



Graphene/activated carbon supercapacitors with sulfonated-polyetheretherketone as solid-state electrolyte and multifunctional binder



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ABSTRACT

Sulfonated polyetheretherketone (SPEEK) has been synthesised by sulphonation process and used as the solid-state electrolyte, binder and surfactant for supercapacitors. Reduced graphene dispersed by SPEEK is used as a high-efficiency conducting additive in solid-state supercapacitors. It is found that SPEEK can improve the stability of the reduced graphene dispersion significantly, and therefore, the solid-state supercapacitors show a large decrease in IR drop and charge-transfer resistance (R_{ct}), resulting in a higher rate capability. The solid-state supercapacitors with the activated carbon/reduced graphene/SPEEK/electrode can be operated from 1 to 8 A/g and exhibit capacity retention of 93%. The noteworthy is more than twice higher value for capacity retention by comparison with the solid-state supercapacitors using activated carbon/reduced graphene/PVDF electrode (capacity retention is 36%). The cell of reduced graphene with SPEEK can be cycled over 5000 times at 5 A/g with no capacitance fading.

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1. Introduction

Electric double-layer capacitors (DLCs), also called supercapacitors or ultracapacitors, are high-power energy-storage devices facilitated by reversible ion adsorption at electrolyte/electrode interfaces upon application of a voltage. Superior properties such as long cycling life and high power density make DLCs suitable for applications in uninterruptible power supplies, peak-power sources for hybrid electric vehicles, and starting powers for fuel-cell systems [1–3].

However, current supercapacitors using ionic liquids or aqueous electrolytes possess the safety hazard of liquid leakage; therefore, robust packages are required. Solid polymer electrolytes are able to address this issue, and have other advantages such as simple assembly, low cost and flexible packages, and possible high-voltage operation. Several materials have been utilized as solid polymer

electrolytes, such as Nafion [4], poly(etheretherketone) (PEEK) [5–7], polybenzimidazole [8], and poly(ethylene oxide) [9,10], which showed reasonable capacitance with limited high-rate capability owing to the low ionic conductivity of solid-state electrolytes. However, current supercapacitor devices still show obvious specific capacitance truncation under ultra-high-rate charge/discharge conditions. Different additives such as carbon black [11,12], carbon nanotubes [13] or acetylene black [14,15] have been incorporated with electrode materials to overcome these difficulties. Graphene is a two-dimensional carbon sheet, and is considered as a state-of-the-art conductive additive [16,17]. Owing to its flexibility and high electron mobility ($15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), graphene provides two-dimensional continuous transport pathways with plane-to-point conductive contacts with active materials [18]. It is therefore a potential candidate as the conductive additive for various energy-storage devices. It has been revealed recently that an enhanced capacity can be achieved by using graphene-grafted metal oxides as the active materials for supercapacitors and lithium-ion batteries [18,19]. However, their dispersion has proved to be a challenge for all applications of graphene. Due to the fact which graphene has a high specific surface area, so they tend to agglomerate irreversibly or even re-stack to form graphites through

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van der Waals interactions. The dispensability of graphene is important because most of their unique properties are only associated with individual sheets. Generally, graphene agglomeration can be reduced by the appropriate dispersants. The presence of dispersants may not be compatible because they are unacceptable impurities, increasing the internal resistance within supercapacitors [20].

In the present study, sulfonated PEEK (SPEEK) is used simultaneously as the solid-state electrolyte, binder, and ion-conducting surfactant for supercapacitors. The effects of reduced graphene additives with SPEEK and conventional polyvinylidene difluoride (PVDF) binders in solid-state supercapacitors have been investigated and compared systematically.

2. Experiments

2.1. Graphene preparation

Graphite oxide was prepared through a modified Hummers method [21]. In brief, natural graphite powder (10 g) was mixed with H₂SO₄ (230 mL, 98 wt%) in an ice bath. Subsequently, KMnO₄ (30 g) was added slowly to the above mixture, which was stirred for 2 h. The mixture was allowed to stand for 1 h, and then, deionized water (500 mL) was added gradually to the mixture. During this process, the temperature was kept below 35 °C by controlling the rate of water addition. The water bath was then heated to 95 °C, and maintained at this temperature for 3 h to increase the oxidation degree of the graphite-oxide product. After oxidation, H₂O₂ solution (30 mL, 30%) was added, and the mixture was then centrifuged and washed to remove any residual salts. The wet graphite oxide was dried under vacuum at 50 °C for 48 h. The resulting graphite oxide was then thermally exfoliated at 500 °C for 5 min in a tubular furnace under an Ar atmosphere to obtain reduced graphene.

2.2. Preparation of the binder and solid-state electrolyte (SPEEK)

Commercially available PEEK powder (Victrex Ltd.) was sulfonated according to the processes reported in the literature [22,23]. PEEK powder was dissolved in 98% sulphuric acid for sulphonation. The solution was poured into cold water (5 °C) to terminate the reaction. For removal of the residual sulphuric acid, the resulting suspension was washed with deionized water until the pH value reached 7. The precipitate was filtered out and dried at 70 °C for 24 h to obtain the sulfonated PEEK polymer. SPEEK (50 mg/mL) was further dissolved in dimethyl sulfoxide (DMSO) at room temperature. The solution was used as a binder and dispersion surfactant. A PVDF binder was also used for comparison.

Reduced graphene was dispersed in the SPEEK or PVDF solution (50 mg/mL) through sonication for 30 min in an ultrasonic bath (Branson 5510R-MT). For characterization of the dispersion stability, homogeneous graphene/SPEEK and graphene/PVDF suspensions were prepared for zeta-potential measurements, which were carried out using a Horbia SZ-100Z instrument with a 532 nm laser [20].

For the solid-state electrolyte, the SPEEK solution (50 mg/mL) was cast into solid membranes by pouring the solution on a Teflon plate and allowing the solvent to evaporate slowly at 150 °C for 24 h. The thickness of the dried membranes was approximately 80 μm [5–7].

2.3. Materials and electrochemical characterization

The morphologies and structures of the graphenes were observed by means of scanning electron microscopy (SEM, JSM-6510) and transmission electron microscopy (TEM, FEI Tecnai G2

T20). X-ray photoelectron spectroscopy (XPS, VGS Thermo K-Alpha) was used to analyse the content of functional groups on the graphene surface.

Electrodes were fabricated by mixing activated carbon (Mitsubishi Chemical, TF-B520) and reduce graphene with binders (SPEEK or PVDF). The activated carbon exhibited pore size 2 nm, pore size distribution 1–3 nm and surface area 1900 m²/g, as measured by BET. The compositions of the prepared slurries are listed in Table 1. The slurries were applied to Ni metal foils, which acted as the current conductors for the electrodes. The weight loading of activated carbon on the electrode is about 3 mg/cm². The coated electrodes were transferred to a dry box for curing at 105 °C for 2 h. The cells were fabricated by rinsing the solid-state electrolyte membrane (SPEEK) lightly with 1 M Li₂SO₄, and using two coated electrodes to sandwich the rinsed membrane. Finally, the solid-state supercapacitor cells (2 × 2 cm) were packed using laminated Al foils.

Cyclic voltammetry measurements were conducted on a Potentiostat/Galvanostat (Princeton Applied Research, Model 263A). The voltage window is between –1 V and 1 V, and the scan rate is 10 mV/s. Galvanostatic charge/discharge measurements were performed on a charge/discharge tester (Arbin SCTS), and the applied current densities were varied from 1 to 8 A/g. The cell capacitance was deduced from the slope of the discharge curve (Equation (1)) [24]:

$$C = I / (dV/dt) \quad (1)$$

where C is the cell capacitance (F), I is the discharge current (A) and dV/dt is the slope of the discharge curve.

The specific capacitance C_{sp} is the capacitance per unit mass for one electrode (Equation (2)) [25]:

$$C_{sp} (\text{F/g}) = 4 \times C / m \quad (2)$$

where C is obtained from Equation (1) and m is the total mass of the active materials in both electrodes. Electrochemical impedance spectra (EIS) were measured with an AC voltage amplitude of 20 mV and a frequency range of 100 kHz to 0.01 Hz. The charge-transfer resistance (R_{ct}) was obtained from the EIS curves. The supercapacitors were cycled 5000 times at 5 A/g for a lifetime test.

3. Results and discussion

3.1. Morphology

Fig. 1(a) and (b) demonstrates the bright-field TEM images of activated carbon, pristine reduced graphene. TEM images of slurries of activated carbon/KS6/SPEEK and activated carbon/reduced graphene/SPEEK are shown in Fig. 1(c) and (d). The activated carbon is composed of individual particles (Fig. 1(a)). The reduced graphene (Fig. 1(b)) exhibits scrolled-like sheet morphology. It is due to the fact that the reduced graphene contents few functional groups and is thermodynamically unstable [26]. As a result, it tends to scroll. The slurry of activated carbon/KS6/SPEEK (Fig. 1(c)) is composed of individual particles, indicating point to point contacts between

Table 1
List of samples with different compositions.

Sample	Electrode composition
A	80% activated carbon + 10% KS6 + 10% PVDF
B	80% activated carbon + 10% KS6 + 10% SPEEK
C	88% activated carbon + 2% graphenes + 10% PVDF
D	88% activated carbon + 2% graphenes + 10% SPEEK

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