTAT 3.0) was set up to measure the electrochemical performance of the EDLCs printed. The electrochemical performance was evaluated by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) tests. Electrochemical impedance spectra (EIS) were measured at an open circuit potential of 0 V between the frequencies from 0.01 Hz to 100 kHz with 10 points per decade. The capacitance (C) can be calculated from the CV curve measured using:

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

Where, C is the capacitance in farads (F), Q_{total} is the supercapacitor charge in coulombs (C), and ΔV is the voltage range in volts (V).

The area specific capacitance (C_a) of the supercapacitor can be calculated from the CV curves using:

$$C_a = (1/2A(\Delta V/\Delta t)(V_f - V_i)) \int_{V_i}^{V_f} I(V)\Delta V \tag{2}$$

Where, A is the area of the electrodes (cm^2), ΔV/Δt is the voltage scan rate ($V\ s^{-1}$), V_f and V_i are the potential limits of the CV curve, and $\int_{V_i}^{V_f} I(V)\Delta V$ is the numerically integrated area of the CV curve.

During the GCD test, the capacitance can be calculated at a constant current of 15 mA by:

$$C = \frac{i.\Delta t}{\Delta V} \tag{3}$$

Where, i is the discharge current in amperes (A), Δt is the discharging time (s) and ΔV is the voltage of the discharge (V). In addition, the specific capacitance (C_s) of the supercapacitor can be calculated using:

$$C_s = \frac{2C}{m} \tag{4}$$

Where, C is the capacitance in farad (F) calculated by GCD, m is the total mass of the active material used for one single electrode (g).