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# Electronic Supporting Information

# Next Generation Additive Manufacturing: Tailorable Graphene / Polylactic(acid) Filaments allow the Fabrication of 3D Printable Porous Anodes for Utilisation within Lithium-ion Batteries

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### *Electrochemical Optimisation and benchmarking of the graphene / PLA filaments of the additively manufactured / 3D printed architectures.*

The potentiostatic electrochemical experiments were carried out utilising a three-electrode setup with either the graphene/PLA filament or a 3D printed anode (3DA) as the working electrode (with a diameter of 3 mm and a thickness of 1 mm), an Ag/AgCl and platinum as the reference and counter electrodes respectively. Each 3DA for the electrochemical characterisation experiments were 3D printed with a connecting strip allowing simple connection to a crocodile clip.

Firstly, the graphene/PLA filaments were subjected to electrochemical characterisation utilising the near-ideal outer-sphere redox probe 1 mM hexaammineruthenium (III) chloride/ 0.1 M KCl, which does not show any changes in its electron transfer rates due to varying surface chemistry and is only dependent upon the electrode's electronic structure (Density of States (DOS) and the Fermi level) [1][2][3], thus making it a commonly utilised redox probe in the academic literature. Figure S1A depicts typical cyclic voltammograms obtained utilising the graphene/PLA filaments with graphene loadings of 10, 15, 20 *wt.* %. A clear trend is apparent, in which a higher percentage of graphene increases the overall electrochemical reversibility of the system. This trend is present over the entire range, (as shown in the inset of Figure 1B) with the filament containing a graphene loading at 20 *wt.* % possessing the lowest $\Delta E_p$. These voltammetric responses are typical when utilising outer-sphere systems, as the increased graphene loading will most likely increase the amount of available electrochemically reactive edge sites [4][5].

Taking into consideration the electrochemical performance of the filament in its bulk form, we subsequently AM/3D printed the 15 and 20 *wt.* % filaments, to understand the effect of re-extrusion (*i.e.* 3D printing) upon their conductivity and electrochemical capabilities. Presented in Figure 1C is a sole cyclic voltammogram of the 20 *wt.* % graphene 3DA, where it is clear there is a difference within the voltammetry recorded. This is postulated to be due to increase within the volume/area of the 3DA when compared to the bulk filament, with the 20 *wt.* % 3DA exhibiting a heterogeneous electron transfer rate constant, $k^0$, of $2.73 \times 10^{-3}$ cm s$^{-1}$, which is typical of graphitic materials. It is important to note that upon 3D printing of the 10 *wt.* % graphene/PLA filament, the resulting 3D print possessed an excessively high electrical resistance and did not give rise to any useful voltammetry, due to the low percolation of the graphene throughout the increased volume of the 3DA. Conversely, loadings above 20 *wt.* % graphene could not be passed through the nozzle of the 3D printer, due to the brittle nature of the filament, as there is a considerably increased volume of graphene within the bulk filament.

Nonetheless, upon the fabrication of 20 *wt.* % graphene loading (*i.e.* larger PLA content), the graphene/PLA filament (Figure S1) can be successfully 3D printed into useful electrochemical geometries,

**Figure S1**: Cyclic voltammetric profiles from the 10, 15 and 20 *wt.* % graphene loaded filaments and 20 *wt.* % graphene 3DA towards 1 mM hexaammineruthenium (III) chloride / 0.1 M KCl; scan rate: 5 mV $s^{-1}$ (B & C respectively). Inset B: plot of increasing graphene loadings (*wt.* %) *vs. peak potential* (*$\Delta E_p$*) (*vs*. Ag/AgCl).

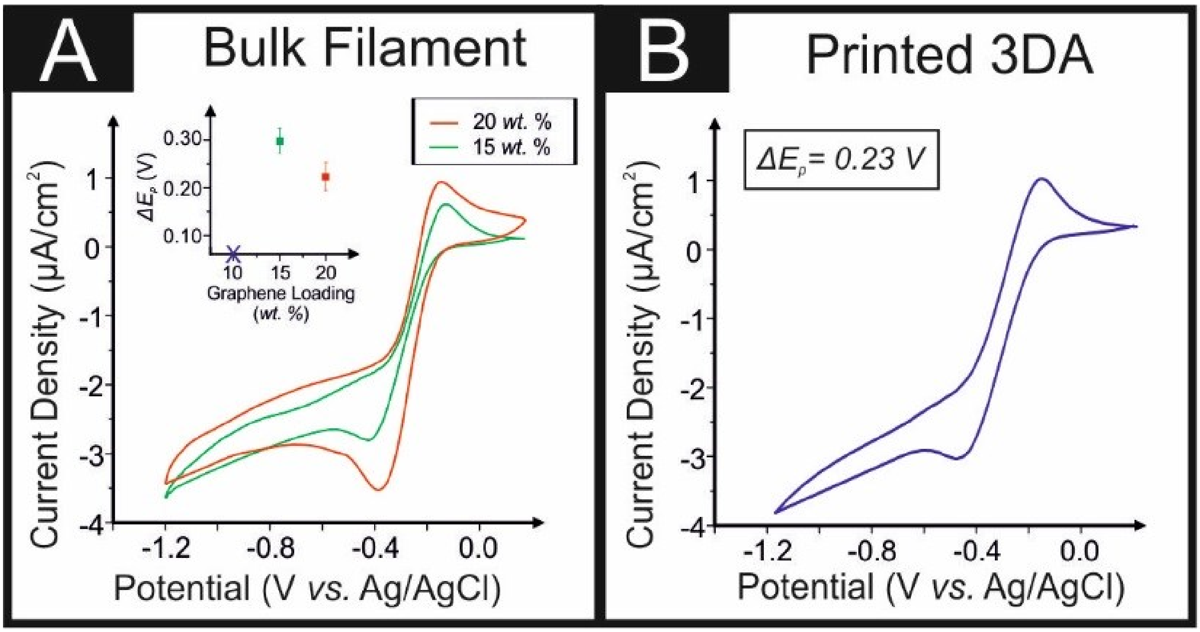


**Figure S2:** SEM imaging of the solution-mixed graphene/PLA powders used to make the graphene/PLA filament (at 15 & 20 *wt.* % graphene loadings, A and B respectively) and 20 *wt.* % graphene 3DA (C).

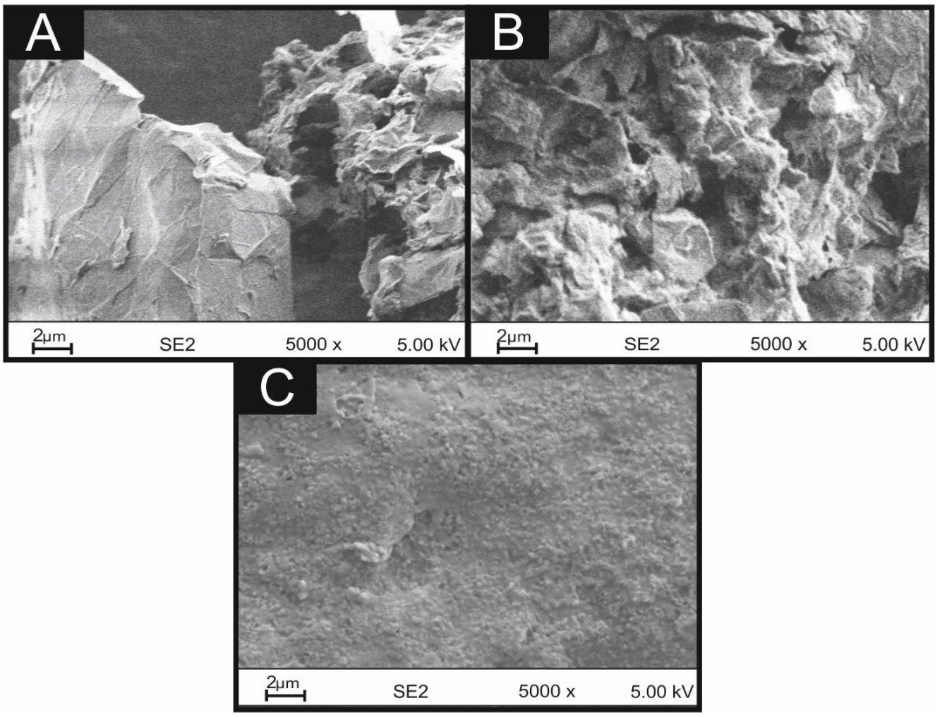


**Figure S3:** XPS spectra and C 1s Region of the 20 *wt*. % graphene 3DA pre and post NaOH treatment.

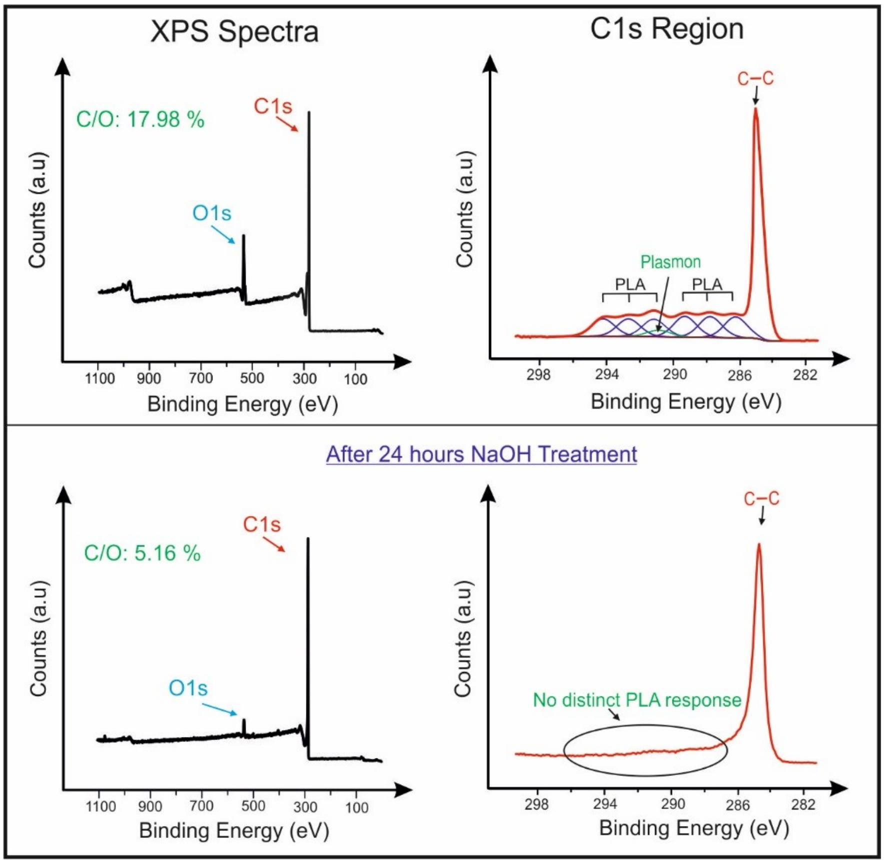


**Figure S4:** SEM imaging of the 20 *wt*. % graphene 3DAs after 24hours exposure to chemical pre-treatment.

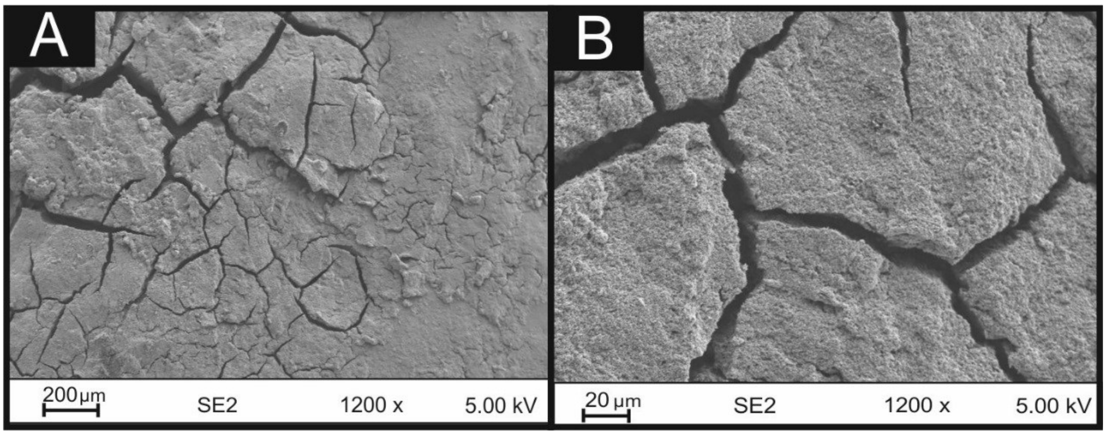


**Figure S5:** XRD analysis of the graphene powder, PLA control, graphene/PLA and chemically pre-treated graphene/PLA.

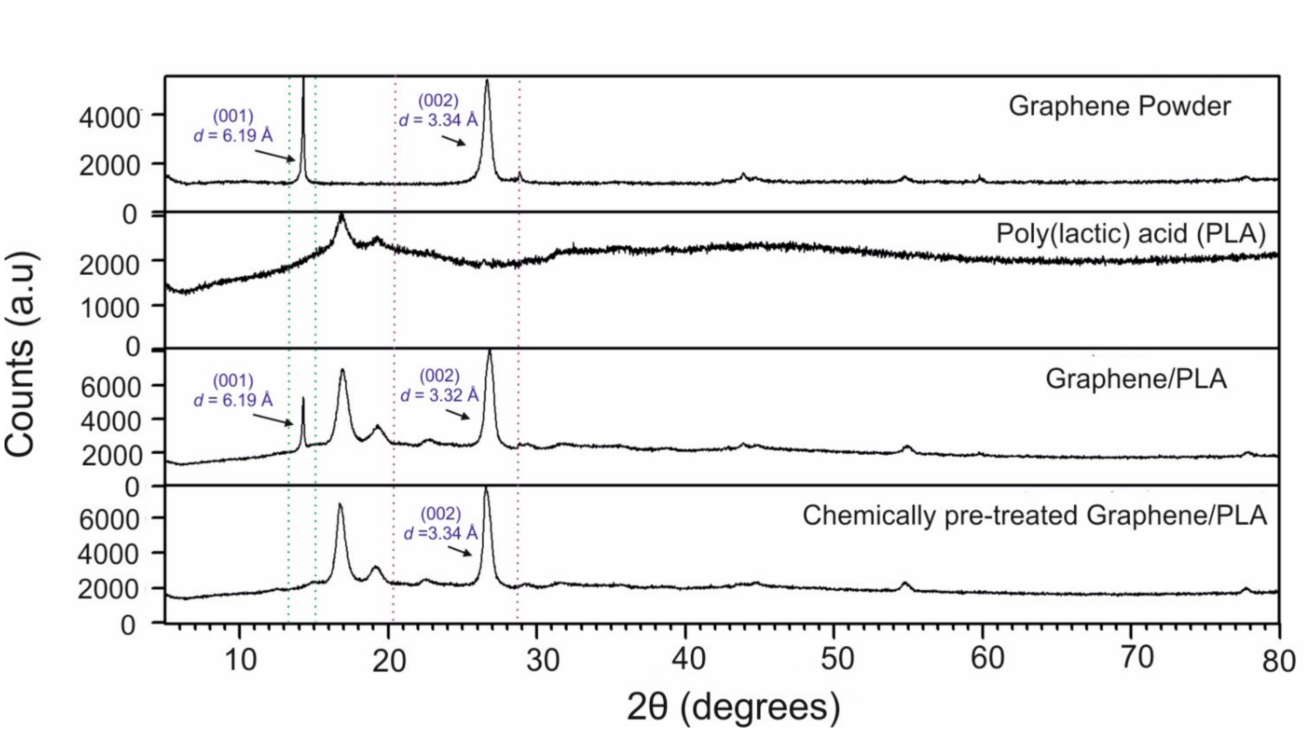


**Figure S6:** Themogravimetric analysis of the 20 *wt*. % graphene 3DA treated with NaOH.

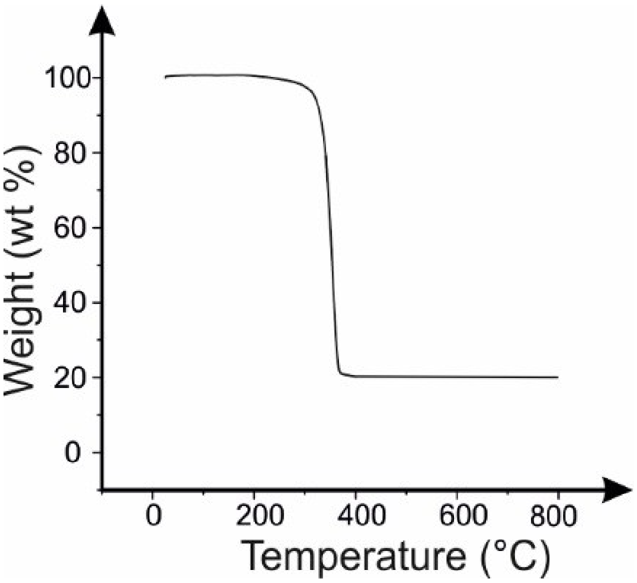
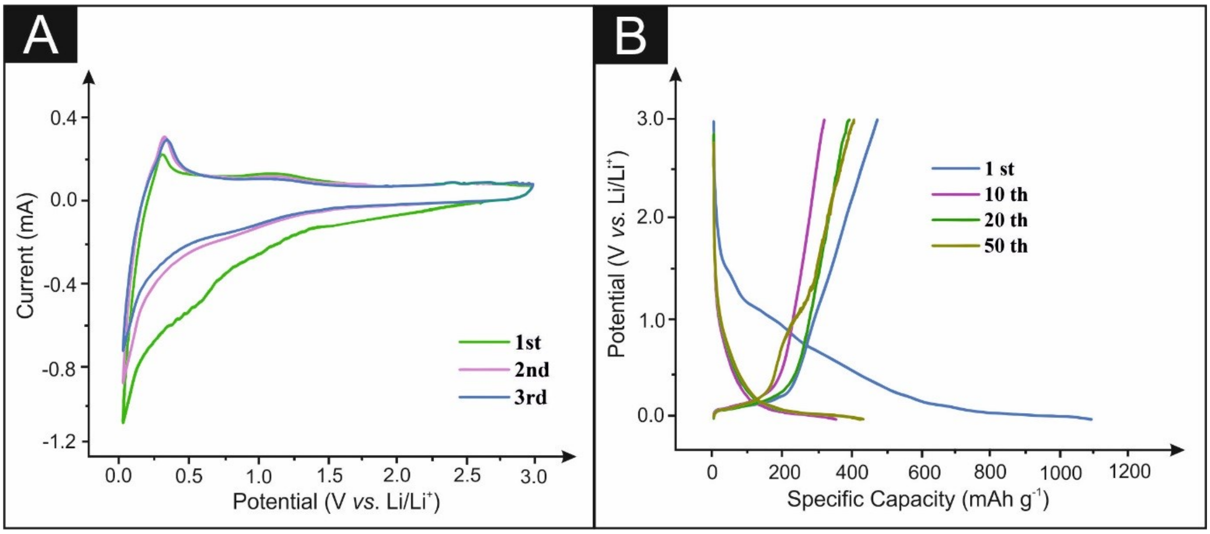


**Figure S7:** Cyclic voltammograms (A) recorded at a scan rate of 0.1 mV $s^{-1}$ over a voltage range of 0.01–3.0 V *vs*. Li/$Li^+$. Galvanostatic charge–discharge profiles (B) at a current density of 40 mA $g^{-1}$.



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