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Research Paper

Graphene-enhanced electrodes for scalable supercapacitors

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ABSTRACT

A scale-up process of high-rate-capability supercapacitors based on electrochemically exfoliated graphene (EEG) and hybrid activated carbon (AC)/EEG are studied in this work. A comparison of the rate capabilities of large-scale EEG and AC/EEG-based pouch cell and commercial high-power supercapacitors are also presented in this paper. The oxygen content of the EEG used in this work is 9.6 at%, with a C/O ratio of 9.36, and the electrical conductivity is 2.68×10^4 Sm^{-1}. The specific capacitance (59 Fg^{-1}) of the EEG-based supercapacitors remained above 80% of the maximum value as the scan rate was increased from 5 mVs^{-1} to 1 Vs^{-1}. Furthermore, our study reveals how the rate capability of activated carbon (AC) based supercapacitors can be improved by adding EEG into the electrodes to form a hybrid AC/EEG supercapacitor. Both the EEG-based and AC/EEG supercapacitors were scaled-up to pouch cells with capacitances of tens of farads. The electrochemical response was unchanged when scaling up from a coin cell to a pouch cell, although the specific capacitance fell slightly. The cycle performance of the AC/EEG pouch cell showed good long-term stability, with better than 95% capacitance retention after 10,000 cycles. Both the EEG and AC/EEG (with 1:1 mass ratio) pouch cells had rate capabilities that compared favourably with the commercial high-power supercapacitors.

1. Introduction

Supercapacitors are an attractive energy storage technology for applications ranging from electronic devices to electric vehicles, and renewable power generation, owing to their very large capacitance and high-power capability when compared to dielectric capacitors or secondary batteries. The performance of a supercapacitor depends greatly on the properties of the electrode materials and the electrode/electrolyte interface, and several carbon materials such as activated carbon (AC) [1], and carbon nanotubes (CNTs) [2,3] have been investigated as supercapacitor electrodes because of their excellent physical and chemical properties. AC is the most commonly used material in commercial supercapacitors due to its large surface area and low cost. However, the low electrical conductivity of AC leads to limitations when used for high-power applications [4]. CNTs have higher electrical conductivity and large readily accessible surface areas. However, single-walled carbon nanotubes are very likely to stack in bundles, leading to only the outermost portion of the CNTs being available for ion accumulation, which results in a lower specific capacitance [3,4].

Recently, graphene-based electrodes for supercapacitor applications have been widely investigated due to the material's high specific surface area, excellent electrical properties and its chemical and thermal stability [5,6]. In order to commercialise graphene-based supercapacitors, efficient large-scale production of appropriate quality graphene is crucial. Large-scale graphene sheets have been produced by chemical vapour deposition (CVD) [7], ultrasonic exfoliation of graphene in solvents such as *N*-methylpyrrolidone (NMP) [8], epitaxial growth on SiC [9], electrochemical exfoliation of graphite [10–13] and solution-based chemical reduction of graphene oxide [14,15]. Although CVD and epitaxial growth can produce high quality graphene on substrates, both methods require high temperatures [16]. Ultrasonic exfoliation of graphene in NMP can give high quality and uniform flakes, but the yield remains low (<50% 1-4 layers graphene) and the lateral flake dimensions are usually small (<1 μm) [8,17]. Electrochemical exfoliation of graphite is very simple, low-cost and less polluting in comparison to the other methods listed, and these features make it ideal for use in commercial graphene-based

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supercapacitors [13,17,18]. In addition, EEG has lower oxygen content and higher conductivity compared to graphene oxide and reduced graphene oxide [19,20]. These factors make EEG a suitable candidate for high-power supercapacitor applications [13,18]. Flexible EEG-based supercapacitors have been demonstrated with high rate capability and gravimetric capacitances ranging from 18.8 to 56.6 Fg^{-1}, depending on the loading of EEG in the electrodes, which varied from 0.6 to 0.2 $mg\,cm^{-2}$ [13]. However, the studies [13] focus on flexible supercapacitors [21–24], but lack of systematic information demonstrating the influence of the scale-up process on the performance of EEG-based high-power supercapacitors. In addition, although the cost-effective nano-graphite has been demonstrated to be scalable for pouch cell supercapacitors, there is a lack of understanding of how nano-graphite improves the performance of pouch cell supercapacitors [25].

In this paper, we demonstrate a successful process can be applied to scale up EEG-based and AC/EEG hybrid supercapacitors with unchanged high-power electrochemical behaviour as in small scale. The information of using high quality graphene in large-scale supercapacitors is limited in the literature. The power density of AC/EEG hybrid electrodes was also revealed to be superior to that of conventional AC electrodes in this work. We prepared high quality graphene by electrochemical exfoliation of graphite foil in aqueous electrolytes to produce EEG with an oxygen content of 9.6 at%, and with a C/O ratio of 9.36. The measured electrical conductivity of the EEG was 2.68 $10^4\,Sm^{-1}$. Supercapacitors made using the EEG show a high rate capability (80% capacitance retention at scan rates over the range 5 mVs^{-1} to 1 Vs^{-1}). This type of supercapacitor has been cycled up to 60,000 times and retained 95% of its initial capacitance value. EEG is also demonstrated to perform well as an enhancer to improve the rate capability of supercapacitors made using AC. EEG has been mixed with AC to make AC/EEG hybrid electrodes for supercapacitors. The electrochemical performance of AC/EEG hybrid electrodes at different ratios has been investigated. The rate capability is significantly improved with only 25 wt% of EEG added to AC electrodes. The best mass ratio of AC/EEG for high-power applications is 1:1 as judged by the optimal capacitance performance seen at a scan rate of 1 Vs^{-1}. A comparison between commercial high-power supercapacitors and the prototype EEG and AC/EEG supercapacitors is also reported. The addition of EEG into AC electrodes could be a cost-effective way to improve the performance due to a small adjustment of production line. The research of using EEG to improve the rate capability of AC electrodes and the scale-up process are successfully conducted in this paper for industrial references.

2. Experimental method

2.1. Materials

Graphene was produced by anodic electrochemical exfoliation according to the previous report by Mullen et al. using 0.1 M ammonium sulfate (aqueous solution) as the electrolyte [13]. The poly(tetrafluoroethylene) binder (60 wt% dispersion in water),

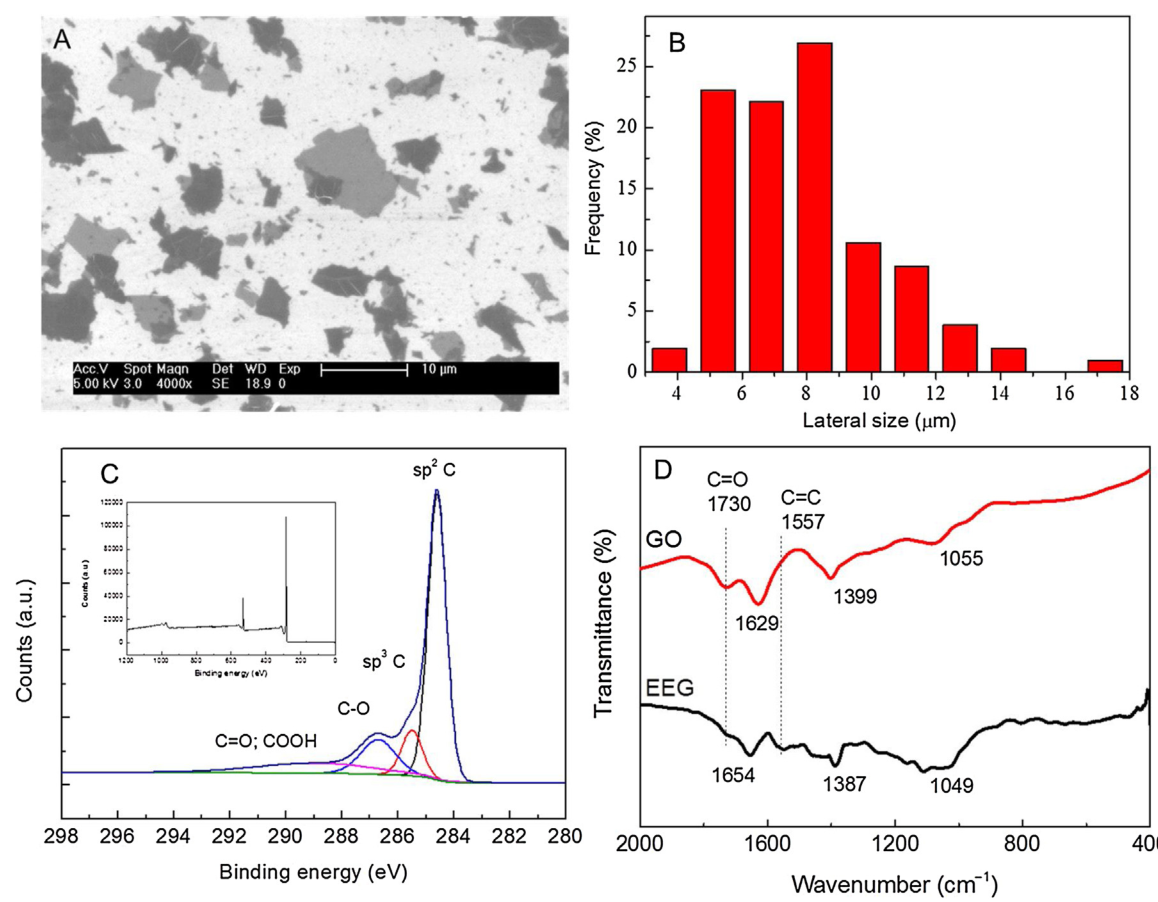

Fig. 1. Characterisation of EEG laminates (a) SEM image (b) statistics of flake sizes over 100 flakes (c) XPS C1s spectra of EEG (inset: survey spectra)(d) FT-IR of EEG (black line) and GO (red line).