



Bifacial carbon nanofoam-fibrous PEDOT composite supercapacitor in the 3-electrode configuration for electrical energy storage



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ABSTRACT

Electrical energy storage properties of supercapacitors based on carbon nanofoam-fibrous PEDOT composite and microporous PEDOT film/graphite electrodes formed by the pulsed current electropolymerization technique are investigated. The 3-dimensional nano-architecture of the composite carbon nanofoam-fibrous PEDOT electrode exhibits high pore connectivity and electrolyte ion diffusivity. By utilizing its bifacial ion transportation ability and reduced ion diffusion impedance, a supercapacitor device in the 3-electrode configuration has been tested which shows high specific capacitance of 210.8 F g^{-1} as compared to 142.5 F g^{-1} observed for the supercapacitor in the conventional 2-electrode design. The voltage scan rate dependence shows high efficacy of the bifacial carbon nanofoam electrode in faster ion transport in the 3-electrode supercapacitor configuration. The 3-electrode supercapacitor cell shows energy density of 8.53 Wh kg^{-1} which is nearly 1.7 times higher than the energy density of the 2-electrode supercapacitor cell. The power density of $\sim 19.7 \text{ kW kg}^{-1}$ for the 3-electrode supercapacitor cell is also superior as the 2-electrode supercapacitor exhibit a typical value of 11.8 kW kg^{-1} .

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1. Introduction

Electrical energy storage using the supercapacitor devices has gained considerable importance for meeting the high power demands in several applications such as electric and hybrid vehicles, industrial automation, mobile communication and sensor networks [1–4]. The two mechanisms by which the supercapacitors store energy are, (i) the electrochemical double layer in which energy storage is based on the separation of charges at the electrolyte-electrode interface, and (ii) the reversible redox reactions which store energy faradically using the pseudocapacitive property. Structured carbons have large surface area and utilize the vast interface with the electrolyte to store capacitive energy in the electrified double layers [5]. The transition metal oxides [6] and the electrically conducting polymers (ECP) [6] are the materials systems which show the pseudocapacitive energy storage functionality with a high energy density [7]. The polypyrrole (Ppy), poly(3,4- ethylenedioxythiophene) (PEDOT)

and polyaniline (PANI) are the prominent ECP electrode materials which undergo reversible redox processes equivalent of doping and dedoping of electrolyte ions to store energy [8–10]. To enhance the energy and the power density, it is important that the ECP electrodes have highly pervasive access to the electrolyte ions and faster kinetics of ingress and extraction of electrolyte ions by diffusion. Towards this objective, the conducting polymers in various nanoscale morphologies such as, nanoporous [11], nanofibers [12,13], nanowires [14] and nanobelts [15] have been investigated. Similarly, the carbons in the nanotube [16], porous [17] and micro-bead [18] structural forms create a large surface area interface which is useful in realizing high rate capable EDLC supercapacitors. The specific storage capacity in these carbon allotropes is still small but it is possible to achieve increased capacitance density by insertion of faradaic materials like conducting polymers as shown earlier for PEDOT [19] and polypyrrole [20] as well as the transition metal oxide nanoparticles [21]. The other carbon systems like carbon aerogels [22] and carbon nanofoams [23] which are characterized by a random network of interconnected pores distributed over its entire 3-dimensional material form are attractive for energy storage in the supercapacitors but rarely investigated [24–26]. In the past

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carbon nanofoam composites with various redox active materials like, RuO_2 [27], birnessite- MnO_x [28,29], LiMn_2O_4 [30], and Fe_2O_3 [31] have been reported. Integration of conducting polymers with carbon nanofoam is rarely studied but appear promising for realizing the enhanced capacitive density as few past studies [32,33] have shown.

In this work, the carbon nanofoam electrode integrated with a conformal thin fibrous PEDOT film is investigated with the objective to combine the contributions from both the double layer and faradic capacitances to boost the specific capacitance of the composite. The choice of PEDOT is based on its high electrical conductivity and excellent chemical and mechanical stability [34,35] which stands out for forming the composite with the carbon nanofoam. The thick PEDOT films as redox active energy storage supercapacitor electrodes are widely studied and its morphological dependencies such as nanowire [36], nanorods [37] nanotube [38,39], and nanocapsules [40] on electrochemical performance in both organic [41] and aqueous [38] electrolytes have been extensively reported. An important aspect of the present work is on the formation of a composite electrode consisting of the carbon nanofoam over coated with a thin conformal PEDOT film having a nanofiber like morphology and the investigation of the effect of the 3-dimensional nano-architecture of the composite electrode over its electrochemical properties. The conformal thin fibrous PEDOT film is deposited over mesoporous carbon nanofoam by controlled pulsed current electropolymerization with the nanoscale morphology. The fibrous PEDOT film has high connectivity though the mesopores of the carbon nanofoam which ensures enhanced access of the electrolyte ions. Furthermore, the transparency of the 3-dimensional mesoporous structure of the carbon nanofoam towards the permeation of electrolyte ions across its both facets provides it a bifacial electrochemical functionality which enables the supercapacitor device design in the three electrode configuration. This paper reports on the capacitive energy storage, charge-discharge, impedance characteristics and power-energy density of the supercapacitor devices formed in the 2 and 3-electrode configurations in aqueous electrolyte.

2. Experimental

2.1. Supercapacitor electrode preparation

The bifacial composite electrode is comprised of a $\sim 250 \mu\text{m}$ thick carbon nanofoam paper over-coated with a PEDOT film in a nanofiber-like morphology on both its facets by the pulsed current electropolymerization [42]. The carbon nanofoam paper is electrically conducting ($\sigma = 10^2 \text{ S cm}^{-1}$) by virtue of the embedded carbon fibers and was used as a self-supporting electrode without a backup current carrying electrode. The BET surface area of the carbon nanofoam was typically $400 \text{ m}^2 \text{ g}^{-1}$ with an average pore size of $\sim 60 \text{ nm}$. The large surface area benefits in enhancing the double layer capacitance by expanding the interface with the electrolyte. A high capacity composite electrode of the carbon nanofoam was prepared by supplementing the double layer capacitance with the redox pseudocapacitive property of the PEDOT conducting polymer. A key requirement for the added PEDOT film component is that it should preserve the nanopores of the carbon nanofoam by not occluding the free flow of the electrolyte ions and thereby not impeding the charge insertion-exchange processes. This was realized by depositing a thin conformal PEDOT film using ultra-short current pulsed electropolymerization [11,41,42] of the 3,4-ethylenedioxythiophene (EDOT) monomer under the action of sodium dodecyl sulfate (SDS) surfactant [43] in a two electrode cell with Pt foil as

a counter electrode. In preparation, first the 0.01 M EDOT monomer (Sigma Aldrich) was dispersed in deionized water in the presence of 0.07 M SDS under continuous stirring at 40°C and subsequently, carbon nanofoam paper was soaked in this medium for $\sim 40 \text{ min}$. The 0.1 M lithium perchlorate (LiClO_4) electrolyte solution was added as the source of dopant ions prior to initiation of electropolymerization. The electropolymerization was carried out using sequential anodic unipolar 4 mA cm^{-2} amplitude current pulses of 10 ms ON period interspaced by a 100 ms OFF period for 3–10 k cycles. The electropolymerization of the monomer is initiated during the ultra-short current ON period. The current OFF period is basically utilized for homogenization of the monomer in the vicinity of the carbon nanofoam interface with the electrolyte as well as to dissolve away any unsustainable adsorbents over the carbon nanofoam surface back into the medium. The pulsed electropolymerization process exerts an effective control over the polymerization kinetics and hence over the film morphology through the choice of both the current pulse amplitude and the ON–OFF periods. Thus formed carbon nanofoam-fibrous PEDOT composite electrode preserves the intrinsic nanopore structure of the carbon nanofoam and enhances the pseudocapacitance property. The other electrode used for assembly of the supercapacitor device is $\sim 10 \mu\text{m}$ thick microporous PEDOT deposited over flexible graphite substrate. This PEDOT layer is also deposited by the pulsed current electropolymerization method wherein the pulsed current profile and the number of cycles were appropriately chosen to yield highly microporous morphology.

2.2. Electrochemical characterization of supercapacitor electrodes

Electrochemical properties of the individual electrodes and the supercapacitor cells were analyzed by the cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and ac impedance spectroscopy techniques. These measurements were performed in a three-electrode cell in 1 M lithium perchlorate aqueous electrolyte medium and the potential was measured with reference to a saturated calomel electrode (SCE). A Pt foil counter electrode was used for measuring the properties of individual electrodes. The CV measurements were performed using Solartron electrochemical interface (Model 1287) by recording the flow of electric current between the working electrode and the Pt counter electrode in the potential range -0.5 to $+0.5 \text{ V}$. The voltage was scanned from the anodic to cathodic voltage direction at different rates between 5 and 100 mV s^{-1} . The specific capacitance, C_{SV} of the electrodes from the CV data was determined by the relation,

$$C_{SV} = \frac{1}{\nu_s m_{ac} (V_a - V_c)} \int_{V_c}^{V_a} I dV \quad (1)$$

where, $(V_a - V_c)$ represents the anodic to cathodic potential range, voltage scan rate is given by ν_s and I is the current response. The electrochemically active mass of the electrode m_{ac} is used in determining the specific capacitance. The CD characteristics were measured in the same cell at $1\text{--}3 \text{ mA cm}^{-2}$ current density in the potential range 0.05 to 0.5 V. The ac impedance measurements were carried out in a two-electrode cell in the frequency range 10 mHz–100 kHz with ac signal amplitude of 10 mV using Solartron gain-phase impedance analyzer (Model 1260). The Nyquist plots based on the impedance data were simulated using the electrical equivalent circuit model representing the electrochemical and electrophysical properties of carbon nanofoam-fibrous PEDOT composite and microporous PEDOT/graphite using the Z-plot software (Scribner Associate) which provide characteristic resistances and various contributing factors to the overall capacitance.

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