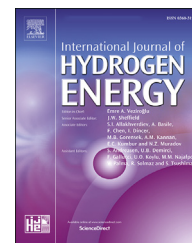




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A facile approach to improve the electrochemical properties of polyaniline-carbon nanotube composite electrodes for highly flexible solid-state supercapacitors

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ARTICLE INFO

Article history:

Received 30 April 2018

Received in revised form

20 July 2018

Accepted 29 July 2018

Available online xxx

Keywords:

Electrochemical energy storage

Electrochemical properties

Electron transport

Polyaniline

Carbon nanotubes

ABSTRACT

We seek to improve the electrochemical properties of supercapacitor via engineering the interface of electroactive material/current collector. A facile electrochemical method is put forward to fabricate expanded graphite (ExGP), and polyaniline-carbon nanotube (PANI-CNT) composite electrodes using ExGP as substrate are prepared by one-step co-electrodeposition. Compared with PANI-CNT/GP electrodes, PANI-CNT/ExGP electrodes show significantly improved electrochemical capacitive performances due to reduced constriction/spreading resistance. This effect is ascribed to the increased area of contact points at the interface of electroactive material/current collector for the latter. The PANI-CNT/ExGP electrodes deliver a specific capacitance of 826.7 F g^{-1} , higher than previous reports based on PANI-CNT composites. A highly flexible solid-state supercapacitor is assembled using PANI-CNT/ExGP electrodes. The device shows high rate capability, superior energy/power characteristics (7.1 kW kg^{-1} at an energy density of 12.0 Wh kg^{-1}), and good cycling stability. This study demonstrates that optimizing electroactive material/current collector interface can implement faster electron transport and represents an effective strategy to promote electrochemical capacitive properties of supercapacitors.

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Introduction

Supercapacitors have attracted wide interests as one kind of energy storage systems, due to their larger energy density relative to conventional capacitors and higher power density and longer cycle life when compared with batteries. These characteristics enable their applications in consumer

electronics, medical devices, and hybrid electric vehicles [1–3]. Depending on electrode materials and operational mechanism, supercapacitors can be classified into two types. One type is electric double-layer capacitors that use carbon materials as electrodes, which store energy via electrostatic charge accumulation at the electrode-electrolyte interface. The other type is pseudocapacitors, commonly utilizing

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<https://doi.org/10.1016/j.ijhydene.2018.07.168>

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transition metal oxides and conducting polymers (CPs) to store energy through fast surface redox reaction [4–6].

Of all known CPs, polyaniline (PANI) has been extensively studied owing to its high pseudocapacitance, small mass density, low cost, and environmental friendliness. However, the low electrical conductivity in dedoped state and poor cycle performance, due to swelling and shrinkage during charging/discharging, restrict its practical applications for supercapacitors [7–9]. Carbon nanotubes (CNTs) are another promising material for supercapacitors with high conductivity, large surface area, long cycle life, and high mechanical strength. Nonetheless, CNTs have rather low specific capacitance due to their charge storage mechanism based on electric double-layer [10,11]. Thus, composites based on PANI and CNT have been explored to achieve enhanced electrochemical performance, which combine the advantages of various electrode materials and make use of their synergetic effects [12–16].

In previous reports, PANI-CNT composites based supercapacitor electrodes were prepared by a variety of methods such as chemical oxidative polymerization with soft template [17], chemical vapor deposition and electrodeposition [18], step electrospinning process [19], enzymatic synthesis [20], reverse microemulsion polymerization [21], dispersion filtration [22], and so on. Broadly, these methods can be categorized into two groups, that is, chemical and electrochemical processes. For chemical synthesis, electroactive materials are usually obtained in the form of powder, which requires mixing thoroughly with a polymer binder. Then the resulting paste is pressed onto the current collectors to construct electrodes. The participation of polymeric binder would decrease electrical conductivity of electroactive materials, leading to reduced electrochemical performances. In contrast, electrochemical synthesis is an attractive way to prepare binder-free electrodes, which directly grows electroactive materials on substrates (that is, current collectors), enabling one-pot preparation. In either chemical or electrochemical synthesis, a high-quality interfacial contact between active materials and current collector is desirable in order to reduce contact resistance. However, frequently used current collectors such as stainless steel, carbon cloth, and graphite foil show a flat surface, resulting in a limited number of contact spots between active materials and current collectors [23]. Small contact spot area will inevitably lead to a constriction/spreading resistance at the interface when current flow passes through it [24,25], thereby lowering the electrochemical performances.

Current collector in a supercapacitor serves to collect/transport electrons from/to electroactive materials during charge/discharge [26]. Unfortunately, its role has not received the attention it deserves as compared to electroactive materials. Graphite (GP) is a commercially available paper-like material, which serves routinely as current collectors, featuring low price, high conductivity, and superior mechanical flexibility [27,28]. In this work, we propose a facile electrochemical method to prepare surface expanded graphite (ExGP) in order to offer substantially increased contact points at the active materials/current collector interface. New type of PANI-CNT/ExGP composite electrodes were fabricated via co-electrodeposition of PANI-CNT composite on ExGP substrate.

Correspondingly, the PANI-CNT/ExGP electrodes demonstrated significantly improved electrochemical performances with respect to PANI-CNT/GP electrodes.

Currently the demand for wearable and portable electronic devices has accelerated the development of flexible supercapacitors, which have high flexibility against deformation. Such electronic devices are required to be integrated with a flexible energy storage component as power supply [29–31]. To verify the feasibility for flexible supercapacitor applications, a symmetrical and flexible supercapacitor device was constructed herein using PANI-CNT/ExGP electrodes. This device shows high flexibility and superior supercapacitive performances, thus holding great promise for use in wearable and portable electronics.

Experimental

Chemicals

Aniline (analytical pure) was purchased from Sinopharm. Pristine multi-walled CNTs (outer diameter: < 8 nm) were obtained from Chengdu Organic Chemicals. Poly (sodium 4-styrenesulfonate) (PSS) was supplied by Alfa Aesar. Graphite papers were obtained from Qingdao Herita graphite. All experiments were implemented using deionized (DI) water (18.25 M Ω cm, 24 °C).

Electrode preparation

Graphite papers were cut into a rectangular shape and insulated with adhesive tape to expose conductive areas of 1 × 1 cm² for electrochemical expansion and electrodeposition. Prior to use, they were cleaned in acetone and DI water, successively. Electrochemical expansion of GP was performed using a two-electrode configuration in 1 mM PSS aqueous electrolyte. Here GP (acting as working electrode) was placed in parallel to the Pt foil (as counter electrode). A static potential of 10 V was applied on GP for 40 min to obtain electrochemically expanded GP (ExGP). To increase conductivity, the ExGP was further reduced in a three-electrode configuration in oxygen-free 1 M LiClO₄ at –1.2 V vs. saturated calomel electrode (SCE) for 5 min. The obtained ExGP was washed with DI water to remove inorganic residuals.

For carboxylation of CNTs, multi-walled CNTs were pre-treated in 3 M HNO₃ at 140 °C under magnetic stirring by refluxing for 96 h. Subsequently, they were transferred into a mixture of concentrated H₂SO₄ and HNO₃ (volume ratio 3:1) and functionalized with carboxyl groups under bath-sonication at 40 °C for 2 h. Finally, the resultant carboxylated CNTs (or CNT-COOH) were rinsed with abundant DI water until the pH reaches about 6.0 and dried at 60 °C for 1 day.

PANI-CNT/ExGP electrodes were prepared via electrochemical co-deposition in the aqueous deposition bath consisting of 0.2 M aniline, 0.5 M HCl, and 1 mg mL⁻¹ CNT-COOH, which were adequately dispersed by stirring and ultrasonication prior to deposition. Here ExGP was used as the electrodeposition substrate. SCE and Pt sheet were used as reference and counter electrodes, respectively. Electrodeposition was

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