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Design and fabrication of modular supercapacitors using 3D printing

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ABSTRACT

Development in multi-material freeform 3D fabrication processes can provide the possibility of building complete functional electronic devices. This paper describes a design and manufacturing process for electrochemical supercapacitors. A combination of two 3D printing systems, i.e. a Fused Deposition Modelling (FDM) printer and a paste extruder, were applied to fabricate these energy storage devices. During the manufacturing process of supercapacitor components, the FDM 3D printer was used to print the packaging frames, the conductive layers, and the electrodes layers; and the separator with electrolyte were deposited using the paste extruder. Several complete energy storage supercapacitors have been made and their electrochemical performances were assessed. The 3D manufacturing process developed was also evaluated in this study.

1. Introduction

Additive manufacturing (AM) (mostly referred to as 3D printing) is a method of manufacturing in which a model designed by Computer Aided Design (CAD) is captured and then consequently constructed on a layer by layer basis. 3D printing is considered as a promising tool for rapid production of 3D objects. At present, the technologies of additive manufacturing are becoming increasingly capable and affordable [1–3]. Current research focuses on the development of novel materials and the improvement of new techniques in order to fabricate a wide range of applications for many purposes. Improvement in 3D printing techniques enhanced with component placement and electrical interconnect deposition can offer the ability to make electronic prototypes. These developments provide integration of electronic components with 3D printed devices. This type of 3D electronics integration is also identified as 3D structural electronics or 3D printed electronics. 3D printed electronics can be designed to any form providing a unique improvement over conventional electronics systems [3–8].

Supercapacitors, also known as electrochemical capacitors, have attracted great attention as an energy storage device. Supercapacitors have several advantages over batteries such as high power densities, long life cycles and high reversibility. These devices have been used as power sources in many applications for example: portable electronic devices, electric vehicles and emergency power supplies [9–11]. Supercapacitors can be divided in two common types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, the energy storage is based on the formation of separated electric charges at the interface of a porous electrode material and an electrolyte. The charge storage process is non-Faradaic and chemical oxidation-reduction (redox) reactions should not occur. In contrast, pseudocapacitors are based on several faradaic mechanisms, for example underpotential deposition, redox pseudocapacitance and intercalation pseudocapacitance. In underpotential deposition, a single layer of metal ion is deposited onto a different metal surface, for example the deposition of lead onto a gold electrode. In redox pseudocapacitance (as in $RuO_2 \cdot nH_2O$), electrons are transferred between the electrolyte and the electrode through a fast a faradiac redox reactions in the charge storage process. Intercalation pseudocapacitance arises from the intercalation of ions into the layers of redox-active electrode materials accompanied by a faradaic charge-transfer without generating phase change [12–14,23]. The manufacturing of supercapacitors can be accomplished by different methods such as inkjet printing and coating methods including the additive manufacturing process that is generally applied in the rapid prototyping industry [11–15].

Recently, there have been great interests in embedding electronic components and electrical interconnections into 3D structures. Palmer [15] presented a 3D printed embedded structure with conductive ink using Direct Printing (DP) which was then expanded by Medina and Lopes [16,17]. In their research, two different 3D printing techniques were integrated, e.g. stereolithography (SL) and a dispensing system. This method was applied to print simple circuits, including a demonstration of simple

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prototype temperature sensors. For 3D printed energy storage devices, Sun [18] introduced 3D interdigitated microbattery architectures (3D-IMA). For the anode and cathode materials of this 3D-IMA, $Li_4Ti_5O_{12}$ (LTO) and $LiFePO_4$ (LFP) were applied respectively. Ho [19] also showed a zinc microbattery with an ionic liquid gel electrolyte using direct write dispenser printing. In this work, a developed dispenser printed a microbattery comprising of zinc and manganese dioxide electrodes which sandwich an ionic liquid gel electrolyte. Zhao [20] presented a 3D printed electrode for fabricating interdigitated supercapacitors using a Selective Laser Melting (SLM) method. In this research, pseudo-capacitors were produced using a 3D interdigitated Ti_6Al_4V electrode which is fine metal powder. Zhu [24] reported fabrication of 3D periodic graphene composite aerogel microlattices for supercapacitor using a direct-ink writing technique. In this study, the 3D-printed graphene composite aerogel (3D-GCA) was produced and fabricated as an electrode. Fu [25] introduced graphene oxide-based electrode inks for 3D printed lithium-ion batteries. In this work, highly concentrated graphene oxide (GO) was selected due to its excellent properties, for example a gel-like behavior and a high elastic modulus. The GO- based electrode inks with high viscosity were used to fabricate lithium-ion battery prototypes using extrusion-based 3D printing. In addition, Zhu [26] reviewed 3D printed functional nanomaterials for electrochemical energy storage. In this literature, manufacturing of batteries and supercapacitors using different types of 3D printing methods were reviewed and showed that 3D printing methods enable fabrication of functional nanomaterials with three-dimensional architectures.

Previous research works have presented 3D printing techniques to create 3D printed electronics in several applications but these have not included EDLC supercapacitors. In this paper, we present a new method of combining 3D printing processes to manufacture EDLC supercapacitors with one continuous process and high reproducibility. In this study, a combination system of Fused Deposition Modelling (FDM) and paste extruder was applied for manufacturing a supercapacitor. The FDM technology was used to print the frame for the supercapacitors, and the paste extruder system was used to print current collector layers, electrodes and separator layer with electrolyte. The method described in this paper showed a new approach for manufacturing embedded energy storage devices.

2. Experiment

2.1. Materials

The material used to build the supercapacitor frame in this experiment is polylactic acid (PLA) filament with a diameter of 2.89 mm. Silver conductive paint was used as the current collector material. The materials used for mixing electrode slurry and electrolyte include activated carbon (AC) (AR grade, 1375 $\mu\Omega$ cm), Sodium carboxymethyl cellulose, CMC ($C_{28}H_{30}Na_8O_{27}$, MW: 250,000), ethanol ($\geq$99.8%, ACS grade), phosphoric acid (H_3PO_4) and PVA (MW 146,000–186,000, >99% hydrolysed). Preparation of the electrode slurry was achieved by mixing the activated carbon (AC) with CMC solution. The CMC binder solution was mixed with distilled water/ethanol (1:1) solvent at room temperature. The concentration of CMC was fixed at 5 wt% based on total mass of AC and CMC, in which 2 g activated carbon was added to the 50 mL of CMC binder solution. The slurry prepared was stirred for 8 h before the experiment in order to make it homogeneous and suitable for printing. The conductivity of the slurry was about 10^2 Ω/sq. The gel electrolyte was made by dissolving 0.8 mL H_3PO_4 and 1.0 g PVA in 10 mL deionized water. All the materials used in the experiment are low cost, nontoxic and easily available.

2.2. Printing system

Fig. 1 shows the schematic diagram of the combination of the two 3D printing techniques applied in this study, i.e. a paste extrusion system (Discovery extruder) is attached to a FDM printing machine (Ultimaker2). FDM technology offers a simple fabrication process, reliability, safe, low cost of material and accessibility to several different types of thermoplastics. In the FDM printer, thermoplastic filament material from feedstock spool was driven using two rollers and forced out through a small temperature controlled extruder as shown in Fig. 2. Then the filament was transformed to the semi-molten polymer and deposited onto a platform in a layer by layer process. To build the sample, filament was deposited from the extruder that moved in the x-y plane. When each layer was complete, the base platform was lowered in order to deposit the next layer and so on. The temperature of the base platform was set at low temperature, so that the thermoplastic filament quickly hardens.

The paste extrusion system was employed for building the current collector layer, electrode layer and separator with electrolyte layer. The system consists of a stepper motor, a syringe connected with a plastic tube and a nozzle. During the manufacturing process of supercapacitor, the frame was printed using the FDM printer, whereas, the other materials of the supercapacitor were printed by the paste extruder. In order to deposit the paste materials, the syringe was forced by the stepper motor and paste material flowed along the plastic tube to the nozzle. This function was automated and controlled by CURA software. CURA software was used to control the manufacturing process, which is compatible with both FDM and paste extrusion system, to set up all specifications of printing including transforming STL file to g-code. G-code is one of many programming languages used in machine automation, which has also been used in this manufacturing process to control the speed of the stepper

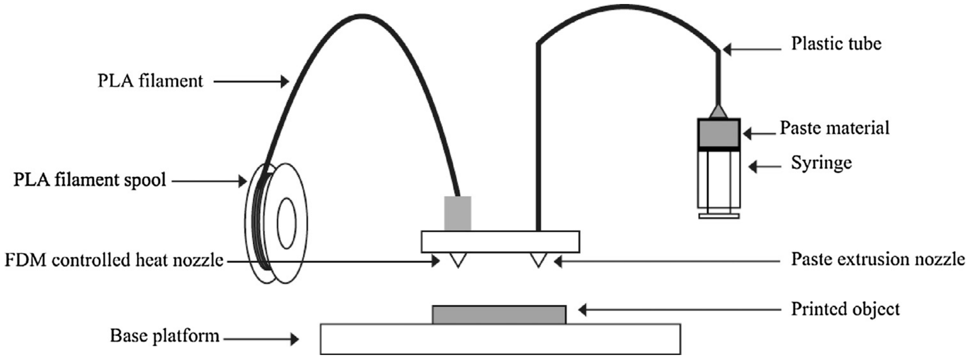

Fig. 1. Schematic of a combination of two 3D printing techniques.