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All-solid state symmetric supercapacitors based on compressible and flexible free-standing 3D carbon nanotubes (CNTs)/poly(3,4-ethylenedioxythiophene) (PEDOT) sponge electrodes

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HIGHLIGHTS

- Porous CNTs sponge acts as both flexible membrane and active materials.
- Homogenous compositing of PEDOT via facile electrodeposition method.
- The inner voids provide accessible ions transmission path to the surface.
- The 3D CNTs framework provides fast electron transmission passageway.

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ABSTRACT

Flexible supercapacitors that maintain electrochemical performance under deformation have attracted much attention for the potential application in the flexible electronics market. A compressible and flexible free-standing electrodes sponge and all-solid-state symmetric supercapacitors based on as-prepared electrodes are presented. The carbon nanotubes (CNTs) framework is synthesized by chemical vapor deposition (CVD) method, and then composited with poly (3,4-ethylenedioxythiophene) PEDOT by the electrodeposition. This CNTs/PEDOT sponge electrode shows highest mass-specific capacitance of 147 Fg^{-1} at 0.5 A g^{-1}, tuned by the PEDOT mass loading, and exhibits good cyclic stability with the evidence that more than 95% of capacitance is remained after 3000 cycles. Furthermore, the symmetric supercapacitor shows the highest energy density of 12.6 Wh kg^{-1} under the power density of 1 kW kg^{-1} and highest power density of 10.2 kW kg^{-1} with energy density of 8 Wh kg^{-1}, which exhibits both high energy density and power density. The electrochemical performance of composite electrode also indicates that the operate voltage of device could be extend to 1.4 V by the n-doping and p-doping process in different potential of PEDOT component. This flexible supercapacitor maintains stable electrochemical performance working on different bending condition, which shows promising prospect for wearable energy storage applications.

1. Introduction

Flexible electronics, such as wearable electronics, electronic skins, flexible displays and bendable smart phones, which have attracted much attention for its properties and wide applications and been required urgently for the characteristics of enduring strain without remarkable loss of their performance [1] [2]. In order to provide energy to such devices, compressible and flexible energy storage systems which could be bent, folded, and compressed while maintaining their electrochemical functions under deformation need to be fabricated [2]. Lithium batteries and supercapacitors are widely studied and commercialized as energy storage system for portable devices, electric vehicles and grid-scale energy-storage systems over the last two to three decades [3] [4] [5]. Supercapacitors, which had attracted researchers' attention for their high power density, long cyclic life and high charge/discharge rates

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against batteries [6] [7]. Therefore, compressible supercapacitors might be a good candidate to match the requirement of flexible electronics.

Stretchable supercapacitors electrodes had been produced by electrochemical active materials composited with insulative substrates of good mechanical property with different structures like fiber [8] [9], paper [10] [11] and sponge [12]. Though the insulated substrate endows the supercapacitors with excellent flexibility, the additive substrate decreases the mass energy and power density of the cell simultaneously. Consequently, free-standing and flexible electrode materials without binders, conductive additives nor flexible insulated substrate had been investigated [13]. Electrochemical active materials contain electrochemical double layer capacitance (EDLC) materials and pseudocapcitance materials [14]. 3D carbon nanotubes (CNTs) sponge consist of 1D carbon nanotube had been synthesized, which exhibit high conductivity and good mechanical strength [15]. While the low specific capacitance derive from the poor specific surface area and EDLC process still limits the application of pure CNTs bulk in supercapacitors [7]. Aiming at improving the energy density, pseudocapacitance materials like conducting polymers (poly (3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polypyrrole (PPY)) [16] [17], transition metallic oxides (ruthenium oxide, manganese dioxide, nickel oxide) [18] [19] had been researched and composited with carbon-based materials [20] [21]. PEDOT was widely investigated for its chemical and thermal stability, non-toxic, high operated potential and good conductivity [22] [23]. In spite of high theoretic specific capacitance of conducting polymer, the active materials tend to aggregate during synthesizing process, which decreases the surface area for participating redox reaction, resulting in decreasing specific capacitance [24]. To solve this problem, different PEDOT nanostructures of controlled morphology with both high energy density and power density had been synthesized by template methods [25] [26] [27], while these procedure companied with sacrifice templates and complicated steps. A facile and steerable method to fabricate high performance electrode with highly opened structure for flexible and high energy density supercapcitors is still in demands.

Here, a three-dimensional (3D) composite electrode with free-standing characteristics was introduced to prepare flexible electrodes and related supercapacitor. By compositing of PEDOT and CNTs sponge through a convenient and controllable method, both excellent electrochemical and mechanical property of electrodes and devices were obtained. Compressible and flexible CNTs framework sponge was fabricated by chemical vapor deposition (CVD) and served as the substrate, and the porous and 3D structure could significantly prevent PEDOT from stacking. To increase packing density and decrease the internal resistance, free-standing and 3D electrodes without current collector nor binder were synthesized by electrodepositing PEDOT on the CNTs framework. This procedure was easy to control by adjust the parameters of precursor solution and electrochemical technics. The high porosity of the stretchable sponge structure facilitates the ion migration to the surface of PEDOT. The mass loading of PEDOT could be easily tuned by adjust the deposition time. Moreover, the mechanical strength and stability provides a strong support for PEDOT, which leads to a long cyclic stability. This work might provide a novel method and structure for flexible energy storage in portable, wearable electronics, bendable smart phones and implantable medical devices.

2. Experiment

2.1. Materials

The 1,2-dichlorobenzene, ferrocene and polyvinyl alcohol (PVA) (molecular weight: 6450 g mol^{-1}) were purchased from Sigma-Aldrich. The 3,4-ethylenedioxythiophene (EDOT) monomer were purchased from Bayer, AG. The nitric acid (68% HNO_3), lithium perchlorate ($LiClO_4$), ethanol, sulfuric acid (98% H_2SO_4), acetone, and other reagents were analytical reagent grade and all the chemicals were used after purchasing without further purufication or treatment. All the experiments were performed under ambient conditions.

2.2. The synthesis of CNTs/PEDOT electrodes and all-solid-state supercapacitor

Fig. 1 shows a schematic illustration of the synthesized procedure of the CNTs/PEDOT composite electrode. Firstly, the sponge structure 3D multiwalled carbon nanotubes (MWCNTs) was produced by CVD method with the 1,2-dichlorobenzene and ferrocene, which had been reported [15]. To purify the CNTs sponge, we boiled it by the nitric acid at 60 °C for 1 h. Next, the CNTs sponge was filtered and washed with deionized (DI) water many times unless the filtrate was neutral. The density of the 3D CNTs sponge could be varied by regulating the feeding rate of the source and CNTs sponges with density of 10 mg cm^{-3} were prepared. Then, PEDOT was deposited on the surface of MWCNTs sponge framework by cyclic voltammetry under the rates of 100 mv s^{-1} for 100 cycles from 0 to 1.0 V. The samples of different mass loading of PEDOT by varying the electrodeposition cycles (100, 200, 300, 400), which labeled CNT/PEDOT-1, CNT/PEDOT-2, CNT/PEDOT-3, CNT/PEDOT-4. Electrochemical deposition of the composite layers was reacted in a aqueous electrochemical reaction system include electrolyte ($LiClO_4$) and monomer, as well as the solvent of DI water. The concentration of $LiClO_4$ and monomer were 0.2 mol L^{-1} and 1 m mol L^{-1} respectively, and a platinum plate and an Ag/AgCl electrode were used as the counter and reference electrode. The CNTs sponge of 10*5*2 mm^3 (1 mg) and indium-tin oxide (ITO) of 20*10 mm^2 glass served as the working electrodes. As a contrast, pure PEDOT electrodes were fabricated by the same way on ITO glass as the substrate. After electrodeposition, these electrodes were dried in the vacuum drying oven at 40 °C under negative pressure for 12 h, and then at 100 °C under negative pressure for 24 h. Before electrochemical measurement, sponges were weighting and kept vacuumize dipping for 4 h.

Preparation of PVA- H_2SO_4 Gel Electrolyte: PVA- H_2SO_4 electrolyte was prepared using PVA (molecular weight: 6450 g mol^{-1}) and H_2SO_4. Firstly, 4 g PVA was dissolved in 40 mL deionized water with continuous stirring and kept at 90 °C for 2 h until a transparent viscous solution was obtained. When the temperature decreased, add the 4 g of H_2SO_4 solution to the solution gradually with stirring until a clear solution was prepared.

Assembling of All-Solid-State Flexible Supercapacitor: The CNTs/PEDOT sponge were dipped into the PVA- H_2SO_4 gel electrolyte (50–60 °C) for 0.5 h and kept in the low pressure condition for 15 min to assure the electrolyte to diffuse into the porous structure of active materials. Then, the two electrodes were pressed against each other and dried in hot air until the gel electrolyte was solidified and the deionized water evaporated. Aluminum foil was used for electric contact between the cell and instrument.

2.3. Characterization and electrochemical measurements

The morphology and microstructure of the electrodes were characterized by scanning electron microscopy (SEM, HITACHI S4800), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Raman Spectroscopy. The 3D-CNTs/PEDOT sponge served as the working electrodes with a working mass of 1 mg directly. Cyclic voltammetry (CV),