



Electrochemical performance of supercapacitors based on carbon nanofoam composite and microporous poly(3, 4-ethylenedioxythiophene) thin film asymmetric electrodes



Navjot K. Sidhu, A.C. Rastogi*

Electrical and Computer Engineering Department and Center for Autonomous Solar Power (CASP), Binghamton University, State University of New York, Binghamton, NY 13902, USA

HIGHLIGHTS

- Carbon nanofoam-nanofibrous PEDOT composite shows large double layer capacitance.
- Pulse current polymerization forms microporous PEDOT of high specific capacitance.
- Aligned Ionic charges at nanopore interiors of carbon nanofoam store energy.
- Carbon nanofoam-PEDOT asymmetric supercapacitor has 13.6 Wh g⁻¹ energy density.
- Asymmetric supercapacitor show power density 29.4 kW g⁻¹ and 10 k cycle stability.

ARTICLE INFO

Article history:

Received 25 January 2016

Received in revised form

22 March 2016

Accepted 23 March 2016

Available online 1 April 2016

Keywords:

Microporous materials

Polymers

Electrochemical techniques

Electrochemical properties

Coatings

Thin films

ABSTRACT

Electrochemical performance of supercapacitors configured using carbon nanofoam enfolded by conformal thin poly(3,4-ethylenedioxythiophene) (PEDOT) film in nanofibrous structure and electrodeposited microporous PEDOT film/graphite as two asymmetric electrodes is described. Cyclic voltammetry data at 20 mV s⁻¹ scan rate show specific capacitance of carbon nanofoam-PEDOT composite electrode operating in the -0.8 to +0.2 V, and microporous PEDOT in the 0 to +0.8 V voltage range are 72 and 159 F g⁻¹, respectively. Paired in an asymmetric supercapacitor, in the balanced charge state, highly symmetrical cyclic voltammetry plots at high scan rates of 100 mV s⁻¹ in -0.8 to +1.2 V voltage range testify highly capacitive behavior with high degree of charge reversibility. This is attributed to unimpeded pore-filling and alignment of ionic charges over vast interiors of carbon nanofoam and a highly pervasive access to electrolyte ions within interconnected void network of microporous PEDOT. Linear charge-discharge characteristic of the supercapacitor at 1.0 to 3.5 A g⁻¹ current density show high rate capability and yield energy density of 13.6 Wh kg⁻¹ at the power density of 19.0 kW kg⁻¹. The long term charge-discharge tests at 1 A g⁻¹ show minimal ~14% loss of specific capacitance of asymmetric supercapacitor for 10,000 cycles.

Published by Elsevier B.V.

1. Introduction

Electrochemical storage of the electrical energy by supercapacitor devices has potential applications in the modern communication, distributed sensors arrays, industrial automation

and electrical vehicles [1–3]. The ability to deliver power at a high rate exceeding 10 kW kg⁻¹ with charge–discharge time of a few seconds are attractive features of energy storage with the supercapacitors distinguishing them from the electrochemical battery storage. Equally important, however, is to attain high energy density capability which stands poor compared to the rechargeable batteries. Supercapacitors which store electrical energy by electrical double layer capacitance (EDLC) are based on activated carbon (AC), carbon nanotubes (CNT) and morphological variants of graphene [4,5]. In EDLC supercapacitors, the capacitive energy density enhancement is achieved by large surface area and

* Corresponding author. Electrical and Computer Engineering Department, Binghamton University, State University of New York, 4400 Vestal Parkway East, Binghamton, NY 13902, USA.

E-mail addresses: nsidhu1@binghamton.edu (N.K. Sidhu), arastogi@binghamton.edu (A.C. Rastogi).

distributed open pore structure making it highly accessible to the electrolyte ions. The materials systems in which the electrical energy is stored via faradaic reversible surface redox reactions are the transition metal oxides [6] and electrically conducting polymers [7]. The basic approach for high specific capacitance in these material systems is to form the nanocomposites and to create various nanostructured forms like nanowires, nanorods, or nanoparticles. This produces mesoporosity which reduces diffusive pathways for ions and increases ion access for rapid surface redox reactions [7–9] which is critical for achieving high energy storage density.

The increase in the energy density can also be achieved in supercapacitors cell that operate at higher voltages based on the relation, $(E = 1/2)CV^2$. This is possible in supercapacitors with two dissimilar electrodes rooted in different storage mechanisms which operate in different electrochemical potential range. This increases the functional voltage range of the assembled supercapacitor [10–12]. In the past, asymmetric combination of the metal oxides and metal hydroxides with the structured carbons electrodes, such as $Ni(OH)_2$ /graphene, RuO_2 /graphene [13], $Ni(OH)_2$ /CNT [14], MnO_2 /AC [15], MnO_2 -graphene [11,16] and $MnFe_2O_4$ /graphene- MnO_2 [17] have been extensively researched. A recent trend is to develop electroactive materials in the nanostructured forms such as $NiO-CoO_2$ nanosheets/CNT [18], $Ni(Co)O$ nanowires/activated carbon [19], RuO_2/TiO_2 nanotube/AC [20], graphene- MnO_2 nanorod/graphene-Ag [21] and MnO_2 nanowire/graphene [12] as electrodes for supercapacitors. The electrically conducting polymers show reasonably high specific capacitance in the symmetrical supercapacitors but have not as widely been studied in the asymmetric combination. A few studies have focused on combination of activated carbon (AC) electrode [22] with various conducting polymers, polyaniline (PANI) [23,24], poly(3,4-ethylenedioxythiophene) (PEDOT) [25], poly(3-(4-fluorophenyl)thiophene) (PFPT) [26], and poly(3-methyl thiophene) (PMeT) [27] as well as its composites with metal-oxides like polypyrrole (Ppy)- MnO_2 [28]. Balancing of the stored charge on both asymmetric electrodes is required in a supercapacitor device in order to achieve high energy density. The pseudocapacitive electrode has high charge density compared to EDLC electrode based on the structured carbons. To compensate for the deficiency in its specific capacity, the EDLC electrode mass is generally increased. However, as EDLC is an interfacial storage mechanism, it is difficult to achieve reasonable balancing of charges. Another approach to create dissimilarity in electrodes is by modifying one electrode of a symmetrical supercapacitor by making composite having both EDLC and pseudocapacitive components in proper proportions. In the past, supercapacitors pairing one electrode of graphene and carbon nanotubes (CNT) with another electrode being the composite graphene and CNT with conducting polymer, for example composites of PEDOT- CNT [29], PANI-graphene [30], PMeT-CNT [31] and PEDOT-carbon fiber [32] have been reported.

We have investigated supercapacitor using the asymmetric electrodes based on the carbon nanofoam with nanofibrous PEDOT forming a composite structure and microporous PEDOT layer over graphite. The PEDOT has high p-conductivity [33] and a wide potential window [34]. In the microporous form, it can achieve higher areal capacitance even with a thin layer of low specific mass. The carbon nanofoam due to its 3-dimensional (3-D) nano architecture and the random network of interconnected nanopores distributed over its entire 3-D material form offers high surface area. Hence, it has vast interface with the electrolyte which contributes to high specific capacitance due to the electrochemical double layer. Its pore structure facilitates faster ion exchange reactions due to extensive electrolyte ion access even with the limitation of short diffusion lengths [35,36]. Herein, we formed a composite by wrapping the carbon nanofoam with a conformal coating of

ultrathin (~100 nm) film of PEDOT in the nanofiber-morphology. Thus, the carbon nanofoam pores have much improved electrical connectivity significantly increasing the areal capacitance density of the carbon nanofoam-fibrous PEDOT composite electrode. The conformal ultrathin PEDOT film formed by not occluding the underlying mesoporous structure, also improves the dynamic performance of the assembled supercapacitor. This paper reports on the electrochemical properties, impedance analysis, charge-discharge characteristics and energy-power density of the supercapacitor assembled with the two asymmetric carbon nanofoam-nanofibrous PEDOT composite and microporous PEDOT/graphite electrodes.

2. Materials and methods

An ultrathin (~100 nm) PEDOT film in the nanofibrous morphology was deposited conformal to the carbon nanofoam by ultra-short pulsed current electropolymerization method in an aqueous medium [37,38]. In preparation, the 0.01 M 3,4-ethylenedioxythiophene (EDOT) monomer (Sigma Aldrich) was dispersed in deionized water in the presence of 0.07 M sodium dodecyl sulfate (SDS) surfactant under continuous stirring at 40 °C. Later, the carbon nanofoam foil was soaked in this medium for ~40 min. The pulsed current electropolymerization was carried out in a two electrode cell with carbon nanofoam as a working and Pt foil as a counter electrode. The electrolyte 0.1 M lithium perchlorate ($LiClO_4$), which is also a source of the dopant anions for PEDOT conjugation, was added just prior to the initiation of electropolymerization. Though the EDOT monomer is sparingly soluble in water, it was possible to achieve aqueous dispersion of EDOT with the support from the SDS surfactant. The ionized SDS molecules with the extended dodecyl alkyls molecular chains being hydrophobic in character attach at the carbon nanofoam surface [39] while the hydrophilic OSO_3 groups project outwardly into the water. The EDOT monomers thus preferentially disperse within the hydrophobic region at the carbon nanofoam created by the attached dodecyl alkyls molecular entities [40] where these polymerize under the action of the current pulses. The PEDOT deposition by electropolymerization was carried out by applying sequential unipolar anodic current pulses of ultra-short 10 ms periods and 4 mA cm^{-2} current density. The film thickness was controlled by the number of pulsed current cycles applied for deposition. The PEDOT film growth essentially takes place when electropolymerization of the EDOT monomer attached at the carbon nanofoam surface is initiated by charge transfer during the ultra-short current ON period. The PEDOT forms in the pulsating manner under the action of the anodic current pulses which results in the formation of a thin conformal layer in the nanofibrous morphology [41]. The other electrode consisted of a ~10 μm thick uniform microporous PEDOT film over a 250 μm thick graphite sheet substrate. It was formed by depositing a PEDOT film by the similar pulsed current electropolymerization method using the modified pulsed current parameters which involves short current off period of 100 ms. The intervention of a short current off time between the successive current pulses is an important factor in the creation of the microporous growth morphology of the PEDOT film. The current OFF period is basically utilized to dissolve away the unsustainable oligomers or adsorbents. It also homogenizes the EDOT monomer and increases its availability by diffusion in the vicinity and across the growing PEDOT film surface over graphite substrate which results in the formation of highly porous PEDOT film. The graphite substrate unlike the carbon nanofoam shows no EDLC capacitance and acts solely as a current carrying support electrode.

The electrochemical properties of the individual electrodes and

Download English Version:

<https://daneshyari.com/en/article/1520570>

Download Persian Version:

<https://daneshyari.com/article/1520570>

[Daneshyari.com](https://daneshyari.com)