

3D printed graphene-based electrodes with high electrochemical performance

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Abstract Three-dimensional (3D) printed graphene pyramids were fabricated through a dual-extrusion FDM-type 3D printer using a commercially available PLA-based conductive graphene. Compared with flat printed graphene, a substantial enhancement in the electrochemical performance was clearly observed for the case of 3D printed graphene pyramids with 5.0 mm height. Additionally, the charge transfer of Li⁺ across the graphene pyramids/electrolyte interface was easier enhancing its performance presenting a specific discharge capacity of 265 mAh g⁻¹ with retention of 93% after 1000 cycles. The importance of thickness control towards the printing of an electrode with good stability and effective electrochemical behavior is highlighted.

1 Introduction

Graphene, a two-dimensional (2D) atomic layer of sp^2 hybridized carbon atoms packed in a honeycomb lattice, has received a great deal of attention in energy-storage devices because of its high electron mobility, good thermal conductivity, and high elasticity generated from their long-

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range π -conjugation [1–3]. Studies dealing with graphenebased materials for lithium-ion batteries (LIBs) applications have focused on flexible batteries with high flexibility and energy capacity [4]. A basic requirement for a flexible battery is that its power and energy supply as well as cycle life are not compromised under frequent large mechanical strains (e.g., bending, folding or deforming) [5]. Nevertheless, the flexibility of the traditional electrodes is largely limited by the metallic current collectors, which is difficult to recover their original shapes after being folded or deformed [6]. Additionally, the active materials could easily detach from the metallic collectors under large deformation due to insufficient adhesion leading to poor cycle life [6]. Hence, it still remains a challenge to achieve the desired patterning of graphene sheets at both the micrometer and the nanometer scale and tackle the above drawbacks.

A variety of techniques including photolithography, soft-lithography and direct-writing have been utilized towards this direction [7–9]. However, they present limitations including additional etching processes, restrictions related to a limited choice of suitable substrates, high operating cost, deformations of the elastomeric stamp, high defect density in the resulting pattern and patterning of 2D or low-aspect-ratio structures of graphene, while three-dimensional (3D) patterning is essential [10].

In that respect, 3D printing is a rapidly growing printing technique and can be employed to produce conductive electrodes with special shapes or compositions. One of the first attempts at producing conductive materials through additive manufacturing was made by Czyżewski et al. who used a binder jetting 3D printing machine to fabricate a plaster-based block [11]. In a recent development, Wei et al. were able to prepare graphene composites with acrylonitrile–butadiene–styrene (ABS) and poly(lactic

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acid) (PLA), which were then used with a commercial fused deposition modeling (FDM) printer to produce conductive 3D models [12]. In another work, Zhu et al. prepared graphene oxide inks with suitable rheological properties to be printed using the direct ink writing method [13]. In 2010, Snowden et al. designed a versatile flow cell, which can easily accommodate different types of electrodes [14]. This was one of the first applications of 3D printing for electrochemistry.

Thickness (and geometry) control is important for tuning the amount of active material in the electrode [4, 15]. The capacity of a cell is directly related to the mass of the material present, so the thicker the electrode the greater its capacity will be. Wei et al. developed a flexible solid-state LIB made with graphene inks composed of anatase TiO₂ nanoparticles mixed with graphene sheets modified with either n-type or p-type anionic groups dispersed in water [16]. The printable electrodes exhibited stable cycling performance at 240 mAh g⁻¹ for 100 cycles, which is comparable to other flexible LIBs [15].

In this paper, we describe a micro/mili-meter scale 3D printing approach that exploits a size-controllable graphene pyramids. The correlation of the height of pyramids with the electrochemical performance comprising cycle life, diffusion coefficient and specific discharge capacity of the 3D printed graphene was explored.

2 Experimental

2.1 3D printed samples' fabrication

dual-extrusion FDM-type 3D printer (Makerbot Α Replicator 2X) was used for the direct fabrication of graphene pyramids, using a commercially available PLAbased conductive graphene with a volume resistivity of $0.6 \ \Omega$ cm. The FMD process of building a solid object involves heating of the fed filament and pushing it out layer-by-layer through a heated (220 °C) nozzle (0.4 mm inner diameter) onto a heated surface (50 °C), via a computer-controlled three-axis positioning system (with a spatial resolution of approximately 100 µm in z-axis and 11 μ m in x and y). Following the approach above, several 3D printed samples were fabricated, which consisted of 4-side pyramids [rectangular base of $2.5 \times 2.5 \text{ mm}^2$; height (H) varying from 1.0 to 5.0 mm] on a 1.0 mm thick graphene-based slab, while the overall size of the samples was 25.4×25.4 mm². One representative geometry, along with the dimensions of the 3D printed samples in this work, is schematically shown in Fig. 1.

2.2 Characterization techniques

The crystal structure of all graphene-based samples was determined by X-ray diffraction (XRD) using a Rigaku (RINT 2000) diffractometer with Cu K α ($\lambda = 1.5406$ Å) X-rays for $2\theta = 10.00^{\circ}$ -60.00° and a step time 60°/s. Moreover, Raman spectroscopy was performed using a Renishaw Invia Raman spectrometer equipped with an integral microscope (Leica DM 2500 M) and a Peltier cooled charged-coupled detector. A 514.5 nm radiation from a 50 mW Ar-ion laser was used as excitation source. The excitation was performed through a 50× objective lens and Raman scattering was detected in a backscattering geometry (180°). The spectral resolution was approximately 1 cm⁻¹ for a 2400 grooves/mm grating.

2.3 Electrochemical performance study

The electrochemical performance of the printed graphene samples was evaluated using a three-electrode electrochemical cell [17-19] and 1 M, LiCl aqueous solution as an electrolyte over 1000 scans. The reference, the counter and the working electrodes were Ag/AgCl, Pt and the printed graphene samples, respectively. The geometrical area of the working electrode was 0.25 cm^2 . The scan rate was 10 mV s⁻¹ over the potential range of -1 to +0.5 V. Additionally, cyclic voltammograms were obtained at scan rates of 5, 10, 20, 50, 100 and 200 mV s⁻¹ for the determination of diffusion coefficient. Chronocoulometric experiments were conducted at +0.5 V, recording the total deintercalated charge versus time over 30 s. Chronopotentiometric (CP) tests were employed in the voltage range from -0.5 to -1 V at a constant specific current of 40 mA g⁻¹. Finally, electrochemical impedance spectroscopy (EIS) curves were obtained using alternating current (AC) amplitude of 0 V and set potential of -0.1 V over the frequency range of 10 mHz-100 kHz. Nyquist plots were fitted and analyzed using Z-view software. All electrochemical tests were carried out at room temperature (25 °C).

3 Results and discussion

3.1 Characterization

A typical XRD pattern of graphene in PLA composites is presented in Fig. 2, verifying their crystalline properties. The XRD patterns depict typical peaks of the PLA profile [20], and all the characteristic diffraction peaks of graphite, according to the JCPDS card, No.75-1621 [21, 22].





Fig. 2 Typical XRD pattern of graphene-based 3D printed samples. One can see the typical XRD peaks of the PLA polymer matrix marked with asterisks

Raman scattering measurements were used to verify the presence of carbon materials in the composite filaments. The position, the shape and the relative intensity of D, G and 2D peaks in this type of materials can provide useful information since they reflect the electronic structure and the electron–phonon interactions [23]. These parameters provide information regarding graphene, graphite, carbon nanotube and fullerene structures, and produce distinct Raman fingerprints as they are linked to the specific carbon sheets organization. D band is connected with the breathing modes of sp2 atoms in hexagon rings activated by the defects such as vacancies. G band is attributed to the bond stretching, while 2D band, which is the second order of the D band, is attributed to breathing modes of sp2 atoms in rings. The I_D/I_G and I_{2D}/I_G ratios reflect the amount of

structural defects and are used as an indicator of the graphitization index. The Raman spectrum of graphenebased samples is shown in Fig. 3 and the characteristic values of the important parameters are listed in Table 1.

The full width at half maximum (FWHM) value of the 2D peak in the Raman spectrum of the graphene-based 3D printed structure is 85.2 cm^{-1} , almost three times bigger than the value of pristine graphene [24] and the I_D/I_G ratio value is 0.49. The other remaining peaks shown in the Raman spectra can be assigned to the PLA polymer matrix of the composites. The strong Raman bands in the 3100–2800 cm⁻¹ range correspond to C–H stretching modes of –CH₃ and –CH₂– groups. The peak at 1455 cm⁻¹ can be assigned to the CH₃ asymmetric deformation whereas the one at 873 cm⁻¹ to the C–COO stretching of the repeated polymer unit [25].



Fig. 3 Typical Raman spectrum of graphene-based 3D printed samples. One can see the typical Raman bands of the PLA polymer matrix marked with asterisks

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Table 1 Characteristic Ramanparameters of graphene-based3D printed samples	D peak (cm ⁻¹)	G peak (cm ⁻¹)	$I_{\rm D}/I_{\rm G}$ ratio	2D peak (cm ⁻¹)	$2D FWHM (cm^{-1})$	$I_{\rm 2D}/I_{\rm G}$ ratio
	1357.46	1581.77	0.49	2708.89	85.2	0.68

3.2 Electrochemical performance

3.2.1 Current–Potential curves

The effect of the pyramids height on the electrochemical performance of the 3D-printed graphene was evaluated by cyclic voltammetry as shown in Fig. 4. It can be observed that the printed graphene pyramids with 5.0 mm height exhibited two redox peaks at -0.3 and -0.1 V (versus Ag/ AgCl), which can be assigned to the reversible Li⁺ intercalation/deintercalation reaction following the equation $x\mathrm{Li}^+ + x\mathrm{e}^- + \mathrm{C}_6 \leftrightarrow \mathrm{C}_6\mathrm{Li}_x$ [26]. Additionally, the sweeping area of this sample is the highest of all presenting enhanced electrochemical activity. On the other hand, the other samples indicated less distinctive redox peaks. One may then suggest that the amount of charge incorporated is increased for the graphene pyramid with 5.0 mm height due to the larger mass of the material present (i.e., thicker electrode) as expected from the literature [4, 15] endowing the transportation of electrolyte ions and electrons throughout the electrode matrix. Figure 4 inset shows the cyclic voltammograms for various scan numbers of the graphene pyramids with 5.0 mm height, where the current was lower as the number of scans increased from 1 to 250 and remained constant afterwards. This behavior indicates prolonged stability of the printed graphene and is supported



Fig. 4 Cyclic voltammograms of first scan at 10 mV s^{-1} for the 3D printed graphene pyramids with heights of 1.0, 2.5 and 5.0 mm along with the flat printed graphene as inset for geometrical electrode surface area of 0.25 cm². Cyclic voltammograms of 1, 250, 500 and 1000 scans of the graphene pyramids with 5.0 mm height are shown as inset

by the voltammograms showing no evident degradation after cycling for 1000 times. This decrease is ought to the immediate detachment of the pyramid top by the electrolyte. Since the electrochemical cell was made of glass, these changes could be observed during the electrochemical measurements. All printed graphene pyramids showed good reproducibility over continuous Li+ intercalation/ deintercalation scans. Finally, it is important to note that the current of the flat printed graphene (Fig. 4 inset) was one degree of magnitude lower than the rest of the samples strengthening the importance of the graphene patterning.



Fig. 5 a Cyclic voltammograms of 3D printed graphene pyramids with 2.5 mm height recorded at 5, 10, 20, 50, 100 and 200 mV s⁻¹ **b** Anodic peak current as a function with the square root of scan rate. Diffusion coefficient values are also included as inset in b

Figure 5a shows the cyclic voltammogram curves of the 3D printed graphene pyramids with 2.5 mm height at scan rates of 5, 10, 20, 50, 100 and 200 mV s⁻¹. The peak current increased with the scan rate [27], while retaining the shape of the curves, suggesting fast redox reaction and transport rates [28]. A similar behavior is observed for the rest of samples (not shown here for brevity). Figure 5b indicates the plots of peak current against the square root of scan rate for all samples. A linear relationship was obtained suggesting a diffusion-controlled process. Taking this into consideration, the diffusion coefficient of Li⁺ can be calculated using the following equations [17]:

$$I_{\rm p} = D^{1/2} 2.72 \times 10^5 n^{3/2} A C v^{1/2} \tag{1}$$

$$D^{1/2} = \frac{a}{2.72 \times 10^5 n^{3/2} AC} \tag{2}$$

where *n* is the number of electrons, i_p is the peak current in *A*, *D* is the diffusion coefficient in cm² s⁻¹, *A* is the area in cm², *C* is the concentration of Li⁺ in mol cm⁻³, *v* is the scan rate in V s⁻¹ and *a* is the slope obtained from Fig. 5b. The diffusion coefficient for the graphene pyramids with 5.0 mm height was the highest in accordance with the discussion above expecting to result in a fast response [29].

3.2.2 Estimation of electrochemical surface area and roughness factor

Chronocoulometry was utilized for surface area measurements [27, 30] based on the Anson equation [30], which defines the charge-time dependence for linear diffusion control

$$Q = 2nFACD^{1/2}\pi^{-1/2}t^{1/2}$$
(3)

$$A = \frac{a}{\frac{2nFCD^{1/2}}{\pi^{1/2}}}$$
(4)

where Q is the charge in C, n is the number of electrons, A is the electrochemical surface area in cm², F is the Faraday constant in C mol⁻¹, D is the diffusion coefficient in cm² s⁻¹, t is time in s and a is the slope obtained from Fig. 6. From the plot if charge versus $t^{1/2}$, a linear relationship is obtained for all printed graphene samples, which is referred to as Anson plot [31]. Using the slope obtained in Fig. 6 and Eq. (4), the electrochemical surface area and the roughness factor were calculated. The roughness factor was obtained from the ratio of the electrochemical to the geometrical surface area. The estimated values indicate a clear dependence of the electrochemical performance on the roughness, with enhanced performance for the 3D printed graphene pyramids with 5.0 mm height.



Fig. 6 Anson plots for 3D printed graphene pyramids with 1.0, 2.5 and 5.0 mm height. Estimated electrochemical surface area and roughness factor are also indicated as inset

3.2.3 Specific discharge capacity

The CP measurements of the 3D printed graphene pyramids with 5.0 mm height under a constant specific current of 40 mA g⁻¹ and potential ranging from -0.6 to -1 V (versus Ag/AgCl) are indicated in Fig. 7a. A faint plateau at approximately -0.9 V is observed suggesting the onestep deintercalated (discharging) process. Additionally, the specific discharge capacity was estimated to be 248 mAh g⁻¹ after 1000 scans from the initial value of 265 mAh g⁻¹, which is a promising performance for practical application in Li⁺ batteries. Similar specific discharge capacity values were observed by others [15, 16]. The mass of the 3D printed graphene pyramids was measured by a 5-digit analytical grade scale and found to be 0.02532 g.

Rate capability is an important parameter for practical Li⁺ batteries and was assessed at different specific current values ranging from 40 to 280 mA g⁻¹ as shown in Fig. 7b. The 3D printed graphene pyramids with 5.0 mm height exhibited a specific discharge capacity of 265, 262, 261, 255, 254, 220 and 200 mAh g⁻¹ for 40, 80, 100, 120, 240 and 280 mAh g⁻¹, respectively. Particularly, when the specific current increased to seven times of the initial value (40 mA g⁻¹), the specific discharge capacity maintained 75% of the original value. Additionally, the 3D printed graphene pyramids could still deliver a specific discharge capacity of 263 mAh g⁻¹, corresponding to specific discharge capacity retention of 99% of the original value suggesting good structural stability and high reversibility.

3.2.4 Electrochemical impedance spectroscopy

To study the effect of pyramids height on the electron transport and recombination properties of the 3D printed



Fig. 7 a Chronopotentiometric curves for 3D printed graphene pyramids with 5.0 mm height under specific current of 40 mA g⁻¹, potential ranging of -0.5 to -1.0 V and scan numbers 1 and 1000. Specific discharge capacity of the same sample as a function with scan numbers as inset. **b** Rate capability of the 3D printed graphene pyramids with 5.0 mm height at different specific current values ranging from 40 to 280 mA g⁻¹ and then back to 40 mA g⁻¹

graphene, EIS measurements were performed as presented in Fig. 8. Nyquist plots show semicircles, which correspond to the charge transfer reaction at the electrode/electrolyte interface [32, 33]. The plots were further fitted using the equivalent circuit as indicated in Fig. 8 inset consisting of the charge transfer resistance (R_p) , the solution resistance (R_s) and a constant phase element. The experimental data is represented by the symbols, while the data fitted by Z-view software by the solid lines. The fitted values of R_p are estimated to be 3200, 1900 and 320 Ω for 1.0, 2.5 and 5.0 mm, respectively, suggesting that the 5.0 mm height is beneficial for the charge transfer across the 3D printed graphene/electrolyte interface enhancing its Li⁺ intercalation performance.



Fig. 8 Nyquist plots of the measured (symbols) and fitted (solid lines) impedance spectra of the 3D printed graphene pyramids with 1.0, 2.5 and 5.0 mm height. Equivalent circuit is also indicated as inset

4 Conclusions

The fabrication of crystalline 3D printed graphene pyramids with good stability under environmental conditions was accomplished by varying their height. Electrochemical analysis revealed that the printed graphene with the longest pyramids exhibited several characteristics that make it promising as a high-performance electrode material including: (a) large mass of the active material available (i.e., thicker electrode), (b) high specific discharge capacity of 265 mAh g⁻¹ with retention of 93% after 1000 cycles and (c) high rate capability suggesting good structural stability and high reversibility. Considering all those features, the proposed 3D printed graphene is promising to be an anode for flexible and lightweight LIBs.

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