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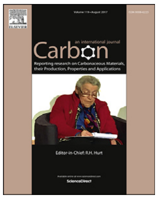

Binder-jet powder-bed additive manufacturing (3D printing) of thick graphene-based electrodes

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ABSTRACT

Additive manufacturing (AM), also known as 3D printing, is emerging as a promising method for the fabrication of complex 3D structures and has the potential to replace the conventional techniques used in the manufacture of commercial devices based on advanced materials. Graphene has shown superior performance in various electronic devices such as electrochemical supercapacitors. However, it remains challenging to produce the thick, high loading graphene-based electrodes required to achieve a high practical energy density in full devices. Herein, we introduce a powder-bed AM technique for the fabrication of crack-free, mm-thick graphene-based electrodes, with high surface area that can be printed in complex shapes. While this technology has the potential to be used in many application areas including energy storage, conversion, and sensing, in this work, we demonstrate their use as high performance supercapacitors. Devices fabricated using thermally exfoliated graphene oxide powder had gravimetric and areal capacitance of ~260 F g^{-1} and ~700 mF cm^{-2}, respectively at 5 mV s^{-1} in 1 M H_2SO_4 electrolyte. The supercapacitors retained 80% of their capacity over 1000 cycles. This technique provides a promising route for the fabrication and commercialization of thick, porous graphene-based devices.

1. Introduction

Additive manufacturing (AM) has revolutionized the way in which we fabricate 3D structures [1–4]. AM is defined as a process through which materials are joined together to build parts using a 3D model and most often involves a layer-by-layer manufacturing process in contrast to subtractive methodologies [5]. To date, various 3D printing strategies have been demonstrated. For example, fused deposition modeling (FDM), stereolithography, selective laser sintering (SLS), microdeposition, inkjet printing, aerosol jet printing, and binder jetting are now being frequently adopted to print complex 3D shapes using various precursor materials [1,6–9]. All these methods have a feature in common, which is layer-by-layer manufacturing of the structure and binding these layers through either melting, photopolymerization, sintering, or injection of a binder. While AM was once only used for rapid prototyping, it is now becoming a commercial end-product fabrication platform with wide potential applications in automotive, aerospace, bio, and particularly, energy-related areas [3]. In particular, AM has the potential to fabricate full energy storage systems including batteries and supercapacitors using advanced materials such as graphene, carbon nanotubes, various metal oxides, and high performance polymers [10–22]. However, AM requires the material to be either easily spread, injected, melted, or sintered which is commonly missing for advanced materials and makes it a challenging endeavor to use them for 3D-printing.

For example, graphene-based supercapacitor electrodes have been prepared through different methods such as inkjet printing [14,16–18,23–38]; however, evaporative drying of the solvent induces stresses in the film which causes film cracking and limits the technique to printing only thin films [39]. While such thin films are sufficient for proof-of-concept demonstrations, commercial high energy density supercapacitors (and batteries) require electrodes to be 100–500 μm thick [40] – a regime currently out of reach for solvent-based printing methods. These thicker films are required to maintain a larger fraction of active material than current collector and separator in the cell to obtain the highest possible energy density for a packaged device [41].

There have been several recent reports describing the fabrication of thick graphene-based electrodes [42–49]. Graphene foams,

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for instance, have been prepared using hydrothermal and self-assembly methods; however, these processes commonly require use of toxic reducing agents such as hydriodic acid (HI) or hydrazine followed by freeze drying [50–53] to prevent the cracking that would otherwise occur during evaporative drying. This process typically takes several days and is thus not particularly amenable to scale-up for rapid manufacturing [39]. Several additive manufacturing approaches have also been used to fabricate thick graphene-based structures. However, all of these processes, again, require freeze drying. For example, García-Tuñon et al. [12] prepared a GO/branched copolymer surfactant suspension with tailored viscoelastic properties and used a robotic deposition device to produce graphene-based 3D structures. These structures were freeze dried and thermally reduced in a tube furnace. Wei et al. [20] developed different graphene-polymer based composite dispersions that were extruded using a similar technique. Zhang et al. [54] froze aqueous droplets of GO suspension onto a super-cooled build-bed to create supported 3D structures which were subsequently freeze-dried in liquid nitrogen. These studies did not assess the performance of these materials as electrodes.

To by-pass these problems, our group has recently demonstrated a technique called binder-jetting powder-bed AM which eliminates the use of a solvent all-together in order to build large, crack-free 3D structures such as porous bone-implants [55–59]. The technique relies on the use of precursors in the form of dry, micron-sized, flowable powders which are uniformly distributed as a layer and patterned with a binder which effectively glues adjacent layers together as the structure is built up layer-by-layer. In this way, it is possible to build complex 3D structures with interconnected pores which has been shown to facilitate material flow [58–61]. We hypothesized that such an interconnected pore structure, resulting from the voids formed between powder agglomerates, would also allow for rapid ion transport inside the electrodes of batteries and supercapacitors.

In this paper, we demonstrate the application of this binder-jetting powder-bed AM technique for the fabrication of thick graphene-based 3D structures and report their use as electrodes in high performance supercapacitors. Using this method, we are able to directly use the high specific surface area powder generated during the rapid thermal expansion of graphene oxide. The wrinkles and folds between aggregated sheets of the resulting thermally reduced graphene oxide (TRGO), that make up the powder, generated by the build-up of gases released during the rapid decomposition and reduction of graphite oxide help to prevent the sheets from restacking and help to maintain the high specific surface area [62]. After evaporatively consolidating this material, to create a higher bulk density powder, the TRGO is built up layer-by-layer using minimal binder into mm-thick electrodes with effectively any shape or form factor. Using the electrodes directly in supercapacitors resulted in capacitances as high as 260 F g^{-1} and areal capacitances of 700 mF cm^{-2}. However, to achieve the best results, a small amount of Pd nanoparticles (<9 wt%) were infiltrated into the printed electrodes to improve the contact resistance between powder agglomerates. Thus, future improvements to this process will need to include improving the bulk density of the electrodes and the contact area between powder aggregates to eliminate the need for such conductive additives which will also improve the volumetric energy density of such devices.

2. Experimental

2.1. Synthesis and reduction of graphene oxide

The Tour method was used to synthesize graphene oxide (GO) [63]. Briefly, 9:1 ratio of sulfuric acid and phosphoric acid were mixed and subsequently, graphite (graphite flake, −10 mesh, Alfa Aesar, MA) and $KMnO_4$ (1:6 ratio) were added to the mixture. The mixture was stirred for 16 h while heated to 45 °C. Next, the mixture was cooled in air to room temperature and then poured on ice very slowly to avoid overheating of the mixture. After stirring, 10 mL of 30% hydrogen peroxide was poured carefully to the mixture to stop reaction. The dispersion was washed with HCl and ethanol (× 3) by centrifugation and eventually stored in ethanol to avoid restacking of the GO sheets.

For thermal reduction, GO dispersed in ethanol was dried and collected. The powder was placed in a fused quartz tube. The air was exchanged with high purity Ar (99.999%) by three vacuum purge cycles. A Lindberg/Blue M™ Mini-Mite™ Tube Furnace was preheated to 1100 °C after which the tube was pushed into the furnace quickly and held at temperature for 1 min. The rapid thermal expansion and reduction process yield agglomerated TRGO sheets in the form of low bulk density black powder, which was collected for further experiments. TRGO sheets were characterized using scanning electron microscopy (SEM) (Zeiss, LEO 1530 Gemini) and X-ray photoelectron spectroscopy (XPS), respectively.

2.2. Synthesis of palladium nanoparticle dispersion

5 mM sodium citrate (Sigma-Aldrich) and 0.025 mM tannic acid were dissolved in 100 mL of distilled water. The solution was heated to 70 °C while stirring. Then, 8 mL of $Pd_2(NO_3)_3$ (25 mM) solution was injected into the sodium citrate/tannic acid solution. After injection, the reactor was kept at 70 °C for 15 min to complete the reaction. The hydrodynamic diameter of resulting Pd was examined by dynamic light scattering (DLS, Zetasizer Nano-ZS90, Malvern) after diluting the dispersion to 0.1 mg/mL. Transmission electron microscopy (TEM) was also used to examine the size of the particles using a JEOL 2010F at 200 kV accelerating voltage. For TEM, samples were prepared by casting a dilute dispersion onto a holey carbon grid.

2.3. Additive manufacturing of electrode disks

A retrofitted binder jetting additive manufacturing machine (3D Systems, Burlington, MA) was used to print the 3D structures of TRGO. The system was retrofitted to use a smaller amount of powder, inject customized binders and provide an open source code to tune process parameters (e.g., layer thickness, binder volume). In this process, a CAD model (STL file) of the electrode disks (diameter: 12 mm, thickness: 300 μm) is prepared and then sliced to be used by the retrofitted machine. As reported elsewhere [55,57,58,64], a layer-by-layer fabrication process is conducted to build the 3D structure. Briefly, as illustrated in Fig. 1, there are two pistons, namely the feed bed and build bed, with adjustable heights in the chamber of the machine. The temperature in the chamber is maintained at 35 °C. The raw powder is first added to the feed bed with an even top layer of powder to provide the material required for the fabrication of the disks. Next, using a micro motion controller, the piston is translated upward according to the pre-adjusted layer thickness (for this study 100 μm) raising one layer of powder on top of the whole substrate. Then, a rotating roller moves pushing the exposed layer of powder forward to cover the build bed. The print head is subsequently directed to the top of the build bed to inject an aqueous-based binder (zb®60 binder clear, 3D Systems, Burlington, MA) to the first layer of powder based on the geometry of the first slice of the CAD model. According to the MSDS, the binder consists of >90% water, 8% glycerol and 2% other humectants. The system injects the binder with 8-bit greyscale colormap distribution at 360 dpi, with 7 drop sizes in the range of 6–42 pL. The shell to core binder concentration ratio was 100:200%