

SULPHUR CROSS-LINKED GRAPHENE NANO PLATELETS AS STRUCTURAL COMPOSITE SUPERCAPACITOR ELECTRODES

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Abstract

Graphene nano platelets cross-linked with elemental sulphur have been used as supercapacitor electrode material to provide successful energy storage in a structural device. Chemical crosslinking of the composite produces a mechanically stable material, with both high conductivity and surface area. Characterisation was conducted using scanning electron microscopy and energy dispersive X-ray spectroscopy. Different concentrations of graphene-sulphur are investigated, along with addition of conductive carbon black and multiwall carbon nanotubes. The effects of these variables on the performance of the sulphur cross-linked graphene as a supercapacitor electrode are presented through impedance spectrometry, cyclic voltammetry and galvanostatic charge-discharge. Analysis of the structural performance of the material is conducted by flexural three-point-bend testing.

1. Introduction

Supercapacitors (or electric double layer capacitors, EDLCs) are a type of capacitive energy storage device where electrical energy is stored in an interface between an electrolyte and an electrode [1] [2]. Supercapacitors store energy in such a way that they fill an operational niche between high power density electrostatic/electrolytic capacitors and high energy density electrochemical battery cells. This paper focuses on structural energy storage, where a solid supercapacitor can be used as a stressed component in an electrical product. Past research includes investigations of carbon fibrous electrode materials [3] and gelled electrolytes [4].

To increase capacitance, supercapacitors include active electrodes of large surface area, which is realised by using highly porous materials as the electrode surfaces, i.e. activated carbon [5]. Electrode choice in EDLCs is the main contributor to enhancing performance. The prime objective is to use a material that will provide high surface area (through porous surface structure), while retaining the high conductivity/low resistance necessary for use in electronic devices. The choice of electrode material has other constraints beyond cost and availability. The high surface area desired must be balanced with the need for electrolyte ion access to the electrode. This is countered by the need for small pore sizes to give maximum surface area.

On the outer layer of the electrode a non-permeable current collector is added, often aluminium or other metallic foil, as most active electrode materials have relatively low bulk

conductivity due to their high porosity [1] [6]. This provides structure to the porous electrode, and some prevention against liquid electrolyte leaks. When using most forms of high porosity carbon for electrode materials, the substance is mixed with a chemical binder to form a composite electrode, which aids application to the current collector and prevents decomposition of the surface [5]. The addition of polymer binders to porous carbon electrodes does however come with a drawback. Polymers are for the most part insulators and so increase resistance of the electrode and by extension the internal resistance of the cell as a whole.

Activated carbon powders provide high specific surface area for supercapacitors, however suffer from low conductivity as well as low contact conductivity at the carbon-current collector interface, and particularly when used with polymer binders. Graphene, with its well-characterised high conductivity and surface area, is emerging as a candidate for energy storage applications [7]. This investigation focuses on construction of a structural supercapacitor, and as such carbon electrodes with polymer binder do not provide enough mechanical stability. Therefore the aim is to create a high conductivity and surface area graphene material, for use as supercapacitor electrodes, which will also provide structural strength to the device.

2. Materials and Experimental Techniques

Carbon nanomaterial cross-linking by sulphur has been developed by Carotenuto et al. [8]. In a process akin to vulcanising rubber, graphene was chemically bonded with elemental sulphur to produce a mechanically stable material. Crosslinking of graphene was performed in a similar procedure to that outlined by Carotenuto et al. [8]. Slurries of graphene nano-platelets (GNPs) and sulphur dispersed in toluene were prepared at different GNP:sulphur compositions. The mass ratio of the total combined solid constituents - GNP and sulphur, and also carbon black (CB) and multiwall carbon nanotubes (MWCNTs) in later experiments to try to improve conductivity [9] [10] - to the solvent (toluene) was maintained at 1:10. Graphene nano-platelets were dispersed into toluene and homogenised, with CB and MWCNTs added in various concentrations. Elemental sulphur was then added to the slurry and stirred to form the basic graphene-sulphur paste, which was poured into moulds for annealing. The annealing process required first drying the mixtures in air to evaporate away the toluene and leave a homogenous dispersion of dry carbon and sulphur. The samples were then transferred to a vacuum oven, where they were annealed at 125°C under vacuum for 4 hours.

Each supercapacitor cell was made by first cutting the cross-linked graphene-sulphur material into electrodes using a razor blade. One electrode was placed on top of its aluminium foil current collector, with a sheet of cellulose separator paper laid on top of the pair. 1M TEABF₄/PC electrolyte was added by pipette, before the second electrode was added, and its current collector placed on the top of the stack. The layup was then sealed inside a polypropylene bag. Every cell in this investigation was made with 1.5×3.0 cm electrodes, for a total electrode surface area of 9.0 cm².

SEM and EDX analysis was used for microstructural and chemical characterization of the graphene-sulphur samples respectively. Impedance spectrometry measures the real and imaginary components of impedance, with varying frequency. Data was collected between 10⁶Hz and 10⁻²Hz. Imaginary impedance Z_{im} is used to determine capacitance C through equation 1.

$$C_{im} = \frac{1}{2\pi f Z_{im}} \quad (1)$$

The data from an impedance spectrograph is plotted as a Nyquist Plot. This displays real impedance Z_{re} on the x-axis (representing resistance) and imaginary impedance on the y-axis. A simplified real capacitor can be modelled as an ideal capacitor and ideal resistor in series and/or parallel [11]. When examining a Nyquist plot, these characteristics appear clearly as two distinct features on the graph. An ideal resistor in parallel appears as a semicircle in the plane of the real axis; the diameter of this semi-circle is the parallel resistance, which is usually the biggest component of the Equivalent Series Resistance (ESR). The left hand side point of this semi-circle on the x-axis represents the in series component of the ESR. An ideal capacitor appears as a straight near-vertical line parallel to the imaginary axis, whose imaginary impedance indicates the capacitance of the cell through equation 1.

Galvanostatic charge-discharge raises the potential of the cell to a set maximum value at constant current, before then discharging at constant current. Data was collected at various currents depending upon the capabilities of the cell, and a voltage range of 0-3V. The capacitance can be determined by equation 2.

$$C_{CD} = \frac{I}{dV/dt} \quad (2)$$

Cyclic Voltammetry was carried out at a fixed scan rate (V/s), up to a maximum target potential difference across the cell, before inverting the scan rate to bring the potential back to zero. It was then repeated for different scan rates. Capacitance can be determined using equation 3, where I_{mid} is the midpoint of the current trace, at which maximal potential difference is reached.

$$C_{cvmid} = \frac{I_{mid}}{dV/dt} \quad (3)$$

3. Results

21 different sample mass compositions were investigated. These are 5 different concentrations of un-doped sulphur-carbon, then the same 5 concentrations each doped with +5%, +10% and +15% carbon black for a total of 20 samples. Upon completing these samples it became apparent that the initial sulphur composition of the samples mattered little, as hard to control evaporation of sulphur in the vacuum oven reduced the sulphur content by an unpredictable amount. Therefore only one graphene-sulphur concentration sample doped at 0.15% with multiwall carbon nanotubes was tested, with an initial composition of 50% carbon and 50% sulphur.

3.1 Microscopy and Spectroscopy Results

EDX analysis was performed, producing spectrums for all 21 samples. Sulphur was shown to be homogeneously distributed over all samples, and some samples contained up to 3.5 wt% elemental oxygen (associated with carbon oxidation). SEM imagery shows in Figure 1 the GNPs to be agglomerations of graphene sheets with lateral dimensions in the micrometre scale. The cross-linked graphene has the appearance of densely packed flakes, and upon

higher magnification inspection each flake is seen to comprise further sheets of graphene. No sulphur agglomerations were seen on any samples, but its presence was indicated by EDX to be homogeneously distributed across all samples. This indicates successful crosslinking of the graphene sheets.

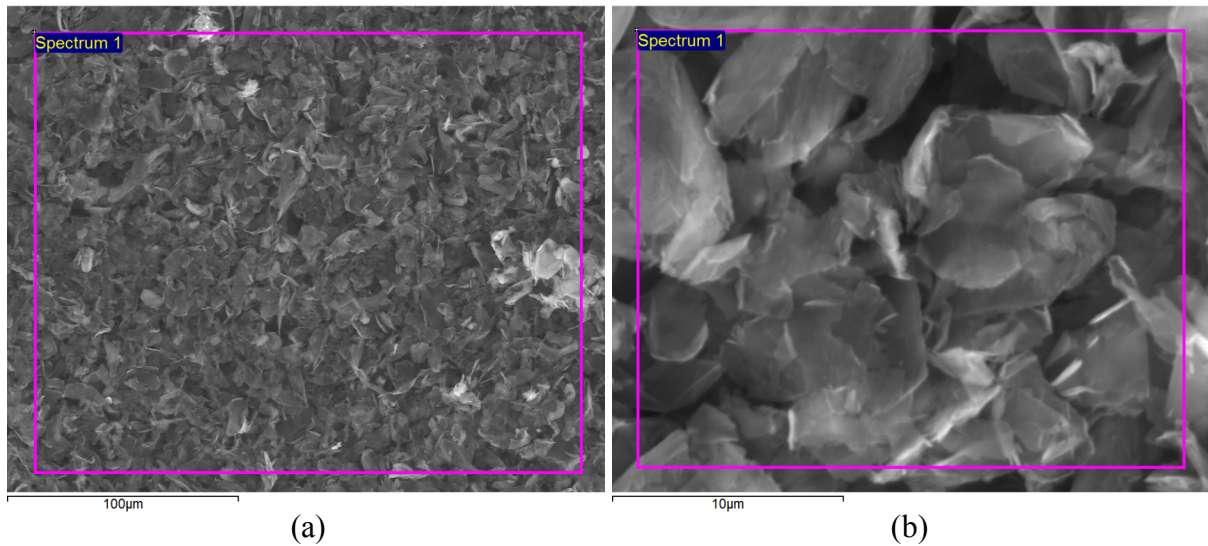


Figure 1 – SEM images of typical graphene-sulphur composite at (a) ×500 and (b) ×5000 magnification.

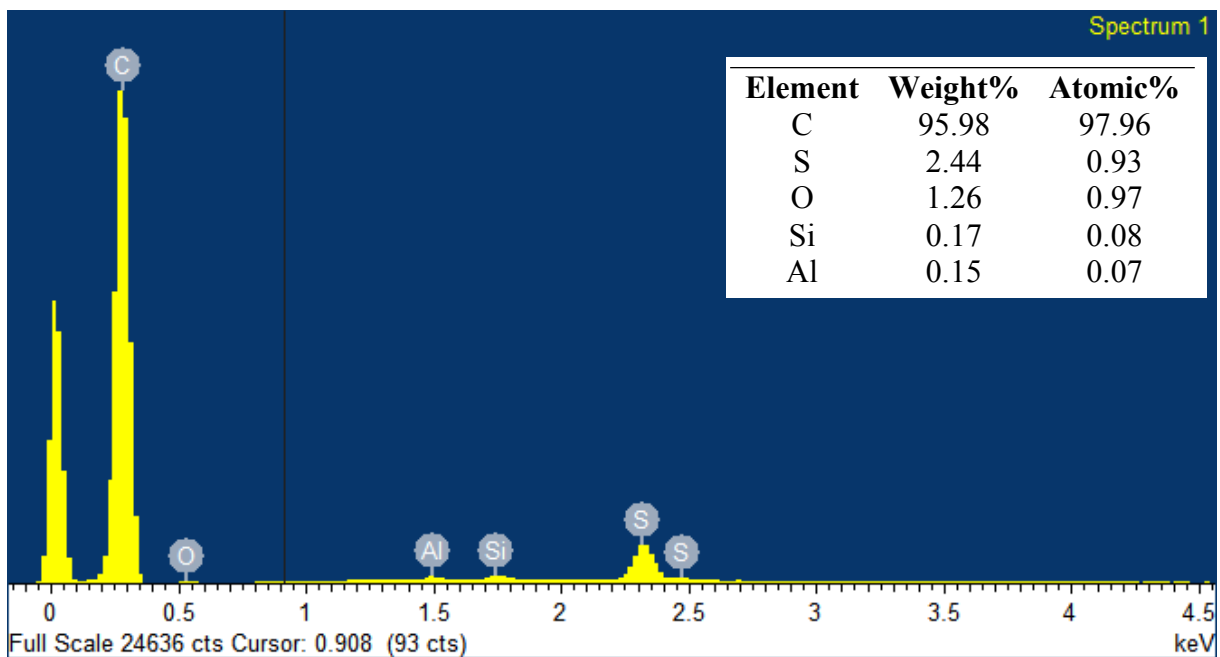


Figure 2 – EDX spectrograph of typical graphene-sulphur composite with weight and atomic elemental percentages.

3.2 Energy Storage Test Results

Electrochemical testing showed that all material combinations when used as electrodes produced successful supercapacitors. Impedance spectrometry showed encouraging Nyquist plots, with low resistances but also low specific capacitances.

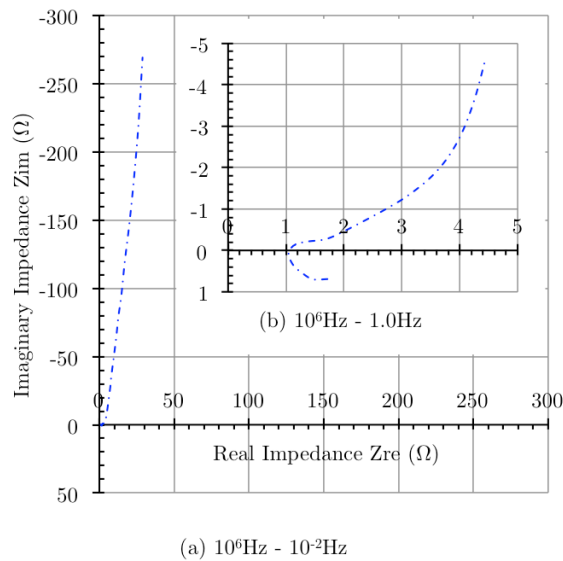


Figure 3 - Nyquist plot of impedance spectrometry data for sulphur cross-linked graphene electrode, with inset high frequency zone depicting resistance.

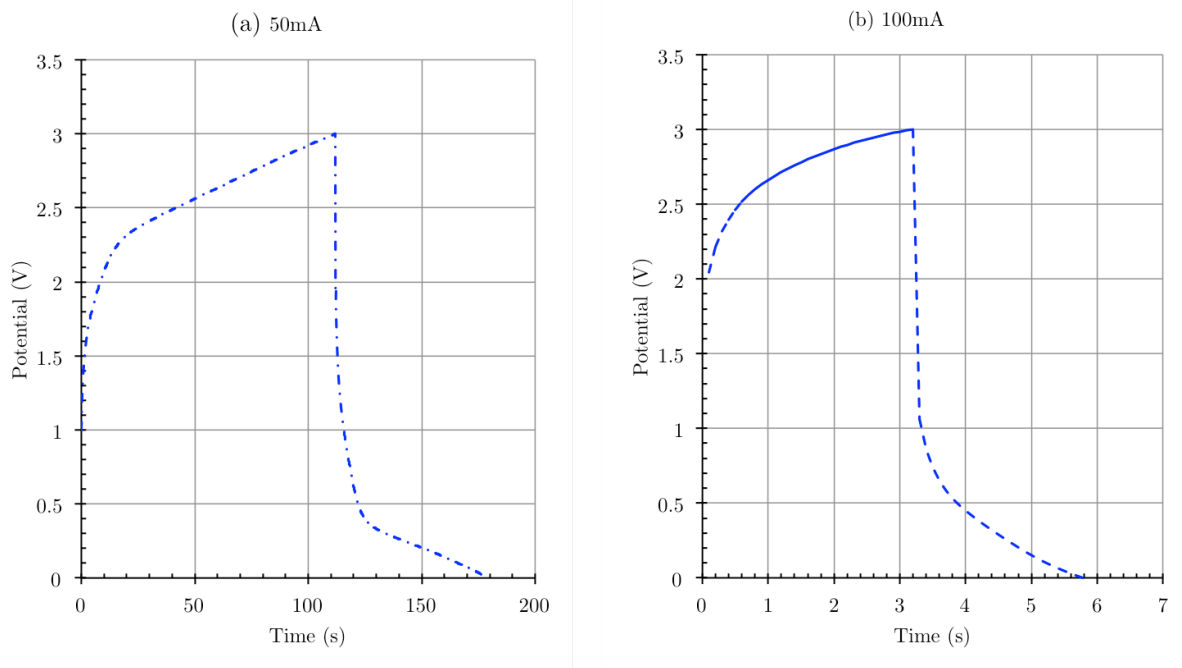


Figure 4 – Galvanostatic Charge-Discharge plots of typical sulphur cross-linked graphene electrode at (a) 50mA and (b) 100mA.

Galvanostatic charge discharge data shows that supercapacitors using sulphur cross-linked graphene electrodes can function as energy storage devices. High voltage drop off is observed

in all samples, which is indicative of high internal resistances in the cells. Using the relation $V=IR$ this voltage drop off can be translated to a discharging internal resistance. The supercapacitor cell tested in Figure 4 exhibits an internal ESR of $\sim 20 \Omega$ at 100 mA. This includes the resistance contribution of slow ion diffusion, corresponding to small pores between bound graphene sheets. The maximum specific energy recorded was 5.79 Whkg^{-1} for the cell with the lowest internal resistance through constant current discharge of 3.5Ω ESR. The electrode material had an initial composition of 5% carbon black, 52.25% sulphur and 42.75% GNPs, and was measured by EDX after annealing to have a final sulphur content of 1.7% by weight.

Cyclic Voltammetry plots in Figure 5 reveal a highly irregular CV plot even at the low scan rate of 0.01V/s, with specific capacitance falling quickly as scan rate is increased.

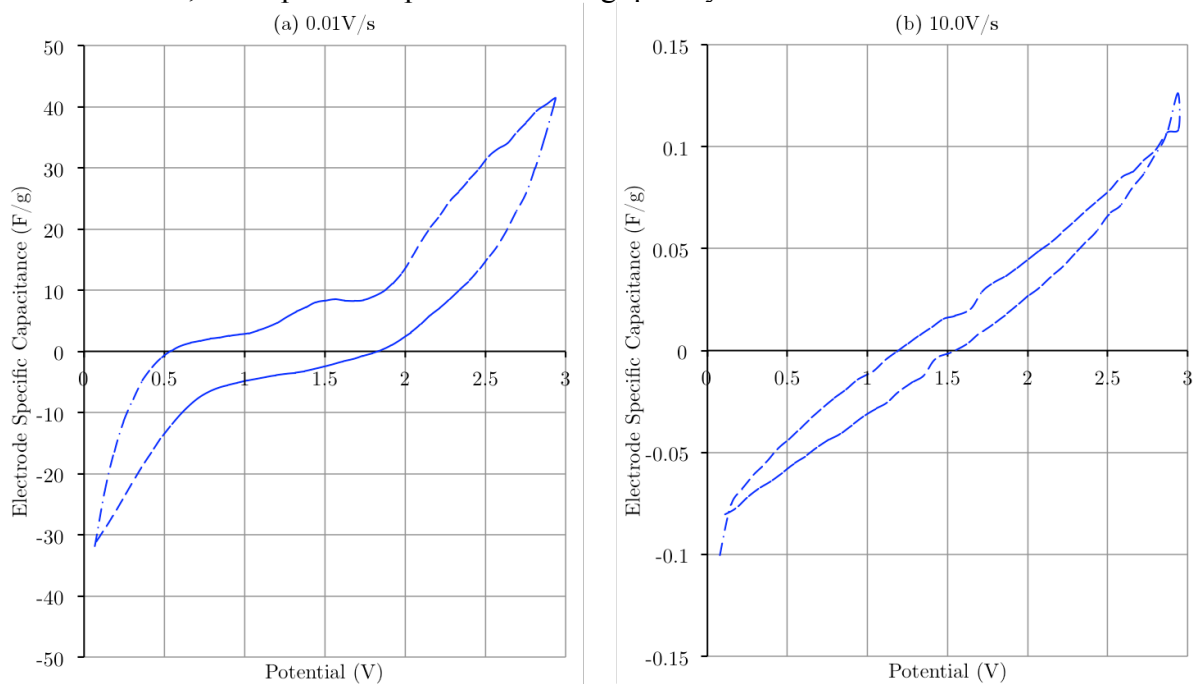


Figure 5 - Cyclic Voltammetry curves for typical sulphur cross-linked graphene electrode at (a) 0.1 V/s and (b) 10 V/s

3.3 Flexural Three Point Bend Results

Flexural three point bend test data was successfully obtained for 7 samples. Three-point bend testing of sample electrodes gave low stress and strain results. The highest modulus was 37 MPa, comparable to stiff rubber. The rest of the samples displayed the flexibility of elastomers. The maximum flexural stress recorded was 0.245 MPa, and the maximum flexural strain was 0.013 mm/mm. These were displayed by the sample with 0.15% MWCNT, with 50% sulphur and 50% GNP initial composition, measured to have a sulphur content after annealing of 20%. This flexural stress of 0.245 MPa does not compare favourably to the strength of mild steel ($\sim 155\text{MPa}$), acrylic polymer ($\sim 75\text{MPa}$), or polypropylene polymer ($\sim 40\text{MPa}$).

4. Concluding Remarks

Methods for the manufacture of a structural graphene supercapacitor electrode were presented. Cross-linking GNPs with elemental sulphur is shown to produce a semi-structural and conductive material with some surface area for use in supercapacitors, although not the high values observed in uncross-linked graphene. BET analysis yields a specific surface area of 11.9 - 18.6 m²g⁻¹ for representative samples. The material is shown to have maximum flexural stress of 0.245 MPa when doped with MWCNTs. Its flexural modulus approaches that of rubbers, with the highest value of 37 MPa for the material doped with MWCNTs. Different initial concentrations of graphene-sulphur are shown to be difficult to maintain through the annealing/cross-linking process, with EDX analysis showing typically 1-2% sulphur remaining for un-doped samples and those doped with 5% carbon black. Impedance spectrometry and galvanostatic charge-discharge test data show little variance across all samples in mean specific capacitance, energy density and power density. Sulphur cross-linking of GNPs accelerates their agglomeration, producing a material with reduced pore surface area and increased sub-nano porosity. This slows ion movement and reduces the number of ion-accessible pore sites at high Voltage scan rates.

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