CARBON 72 (2014) 381–386

Available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/carbon

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 $m^2 g^{-1}$), 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 76 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.

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 high-standard safety encapsulation materials, this in practice 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.

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http://dx.doi.org/10.1016/j.carbon.2014.02.029
0008-6223/

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)–H_2SO_4, PVA–H_3PO_4, 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-solid-state 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 graphene-doped 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 g mL^{-1}) was mixed with a GO aqueous solution (50 mL, 10 mg 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 fluoride-hexafluoro propylene (P(VDF-HFP)) (600 mg) and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) (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 cm × 8 cm) to evaporate the DMF at 80 °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 μm 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