The effect of dispersion status with functionalized graphenes for electric double-layer capacitors

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ABSTRACT

Graphene with oxygen (M-rGO and H-rGO) and nitrogen (N-rGO) related functional groups have been fabricated. Reduced graphenes including H-rGO, M-rGO and N-rGO were mixed with activated carbons as the composite electrodes and characterized for supercapacitors. The effects of the functional groups on graphenes as the conductive additive have been investigated. It was found that a suitable content of functional groups can improve the stability of dispersion, and therefore reduce the internal resistance (IR drop) and charge transfer resistance (R_{ct}) resulting in higher rate capability. The supercapacitor with M-rGO and KS6 as additive at the activated carbon electrode can be operated at a rate as high as 6 A/g and exhibits a capacitance of 208 F/g, whereas the supercapacitor using only KS6 as additive shows a capacitance of only 107 F/g. The graphene contained supercapacitor has been cycled over 2000 times at 4 A/g with almost no capacitance fading.

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1. Introduction

The electric double-layer capacitor (EDLCs), also called supercapacitor or ultracapacitor, is a high power energy storage device facilitated by reversible ion adsorption at electrolyte–electrode interfaces upon applying a voltage. Desirable properties such as a long cycling life and high power density make the devices suitable for the uninterruptible power supplies, peak-power sources for hybrid electric vehicle, and starting powers for fuel cell systems [1–4]. However, current supercapacitor devices still show obvious specific capacitance truncation under ultra high rate charge/discharge conditions. In order to solve this issue, different additives such as carbon blacks [5,6], carbon nanotubes [7] or acetylene blacks, [8,9] have been incorporated with electrode materials to lower the internal resistance of the supercapacitors.

Graphene is a two-dimensional carbon sheet, which is considered as a state-of-the-art transparent conductive material [10,11]. Due to its flexibility and high electron mobility (15,000 cm^2 V^{-1} s^{-1}), graphenes provide two dimensional continuous transport pathways with plane-to-point conductive contacts with active materials [12]. It is therefore a potential candidate as a conductive additive for various energy storage devices. It has been revealed that enhanced capacity can be achieved by using graphenes grafted metal oxides as the active materials for supercapactitors and lithium-ion batteries [12,13]. However, similar to other nanomaterials, a key challenge in synthesis and processing of graphenes sheets is aggregation. Due to the fact that graphenes possess high specific surface area, they tend to form irreversible agglomerates or even restack to form graphite through van der Waals interactions. The dispersion of graphenes is important because most of their unique properties are only associated with individual sheets. Aggregation can be reduced by the appropriate dispersant. However, the presence of disperant is undesirable for most applications [14].

In the present study, graphenes with different functional groups are dispersed in N-methyl-2-pyrrolidone (NMP) solvent to study the effects of the functional groups distinguish on graphenes

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dispersion in NMP. The method is applied in fabrication of electrodes for supercapacitors, and the influence of functionalized graphenes blended activated carbon electrodes has been studied systematically.

2. Experimental

2.1. Preparation of graphene oxide

Graphene oxide was prepared by a modified Hummers method [15]. 10 g of nature graphite powder was mixed with 230 ml of 98 wt% H_2SO_4 in an ice-bath. Afterwards, 30 g of $KMnO_4$ was slowly added in the above mixture, which was stirred for 2 h. The mixture was kept still for 1 h. Deionized water 500 ml was then gradually added into the mixture. During this process, the temperature was kept lower than 35 °C by controlling the rate of water addition. The water bath was then heated up to 95 °C, and kept for 3 h in order to increase the degree of oxidation of graphene oxide product. After oxidation, 30 ml of 30% H_2O_2 solution was added, followed by centrifugation and washing to clean out any remaining salts. The wet graphene oxide was dried under vacuum at 50 °C for 48 h.

2.2. Exfoliation of graphene oxide

The resulted graphene oxide was then thermal exfoliated at 500 and 1000 °C for 5 min in the tubular furnace under Ar ambient to obtain moderate reduced graphene (M-rGO) and heavily reduced graphene (H-rGO), which content of oxygen related functional groups is controlled. The graphene oxide was also annealed at 1000 °C in ammonia for 1 h to obtain graphenes with nitrogen related functional groups (N-rGO) [16].

The functionalized graphenes powders (H-rGO, M-rGO and N-rGO) fabricated by the above process were dispersed in NMP solvent by sonicating for 30 min using a ultrasonic bath (Sonics VCX-750, 750 W, 20 kHz), followed by centrifugation at 4000 rpm for 90 min using a Hettich zentrifugen universal 32 centrifuge to remove any large aggregates [17]. The homogeneously functionalized graphene dispersions were obtained for further experiments by decanting out the top half of the centrifuged dispersions. The functionalized graphenes/NMP solutions with concentrations of 0.1 mg/ml were obtained. The colloidal stability of functional graphenes/NMP solutions was measured by the Zeta potential.

2.3. Morphologies and dispersion stability of functionalized graphenes

Morphologies and structures of the graphenes were observed by the 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 analyze the functional groups bear on the surface of the graphenes.

Zeta potential measurements were carried out on a Horbia SZ-100Z with irradiation from a 532 nm laser. The functionalized gaphenes/NMP solutions were injected in folded capillary cells, and the electrophoretic mobility (μ) was measured using a combination of electrophoresis and laser Doppler velocimetry techniques. The electrophoretic mobility relates the drift velocity of a colloid (V) to the applied electric field.

2.4. Electrochemical performance

Electrode materials were facilitated by mixing activated carbon (AC, Mitsubishi Chemical Holdings, TF-B520), carbon black (KS6, TIMCAL), binder (PVDF, Acros) and above mentioned functionalized graphenes/NMP mixtures (pure NMP, H-rGO/NMP, M-rGO/NMP

Table 1
List of samples with different compositions.

Parameter	Activated layer composition
Sample 1	80 wt% AC + 10 wt% KS6 + 10 wt% PVDF
Sample 2	80 wt% AC + 9.96 wt% KS6 + 10 wt% PVDF + 0.04 wt% H-rGO
Sample 3	80 wt% AC + 9.96 wt% KS6 + 10 wt% PVDF + 0.04 wt% M-rGO
Sample 4	80 wt% AC + 9.96 wt% KS6 + 10 wt% PVDF + 0.04 wt% N-rGO

and N-rGO/NMP). The compositions of the above prepared slurries are listed in Table 1. The slurry was applied to Ni metal foils, which acted as the current conductors for the electrodes. The coated electrodes were transferred to a dry box for curing at 105 °C for 2 h. Supercapacitor cells were packed using laminated Al foils with the coated electrodes, porous Polypropylene (PP) separators (2 cm × 2 cm), and 6 M KOH electrolyte.

Cyclic voltammetry measurements were conducted on a Potentiostat/Galvanostat (Princeton Applied Research, Model 263 A). 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 0.5 to 6 A/g. Charge transfer resistance (R_{ct}) resistance analysis was carried out by measuring electrochemical impedance spectra (EIS) with an AC voltage amplitude of 20 mV and a frequency range of 100 kHz to 0.01 Hz. The supercapacitors were cycled 2000 times at 4 A/g for life test.

The cell capacitance was deduced from the slope of the discharge curve (Eq. (1)) [18].

$$C = I/(dV/dt) \tag{1}$$

where C is the cell capacitance in Farad (F), I is the discharge current in Ampere (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 (Eq. (2)) [17].

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

where C is obtained from Eq. (1) and m is the total mass of the active materials in both electrodes.

3. Results and discussion

3.1. Morphology

The morphologies of H-rGO, M-rGO and N-rGO are shown in Fig. 1(a)–(c). The functionalized graphenes exhibit scrolled-like sheet morphology due to the fact that the reduced graphene contents few functional groups and is thermodynamically unstable. However, it is difficult to distinguish the difference of functionalized graphenes (M-rGO, H-rGO and N-rGO) from the SEM images. Fig. 2(a) and (b) show bright-field HRTEM images of graphene nanosheets, which scroll slightly, owing to their flexible and ultra-thin nature [12]. The inset exhibits the corresponding HRTEM image (Fig. 2(b)), interplanar distance deduced from the HRTEM image was 0.35 nm, which can be assigned to the (0 0 2) reflection. Compare with ideal value in natural graphite ($d_{002} = 0.34$ nm), this value in d_{002} is resulted from the graphenes exfoliation, which expanses the interplanar spacing along vertical direction of (0 0 2) [19,20].

3.2. Functional groups

The functional groups on the surfaces of the graphene oxide, M-rGO, H-rGO and N-rGO were characterized using XPS. Fig. 3(a)–(d) show the C1s XPS spectrum of graphene oxide, M-rGO, H-rGO and N-rGO, respectively. For graphene oxide, six individual components are de-convoluted with bands around 284.6, 285.8, 286.6, 287.9, 288.8, and 289.5 eV, which are attributed to the binding energies of