Materials Research Bulletin 83 (2016) 167–171

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Printable multi-walled carbon nanotubes thin film for high performance all solid state flexible supercapacitors

Sanjeev K. Ujjain[a,b,*], Preety Ahuja[c,1], Rohit Bhatia[d,1], Pankaj Attri[e,*]

[a] Department of Physics, Indian Institute of Technology Kanpur, Kanpur, UP 208016, India
[b] Center for Energy and Environmental Science, Shinshu University, 4-17-1 Wakasato, Nagano-city, Japan
[c] Department of Chemistry, Jamia Hamdard, Delhi 110062, India
[d] Lady Shri Ram College for Women, University of Delhi, Delhi, India
[e] Plasma Bioscience Research Center/Department of Electrical and Biological Physics, Kwangwoon University, Seoul 139-701, Korea

ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form 25 May 2016
Accepted 4 June 2016
Available online 4 June 2016

Keywords:
A. MWCNT
B. Aromatic azide
C. Ionic liquid
D. Gel polymer electrolyte
D. Flexible supercapacitor

ABSTRACT

All-solid-state flexible supercapacitor is assembled using multi-walled carbon nanotubes (MWCNT) and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4] based gel polymer electrolyte. Flexible electrodes on polyethylene-terephthalate (PET) substrate were made by inkjet printed azide functionalized MWCNT (*f*-MWCNT), serving both as electrodes and charge collector. Fabricated supercapacitor *f*-MWCNT/gel polymer electrolyte/*f*-MWCNT (*f*-MWCNT SC) demonstrated high power and energy performance as a gel polymer electrolyte based all solid-state flexible supercapacitor. *f*-MWCNT SC demonstrates high specific capacitance 235 F/g at 5 mV/s in wide operating potential range of 3 V. Short relaxation time constant (τ_o) (248 ms) with high apparent diffusion coefficient (D_a) 2.25×10^{-8} cm^2/s resulted in very high energy density 16.2 Wh/kg and power density 45 kW/kg at 1 A/g. *f*-MWCNT SC exhibits high flexibility and excellent cycling stability with capacity retention >90% after 5000 galvanostatic charge discharge cycles.

1. Introduction

The advanced modern society demand for miniaturized, portable and flexible electronics (e.g., mobile phones, notebooks, cameras) has engendered immense interest among materials scientists in their pursuit for compatible energy storage devices [1–4]. In addition, future developments are moving towards flexible energy and display devices for application in emerging field of wearable electronics, electronic newspapers, wrist mobile phones, curved screens and other flexible gadgets [5,6]. Designing highly efficient, miniaturized energy storage systems that can achieve high energy and power delivery with long cycling stability remains a challenge. Of all energy storage media, electrochemical mean of storage has shown potential for future generation energy needs. However, the high energy storage in conventional batteries is limited either by volumetric alterations or by the slow rate of solid-state diffusion as in lithium-ion batteries [7]. Supercapacitors, also called electrical double layer capacitors (EDLC) or ultracapacitors, store energy via reversible electrolyte ions adsorbed in form of diffused layer close to active electrode materials which are electrochemically stable and possess high surface area [8]. This electrostatic surface charge storage mechanism allows very swift energy with high power uptake and release over millions of cycles [8]. Hence, they bridge the gap between electrolytic capacitors and batteries to power portable electronic equipment and other devices [7].

Significant progress in improving the energy/power density of supercapacitors have been realized in the course of investigating a variety of materials such as activated carbon, multi – and single-walled carbon nanotubes (CNT), graphene, onion-like carbon and metal oxide and their carbon composites [8–10]. However, very few studies have been performed on solution based roll-to-roll processing over large scale, for all solid state flexible charge storage devices. Several group projected ink-jet printed carbide-derived carbon, activated carbon, CNT and graphene based supercapacitor electrode [11–16]. While this techniques hold promise, it requires complex ink formulation technique involving binder and surfactant material resulting in high contact resistances with current collector. High contact resistance enhance the equivalent series resistance (ESR) limiting the power delivery rate of the device [17]. So it can be realized that electrode material demonstrating low ESR

* Corresponding author.
E-mail addresses: drsanjeevkujjain@gmail.com (S.K. Ujjain), chem.pankaj@gmail.com (P. Attri).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.materresbull.2016.06.006
0025-5408/

along with solution processability would permit full integration into the development of future generation wearable electronics.

Here, we have demonstrated a simple and scalable method for fabricating completely printable high performance flexible supercapacitors based on surfactant/binder free thin films electrode of aromatic azide functionalized multiwalled carbon nanotubes (*f*-MWCNT). The *f*-MWCNT thin film electrode served both as active materials for charge storage and charge collector, while free standing gel polymer is used as electrolyte. Utilizing same material for dual role eradicates the high contact resistance at CNT/current collector interface, resulting in a simplified and lightweight architecture [18]. The elevated chemical stability and electrical conductivity along with the excellent mechanical strength of the MWCNT network permits assembling flexible yet robust devices, which are essentially required for portable electronics.

2. Experimental

2.1. Materials

Ionic liquid (IL) 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4], Poly(vinylidenefluoride hexafluoropropylene) [PVdF-HFP] polymer were purchased from Sigma-Aldrich. Chemical reagents of AR grade were used for experimental work. Ortho dichlorobenzene (ODCB), chlorobenzene, acetone and isopropanol (IPA) were purchased from Merck. MWCNT were purchased from Shenzhen Nanotech Port, Co. Limited, China, diameter 10–20 nm and length ~1 μm.

2.2. Characterization

2.2.1. Transmission electron microscopy (TEM)

TEM measurements were performed with a Philips Technai $G^2$30 transmission electron microscope.

2.2.2. Scanning electron microscope (SEM)

Surface morphological characterization of *f*-MWCNT inkjet printed electrode on PET substrate was done on a Zeiss Ultra 55 field emission scanning electron microscope (FESEM).

2.2.3. Electrochemical analysis

The supercapacitor (SC) cell performance was evaluated using electrochemical impedance analysis (EIS), cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) studies. EIS (1 mHz to 1 MHz), CV and GCD characteristics of the SC cells were performed using CHI 604D electrochemical analyzer and an Arbin instrument (model: BT2000, USA). Specific capacitance (C_{SP}), energy density and power density were calculated as described in our earlier article [19]. Resistivity of samples at room temperature was measured by a four-probe method using Keithley Digital Multimeter.

2.3. Functionalization of multiwalled carbon nanotubes

The functionalized MWCNT was synthesised as per our previous report [20]. The precipitated product (*f*-MWCNT) was obtained by centrifugation with repeated washing by millipore water and dried in oven at 70 °C. Yield: 3 mg; Spectral data; IR (cm^{-1}): 1733 (C=O), 1598 (C=C), 1435 (C—N),1254 (C—O stretch), 1139 (C—O out of plane deformation) and 836 (C—H).

2.4. Printed f-MWCNT electrode and gel polymer electrolyte film for solid state supercapacitor

f-MWCNT was dispersed ultrasonically in distilled water to prepare *f*-MWCNT ink (*f*-MWCNT concentration is 3 mg/ml). Black ink cartridge of inkjet office printer (HP Deskjet D2360) was removed and the cartridge was thoroughly washed with IPA, water and dried in air. *f*-MWCNT ink prepared above was then loaded in the cartridge. *f*-MWCNT films (1 × 8 cm) were printed on PET substrate. Afterward, the *f*-MWCNT coated PET substrates were cut into 2 × 1 cm pieces and used as electrodes without any treatment. The mass loading of *f*-MWCNT coated on each electrode, determined by weighing the electrodes before and after the deposition was found to be ~0.5 mg/cm^2.

In order to make our devices fully printable, we explored the use of gel polymer electrolytes. The flexible devices based on [EMIM][BF_4]/[PVdF-HFP] gel polymer electrolyte have already been demonstrated in our earlier report [21,22]. The gel electrolyte was prepared by dissolving host polymer PVdF-HFP and IL [23,24] [EMIM][BF_4] separately in acetone. Afterward, solutions were mixed and stirred magnetically for 12 h. The weight ratio of the ionic liquid to polymer was kept at 4:1. The viscous solution was cast on glass petri-dishes and acetone was allowed to evaporate slowly. It resulted in formation of a transparent and free-standing gel electrolyte. The electrolyte films were dried in a vacuum and stored in inert atmosphere to avoid moisture adsorption.

2.5. Device fabrication

We have employed a simple device architecture consisting of two *f*-MWCNT thin film electrodes enclosing gel polymer electrolyte film. Gel polymer electrolyte offer dual functionality of separator (to avoid electrical contact between the electrodes) and electrolyte.

3. Results and discussion

The structure and morphology of the functionalized MWCNT (*f*-MWCNT) were evaluated by transmission electron microscopy (TEM). Figs. 1a and 1b shows the TEM image of *f*-MWCNT demonstrating smaller bundles of carbon nanotubes instead of super bundles. Typically, *f*-MWCNT are several micrometer long with average diameter of 20–40 nm. From high-resolution TEM (HRTEM) image (Fig. 1c), inter layer spacing of 0.34 nm corresponding to (002) plane of MWCNT is observed [25]. Micrograph shows that the *f*-MWCNT is formed by ~45 concentric, single walled carbon nanotubes. Functionalization inhibits super bundles formation by disrupting strong van der waal forces of attraction between the tubes increasing its solubility in common organic solvents. Inset illustrates a vial of *f*-MWCNT dispersed in DI water (3 mg/ml). The *f*-MWCNT aqueous dispersion was stable without any precipitation all through observation period of a month. This *f*-MWCNT aqueous dispersion was used as an ink for ink-jet printing on flexible PET substrate to form supercapacitor electrodes (Inset 1d). Such formed *f*-MWCNT thin film had a low sheet resistivity of ~65 Ω cm. Introduction of nitrogen during cycloaddition of azides on MWCNT influences the electronic properties of nanotubes resulting in very low *f*-MWCNT sheet resistivity. Figs. 1d and 1e are SEM of *f*-MWCNT thin film. It demonstrates that *f*-MWCNT film exhibits open spaces between intertwined networks of nanotubes forming uniform porous architecture. Consequently, high surface area remains accessible for the solvated ions at electrode/electrolyte interface, which is essential for charge storage in form of electric double layer [26]. This *f*-MWCNT thin film electrode, configured in symmetric SC assembly, *f*-MWCNT/gel polymer electrolyte/*f*-MWCNT (*f*-MWCNT SC) is schematically illustrated in Fig. 2. All-solid-state SC was fabricated by the assembly of [EMIM][BF_4]/[PVdF-HFP] free standing gel polymer electrolyte (Fig. 2a) with two *f*-MWCNT electrodes face-to-face. Edge of each electrode was connected to the alligator clip connecting the electrochemical testing machines (Fig. 2b).