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A high-performance all-solid-state supercapacitor with graphene-doped carbon material electrodes and a graphene oxide-doped ion gel electrolyte



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ARTICLE INFO

Article history: Received 13 January 2014 Accepted 9 February 2014 Available online 13 February 2014

ABSTRACT

Two major issues of conventional supercapacitors, composed of a separator, two electrodes, and liquid electrolyte, are their low package energy density and the leakage of the liquid electrolyte. Therefore, great efforts have been dedicated in development of all-solid-state supercapacitors with higher energy density. Here we demonstrate a high-performance all-solid-state supercapacitor with a graphene-doped carbon electrode material and a graphene oxide (GO)-doped ion gel as a gel polymer electrolyte and separator. Because of the ultrahigh specific surface area (3193 m² g⁻¹), suitable pore-size distribution (primarily 1–4 nm), and excellent electrical conductivity (67 S m⁻¹) of the graphene-doped carbon material, as well as the broad electrochemical window (0–3.5 V) and high ionic conductivity of the GO-doped ion gel, the all-solid-state supercapacitor demonstrates outstanding performance with a specific capacitance of 190 F g⁻¹ and energy density of 57 Wh kg⁻¹ at 1 A g⁻¹, and a specific capacitance of 160 F g⁻¹ and energy density of 57 Wh kg⁻¹ at 10 A g⁻¹. In addition, the all-solid-state supercapacitor exhibits similar and excellent performance as does the compared conventional liquid supercapacitor in respect of specific capacitance, capacitance retention, internal resistance, and frequency response.

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1. Introduction

A dramatic expansion of research in the area of energy storage systems during the past decade has been driven by the demand for electronic devices, electric vehicles, and renewable energy products [1]. Supercapacitors are attractive energy storage devices, which fill the gap between batteries and conventional capacitors [2,3]. A typical supercapacitor is composed of a separator, two electrodes, and liquid electrolyte. However, the use of a liquid electrolyte results in two major drawbacks. First, liquid electrolyte requires tice causes supercapacitors to have clumsy bulk shapes (button or spiral wound cylinder) [4] and low package energy density (encapsulation materials bring down the weight percent of electrode material in the entire device) [5]. Second, once there is leakage of electrolyte, harmful materials cause solvent corrosion and have a bad effect on the environment. These two points make it difficult for conventional supercapacitors to meet the more stringent requirements of future practical applications in the advanced thin and light electronics area.

high-standard safety encapsulation materials, this in prac-

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http://dx.doi.org/10.1016/j.carbon.2014.02.029

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Recently, great efforts have been dedicated to the development of all-solid-state supercapacitors [4,6-11]. It should be noted that most work in this direction has used an aqueous ion gel electrolyte [4,6-10], such as poly(vinyl alcohol) (PVA)-H₂SO₄, PVA-H₃PO₄, to construct all-solid-state supercapacitors. However, the narrow electrochemical window of an aqueous gel electrolyte (0-1 V) leads to a low cell voltage and hence low energy and power densities. Besides, when aqueous gel electrolytes are used in a wide temperature range, there is a critical problem of water evaporation, which will dramatically affect the performance and long-term stability of the devices [12]. Ion gels (ionic liquids trapped in polymers) have a wide electrochemical window (0-3.5 V), excellent thermal stability, nonvolatility, nonflammability, and non-toxicity, but suffer from low ionic conductivity [13,14]. However, our previous results demonstrated that the ionic conductivity of ion gels can be greatly improved by doping with graphene oxide (GO) [14,15], which further suggests great potential for using GO-doped ion gels for high-performance all-solid-state supercapacitor applications.

On the other hand, to successfully realize high-performance all-solid-state supercapacitors, an excellent electrode material is another essential component [3,16]. At present, activated carbons are the most commonly used electrode materials in commercial supercapacitors. However, the current state-of-the-art commercial activated carbons suffer from a moderately low specific surface area (SSA) (1000-2000 $m^2 g^{-1}$), porosity that is mainly in the micropore range (below 1 nm), and too low an electrical conductivity (requiring 5-10 wt% conducting filler), which limit their use in high-performance all-solid-state supercapacitors. Recently, there has been intense research on developing high-performance electrode materials with a high SSA to ensure a high specific capacitance, a suitable pore-size distribution (PSD) that allows easy access for electrolytes, and excellent electrical conductivity to facilitate electron transport in the electrodes [3,16-22]. Nevertheless, there are few materials in the bulk state that exhibit good performance for all of the above properties simultaneously. Consequently, if we can prepare a high-performance electrode material with an ultrahigh SSA, optimized PSD and high electrical conductivity, and combine this with a solid electrolyte with high ionic conductivity and a wide electrochemical window, a high-performance all-solidstate supercapacitor could be achieved.

In this work, we demonstrate the fabrication of an all-solid-state supercapacitor by exploiting a high-performance graphene-doped carbon material as the electrode material, and a GO-doped ion gel as both a gel polymer electrolyte (GPE) and separator. Due to the ultrahigh SSA (3193 $m^2 g^{-1}$) with a suitable PSD (primarily 1-4 nm), and an excellent intrinsic electrical conductivity (67 S m^{-1}) of this graphenedoped carbon material, as well as the wide electrochemical window (0-3.5 V) and high ionic conductivity of the GO-doped ion gel, an all-solid-state supercapacitor with outstanding performance is demonstrated with both a high energy density and a high power density. Furthermore, it has almost as good an electrochemical performance as the compared conventional liquid supercapacitor in respect of specific capacitance, capacitance retention, internal resistance, and frequency response.

2. Experimental

2.1. Materials synthesis

2.1.1. Synthesis of graphene-doped carbon material

An aqueous solution of poly(vinyl alcohol) (PVA) (100 mL, $0.1 \,\mathrm{g}\,\mathrm{mL}^{-1}$) was mixed with a GO aqueous solution (50 mL, $10 \,\mathrm{mg}\,\mathrm{mL}^{-1}$) to obtain a homogeneous PVA/GO solution. The PVA/GO mass ratio is fixed at 20. A glutaraldehyde aqueous solution (1 mL, 50 wt%) and concentrated hydrochloric acid (1.5 mL) were then added to obtain the cross-linked PVA/GO hydrogel. The hydrogel was transferred to a sealed Teflon-lined autoclave and heated at 180 °C for 12 h. The resulting hydrochar was dried in vacuum at 120 °C for 24 h. After crushing, the hydrochar was mixed with 4 times of its weight of KOH, and heated to 900 °C for 1 h at 5 °C min⁻¹ under Ar. The activated product was thoroughly washed with 0.1 M HCl and then with distilled water until the pH value reached 7. Finally, the graphene-doped carbon material was obtained after drying in vacuum at 120 °C for 24 h.

2.1.2. Preparation of GO-doped ion gel membrane

GO with particle size mainly less than 500 nm (6 mg) was dispersed in anhydrous DMF (6 g) in an ultrasonic bath to obtain a clear solution. Then, copolymer poly(vinylidene fluoridehexafluoro propylene (P(VDF-HFP)) (600 mg) and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) (3 g) were added to the GO/DMF solution to form a homogeneous viscous mixture under vigorous stirring. Finally, this homogeneous viscous solution was cast onto an aluminum substrate ($8 \text{ cm} \times 8 \text{ cm}$) to evaporate the DMF at $80 \,^{\circ}\text{C}$ for 24 h, and the resulting GO-doped ion gel film was finally peeled off of the substrate and punched into a round film with diameter of 1.8 cm for further use.

2.2. Characterization

Nitrogen adsorption/desorption analysis was done at 77 K on a Micromeritics ASAP 2020 apparatus. The structure was analyzed by scanning electron microscopy (SEM) using a LEO 1530 VP field emission scanning electron microscope with an accelerating voltage of 10 kV. Transmission electron microscopy (TEM) was carried on a JEOL TEM-2100 electron microscope at an accelerating voltage of 200 kV.

2.3. Fabrication and measurement of all-solid-state supercapacitor

2.3.1. Fabrication

90 wt% electrode material and 10 wt% PTFE were homogeneously mixed in an agate mortar. The mixture was then rolled into 60–80 μ m thick sheets and punched into 12 mm diameter electrodes. After drying at 120 °C for 6 h under vacuum, the electrodes were weighed (3.00–4.00 mg) and hot pressed onto the carbon-coated aluminium foils and then dried at 180 °C for 6 h under high vacuum to completely remove water. The dry working electrodes were transferred into a glove box filled with Ar to construct the all-solid-state supercapacitors and conventional supercapacitors. The all-solid-state supercapacitors consist of two working electrodes and

use the GO-doped ion gel as GPE and separator, while the conventional supercapacitor consists of two working electrodes and a separator using neat $EMIMBF_4$ as electrolyte.

2.3.2. Measurement

All the electrochemical tests were carried out at room temperature. Galvanostatic charge–discharge tests were measured using an Arbin testing system (Arbin MSTAT, America). Cyclic voltammetry (CV) and electrical impedance spectroscopy (EIS) studies at an AC amplitude 10 mV in the range of from 100 to 10 mHz were performed using an Autolab system (Metrohm).

According to the galvanostatic charge–discharge tests, the gravimetric specific capacitance, C_s (F g⁻¹), was calculated using the following formula:

$$C_{s} = \frac{4i}{mdV/dt}$$
(1)

where I is the constant current (A), m is the total mass of the two electrodes (g), dV/dt (V s⁻¹) is the slope obtained by fitting a straight line to the discharge curve.

The energy density, E_{cell} (Wh kg⁻¹), was estimated using the formula:

$$E_{cell} = C_s V^2 / 8 \tag{2}$$

where the V is the discharge voltage.

The power density, P_{cell} (kW kg $^{-1}$), was calculated using

$$P_{\rm cell} = E_{\rm cell} / \Delta t \tag{3}$$

where the Δt is the discharge time.

3. Results and discussion

The configuration of the all-solid-state supercapacitor described here is schematically shown in Fig. 1a. Two

graphene-doped carbon material electrodes sandwich the GO-doped ion gel membrane and all were hot pressed into an all-solid-state supercapacitor, where the GO-doped ion gel acts as both the electrolyte and the separator. The GOdoped ion gel membrane was obtained using copolymer poly(vinylidene fluoride-hexafluoro propylene (P(VDF-HFP)) as the polymer matrix, with 5 times of its weight of ionic liquid of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-MBF₄) as the supporting electrolyte, and 1 wt% GO as the ionic conducting promoter, using a simple solution-mixing/casting method (Section 2). The GO-doped ion gel has a very high ionic conductivity (\sim 25 mS cm⁻¹), which is comparable to that of the pure supporting EMIMBF₄ electrolyte [14]. This GO-doped ion gel demonstrated so high ionic conductivity, which is due to the homogeneously distributed GO as a 3D network throughout the GO-doped ion gel by acting like a ion "highway" to facilitate the ion transport [14]. Fig. 1b shows the porous morphology of the GO-doped ion gel.

The high-performance graphene-doped carbon electrode material was prepared by hydrothermal carbonization and chemical activation by KOH [23–25], using cross-linked PVA/GO hydrogel as precursor (Fig. S1). PVA is selected as the primary carbon source due to its low cost, good water solubility, and great compatibility with GO [26]. A low-magnification scanning electron microscopy (SEM) image shows that the morphology of graphene-doped carbon material has the fluffy structure, shown in Fig. 1c, which is significantly different from the morphology of pure activated carbon derived from a pure cross-linked PVA hydrogel, which has blocky structure with a rather large particle size (Fig. S2). With the addition of a few percent of graphene, the activated carbon derived from the cross-linked PVA is dispersed and coated on the graphene



Fig. 1 – (a) Diagram of an all-solid-state supercapacitor. (b) Low-magnification scanning electron microscopy (SEM) image of the morphology of the GO-doped ion gel. (c) SEM image of graphene-doped carbon material. The activated carbon is dispersed and coated on the graphene sheets. (d) Schematic of the structure of the graphene-doped carbon material. (e) Transmission electron microscopy (TEM) image of the graphene-doped carbon material. (f) High-resolution transmission electron microscopy (HR-TEM) image of the activated carbon, coated on the graphene sheets. (A colour version of this figure can be viewed online.)

sheets. A schematic of the structure is shown in Fig. 1d, and is consistent with the transmission electron microscopy (TEM) characterization, shown in Fig. 1e. The microstructure of activated carbon attached to the graphene was studied by high-resolution transmission electron microscopy (HR-TEM), which shows abundant pores surrounded by highly curved nanographene fragments (Fig. 1f). The short, linear features could be identified as individual nanographene fragments viewed edge-on [19,23,27].

Furthermore, the graphene-doped carbon material has a very high nitrogen Brunauer–Emmett–Teller (BET)–SSA of $3193 \text{ m}^2 \text{ g}^{-1}$, which is about 200% higher than that of the widely used commercial activated carbon RP-20 (Fig. S3a). The PSD shows that most pores are between 1–4 nm, which is suitable for ionic liquid or ion gel electrolyte-based supercapacitor applications (Fig. S3b) [28,29]. In addition, due to the initial molecular-level dispersion of GO, the graphene sheets are homogeneously distributed in the whole carbon matrix and work as a conducting filler to increase the overall conductivity. The graphene-doped carbon material has a high conductivity of 67 S cm⁻¹, which is much higher than that of RP-20 in its pristine state (4.6 S cm⁻¹) and even higher than that of RP-20 mixed with 10 wt% of Super P (44 S cm⁻¹) (Fig. S3c).

The all-solid-state supercapacitor showed excellent electrochemical behavior and capacitor performance as shown in Fig. 2. Cyclic voltammetry (CV) (Fig. 2a) shows rectangular curves from 0 to 3.5 V over a wide range of voltage scan rates, which is characteristic for ideal supercapacitor behavior in this voltage range. Even at the fast sweep rate of 200 mV s^{-1} , there is only a little distortion of the ideal rectangular shape, which indicates the capacitor's low internal resistance and excellent power characteristics. Galvanostatic charge/discharge curves at different current densities are shown in Fig. 2b. All the curves are nearly isosceles triangles, which indicate the high coulombic efficiency and standard double layer capacitor behavior. According to the galvanostatic charge/discharge curves, outstanding specific capacitance values at various current densities are obtained. The specific capacitance values have only decreased a little from 190 F g^{-1} at a current density of 1 A g^{-1} to 160 F g^{-1} at a high current density of 10 A g^{-1} (about 84% capacitance retention), demonstrating excellent power characteristics. Furthermore, the supercapacitors achieve an impressive performance with both very high energy and power densities, as shown in Fig. 2c. The energy density can reach as high as 76 Wh kg^{-1} at a power density of 0.84 kW kg⁻¹ at a current density of 1 Ag^{-1} and 57 Wh kg⁻¹ at a power density of 7.4 kW kg⁻¹ at a current density of 10 Ag^{-1} . With the total electrode weight of the supercapacitor system being typically one-fourth to one-half of the total system weight [30], the system-level specific energy of the supercapacitors can be 19–38 Wh kg⁻¹ at 1 A g^{-1} and 14–28 Wh k g^{-1} at 10 A g^{-1} , which is comparable to lead-acid batteries, but with a much higher power density than they have.

Nyquist plots of the all-solid-state supercapacitor were obtained by a frequency response analysis (FRA) in the frequency range 100–10 mHz, as shown in Fig. 2d with an



Fig. 2 – Performance characteristics of the all-solid-state supercapacitor. (a) Cyclic voltammetry (CV) curves at various scan rates. (b) Galvanostatic charge/discharge curves under different current densities. (c) Ragone plot. (d) Nyquist impedance plots in the frequency range 10–100 kHz. The inset shows a magnified view of the high frequency region of the impedance spectra. (A colour version of this figure can be viewed online.)

expanded view provided in the inset, which show the typical response of a porous electrode. The Nyquist plots exhibit (a) an intercept on the real axis (X axis) at a high frequency (close to 100 kHz), which represents the intrinsic internal resistance of the electrode material and the electrolyte of the device; (b) an approximate semicircular behavior at the high to mid frequency region corresponding to the parallel connection of the interfacial charge transfer resistance and the double-layer capacitance; (c) a 45° Warburg region at the middle frequency region, which is related to the diffusion of the ions into the bulk of electrodes, and (d) an almost vertical line at low frequencies, indicating the ideal capacitive performance of the device [31]. The supercapacitor shows a quite low intrinsic internal resistance, $\sim 0.50 \Omega$, which is due to the high electrical conductivity of the electrode material and the high ionic conductivity of the GO-doped ion gel. The migration of electrolyte occurred at a frequency of \sim 199 Hz and diffusion stopped at \sim 1.6 Hz. Thereafter the total capacitance was reached, which demonstrates a good frequency response and indicates that the full capacitance could be reached with very fast recharging [24,25].

Fig. 3 shows an acceptable cycle stability of the supercapacitor. After more than 5000 charge/recharge cycles at a current density of 10 A g^{-1} , it still retained ~80% capacitance. The good adhesion between the electrodes and the GO-doped



Fig. 3 – Cycling performance of the all-solid-state supercapacitor at a charge/discharge current density of 10 A g⁻¹. (A colour version of this figure can be viewed online.)

ion gel led to the long-term stability of the electrochemical behavior [7].

Furthermore, the all-solid-state supercapacitor has an electrochemical performance that is almost equal to that of a conventional liquid supercapacitor in respect of specific capacitance, capacitance retention, internal resistance, and frequency response (Fig. 4). Fig. 4a shows the specific capacitances at different discharge current densities. The specific capacitance is slightly higher than that of the conventional supercapacitor. This is may be because that the good adhesion between the electrodes and the GO-doped ion gel led to more favorable interfacial electrochemical behavior than that between electrodes and a liquid electrolyte. In galvanostatic charge/discharge measurements, the voltage drop appearing at the beginning of the discharge is associated with the overall internal resistance of the device. Fig. 4b summarizes the voltage drop at different current densities. The voltage drop increases linearly with an increase of current density for each device, and the slope of this linear relationship corresponds to the overall internal resistance value [32]. The all-solid-state supercapacitor showed a similar internal resistance to that of the conventional supercpacitor, which is due to the high ionic conductivity of the GO-doped ion gel. Electrochemical impedance spectroscopy (EIS) provides complementary information about the frequency response of the devices. Based on a series RC model, the normalized capacitances from the FRA data as a function of frequency are shown in Fig. 4c. The all-solidstate supercapacitor demonstrated better frequency response, suggesting better compatibility of the electrodes with the GO-doped ion gel than with the liquid electrolyte [14].

4. Conclusion

In summary, we demonstrated a high-performance all-solidstate supercapacitor with a graphene-doped carbon electrode material without the addition of any conductive filler and a graphene oxide-doped ion gel as a gel polymer electrolyte and separator. The supercapacitor demonstrated outstanding performance with both high energy and power densities, which are much higher than those of current commercially available supercapacitors and are comparable to lead-acid batteries, but with a much higher power density. The



Fig. 4 – Performance comparison of all-solid-state supercapacitors with a conventional liquid electrolyte based supercapacitor. (a) Specific capacitances at different current densities. (b) Voltage drop associated with the internal resistance at different discharge current densities. (c) Frequency response in the frequency range 10–10 kHz. (A colour version of this figure can be viewed online.)

realization of the high-performance all-solid-state supercapacitor strongly depends on both the graphene-doped carbon material with an ultrahigh SSA ($3193 \text{ m}^2 \text{ g}^{-1}$), suitable PSD (primarily 1–4 nm), and excellent electrical conductivity (~67 S m⁻¹), as well as the GO-doped ion gel with a wide electrochemical window (0–3.5 V) and high ionic conductivity. In addition, the supercapacitor exhibits almost as excellent an electrochemical performance as a conventional liquid supercapacitor in the respect of specific capacitance, capacitance retention, internal resistance, and frequency response.

Acknowledgements

The authors gratefully acknowledge financial support from MoST (Grants 2012CB933401 and 2011DFB50300), NSFC (Grants 50933003 and 51273093).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon. 2014.02.029.

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