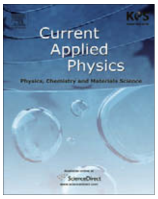
Current Applied Physics 10 (2010) 904–909

Contents lists available at ScienceDirect

Current Applied Physics

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



Hydrophilic polyaniline nanofibrous architecture using electrosynthesis method for supercapacitor application

D.S. Dhawale [a], R.R. Salunkhe [a], V.S. Jamadade [a], D.P. Dubal [a], S.M. Pawar [b], C.D. Lokhande [a,*]

[a] Thin Film Physics Laboratory, Department of Physics, Shivaji University, Vidyanagar, Kolhapur 416 004, Maharashtra, India
[b] Department of Materials Science and Engineering, Chonnam National University, 500-757 Gwangju, Republic of Korea

ARTICLE INFO

Article history:
Received 24 March 2009
Received in revised form 2 July 2009
Accepted 23 October 2009
Available online 29 October 2009

Keywords:
Polyaniline
Electrosynthesis
Nanofibers
Supercapacitor

ABSTRACT

An electrosynthesis process of hydrophilic polyaniline nanofiber electrode for electrochemical supercapacitor is described. The TGA–DTA study showed polyaniline thermally stable up to 323 K. Polyaniline nanofibers exhibit amorphous nature as confirmed from XRD study. Smooth interconnected fibers having diameter between 120–125 nm and length typically ranges between 400–500 nm observed from SEM and TEM analysis. Contact angle measurement indicated hydrophilic nature of polyaniline fibers. Optical study revealed the presence of direct band gap with energy 2.52 eV. The Hall effect measurement showed room temperature resistivity $\sim 3 \times 10^{-4}\ \Omega$ cm and Hall mobility 549.35 cm^{-2}V^{-1} s^{-1}. The supercapacitive performance of nanofibrous polyaniline film tested in 1 M H_2SO_4 electrolyte and showed highest specific capacitance of 861 F g^{-1} at the voltage scan rate of 10 mV/s.

1. Introduction

In recent years, growing demands for power sources of transient high-power density have stimulated a great interest in electrochemical supercapacitor with project applications in digital communications, electric vehicles, burst power generation, memory back-up devices and other related devices which require high-power pulses. Electrochemical supercapacitors are divided into two categories according to different energy-storage mechanisms, as electrochemical double layer capacitors and redox supercapacitors. Supercapacitors store energy in the form of charge at the electrode material and electrolyte solution interface [1] and can be divided into two categories: (i) redox supercapacitors, in which the pseudocapacitance arises from faradic reactions occurring at the electrode interface and (ii) electric double layer capacitors (EDLCs), in which the capacitance arises from the charge separation at the electrode/electrolyte interface. The main materials that have been studied for the supercapacitor electrode are (i) carbons, (ii) metal oxides and (iii) polymers. The conducting polymers have received increasing interest as an alternative to carbons and metal oxide semiconductors for supercapacitor as well as for sensor application. This is due to their room temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates and their rich structural modification chemistry [2,3]. Due to its interesting properties such as electrical conductivity and environmental stability, polyaniline has applications in the areas of sensors [4,5], light-emitting diodes [6], rechargeable batteries [7], gas separation membranes [8], non-linear optical devices [9], etc. Polyaniline exists in a variety of protonation and oxidation forms [10]. Doping and oxidation levels are the most important factors affecting the electrical and optical properties. Polyaniline offers extensive chemical versatility, allowing its properties to be tuned to appropriately meet the needs of a given application. Compared to other conducting polymers, polyaniline can easily switched from an insulating form to a conducting form via either protonic acid doping or base de-doping processes. Depending on the oxidation level, polyaniline can be synthesized in various insulating forms such as the fully reduced leucoemeraldine base, the half oxidized emeraldine base and the fully oxidized pernigraniline base. Among all its forms, the protonate emeraldine form is produced by the oxidative polymerization of aniline in aqueous acids [10]. Polyaniline emeraldine base differs substantially from leucoemeraldine base and pernigraniline base in the sense that its conductivity can be tuned via doping from 10^{-10} S/cm up to 100 S/cm and more whereas the leucoemeraldine base and pernigraniline base forms cannot be made conducting. The insulating emeraldine base form of polyaniline consists of equal numbers of reduced [–(C_6H_4)–N (H)–(C_6H_4)–N(H)–] and oxidized [–(C_6H_4)–N═(C_6H_4)═ N–] repeated units. The conducting emeraldine salt form is achieved by doping with aqueous protonic or functionalized acids where protons are added to the –N═sites while maintaining the number of electrons in the polymer chain constant. In addition, polyaniline has been considered as a potential candidate for the application of electrochemical supercapacitors [11,12]. Prasad and Munichandraiah [13] obtained a maximum specific capacitance of 815 F g^{-1} by

---

[*] Corresponding author. Tel.: +91 231 2609229; fax: +91 231 2609233.
E-mail address: l_chandrakant@yahoo.com (C.D. Lokhande).

1567-1739/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cap.2009.10.020

potentiodynamically depositing polyaniline onto stainless steel substrates. The high value of the specific capacitance was attributed to the high porous morphology obtained at a high sweep rate for the polyaniline deposition. Gupta and Miura [14] reported the maximum specific capacitance of 742 F g^{-1} for polyaniline deposited by potentiodynamically. Zhao and Li [15] also reported the highest specific capacitance of 1142 F g^{-1} for nanowire network of polyaniline. Fusalba et al. [16] also considered that it is important to obtain a high-porosity electrode since this kind of morphology is required to achieve material with high ionic conductivity and a capacitor with high energy and power densities. Thus, the performance electrochemical supercapacitor of polyaniline may be influenced by the morphology, which is closely related to the preparation methods and conditions.

The cost effectiveness and ease of synthesis are the important factors in the successful commercialization of high conductivity. Recently, different morphological forms of polyaniline including nanowire, nanotube, nanofiber, hollow microspheres [17–21] have been investigated. Nanostructured polyaniline, with different morphologies, has been synthesized using various methods such as template synthesis [22], self-assembly [23], emulsions [24] and interfacial polymerization [25]. However, such methods require relatively large amounts of surfactants and it is tedious to recycle the surfactants after polymerization. This drawback can be overcome by directly depositing polyaniline nanofibers onto the substrate without the involvement of surfactants by electrosynthesis method. Another advantage of the electrosynthesis is that it allows large-area film formation at room temperature. Furthermore, it was observed that electrochemically generated polyaniline films show an unusual variety of redox transitions, suggesting that the film conductivity could be controlled to some extent. Electrosynthesis processes such as galvanostatic [26] and potentiodynamic [14] modes in an aqueous acid have been widely used for the preparation of polyaniline thin films.

In the present research work, the deposition of conducting interconnected nanofibrous architecture of polyaniline by using room temperature electrosynthesis method has been reported for electrochemical supercapacitor application. The deposited films have been characterized using thermo-gravimetric (TGA) and differential thermal analysis (DTA), X-ray diffraction (XRD), fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), contact angle, optical absorption and Hall effect measurements. The supercapacitive properties of the polyaniline electrode were investigated by cyclic voltammetry (C–V) technique.

2. Experimental details

Polyaniline nanofibers were electrosynthesized by employing a standard three electrode configuration comprising stainless steel substrate, a graphite rod and saturated calomel electrode as a working, counter and reference electrodes, respectively. Polyaniline nanofibers were deposited from a solution containing 0.2 M H_2SO_4 + 0.2 M aniline ($C_6H_5NH_2$) at room temperature (300 K) in potentiostatic mode (EG& G Princeton Applied Research Model 263-A) by applying a constant potential of +0.75 V/SCE for the deposition period 420 s. The thickness of the film was calculated by the weight-difference method, employing a sensitive microbalance and the maximum thickness found to be 0.31 μm and characterized by using following techniques.

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) of polyaniline in powder form were carried out to study endothermic and exothermic reactions taking place with DSC–TGA (TA Instruments model SDT 2960) at a heating rate of 10 K/min in air atmosphere from 273 to 1273 K. The X-ray diffraction (XRD) analysis was carried out using Philips PW – 3710 diffractometer with chromium target at 38 kV and 50 mA of wavelength 2.2896 Å. Fourier transform infrared spectrum (FT-IR) was recorded between 4000 and 450 cm^{-1} at a spectral resolution of 2 cm^{-1} on a Perkin–Elmer 1710 spectrophotometer to identify the specific bonds of polyaniline. Morphological analyses of polyaniline was performed using scanning electron microscopy, SEM (JEOL-6360) for which, substrate was coated with a 10 nm platinum layer using a Polaron scanning electron microscopy (SEM) sputter coating unit E-2500, before taking the image. The TEM micrographs were obtained with Philips CM-30 TEM unit (Point resolution = 2.4 Å) with acceleration voltage of 300 kV coupled with EDAX-DX-4 analyzer. For the structural confirmation, selected area electron diffraction (SAED) pattern was preferred. Water contact angle was measured by a contact angle meter (Rame-Hart USA) equipped with a CCD camera. The UV–visible absorption of the polyaniline nanofibers deposited on FTO coated glass substrate was recorded on a Systronic spectrophotometer-119 in the wavelength range of 300–850 nm. The electrical properties of the polyaniline nanofibers were studied at room temperature by Hall effect measurements using the van der Pauw configuration. All the electrical parameters such as sheet resistance (R_s), conductivity (s), carrier concentration (n) and Hall mobility (μ_H) were measured. The electrochemical supercapacitor performance of the polyaniline electrode was studied by cyclic voltammetry (C–V) using the 263 A EG&G Princeton Applied Research Potentiostat and forming an electrochemical cell comprising platinum as a counter electrode, saturated calomel electrode (SCE) as a reference electrode in 1 M H_2SO_4 electrolyte. To avoid the oxidation and dissolution of substrate during measurement of capacitance by C–V, surface of substrate is covered by epoxy coating.

3. Results and discussion

3.1. Deposition of polyaniline thin films

Fig. 1 shows typical current versus time response plot of potentiostatic deposition of polyaniline film at potential +0.75 V/SCE for period of 420 s. Initially increase in current is observed due to faster attraction of monomer molecules towards the stainless steel electrode surface and then remained constant suggesting continuous growth of polyaniline as the deposition progresses. Similar type of transient is also reported [23] for the deposition of polyaniline. The electro-oxidation of aniline at constant potential produces green colored, uniform polyaniline thin films.

3.2. Thermo-gravimetric analysis and differential thermal analysis

In order to study the thermal stability of polyaniline fibers, the thermo-gravimetric (TGA) and differential thermal analysis (DTA)

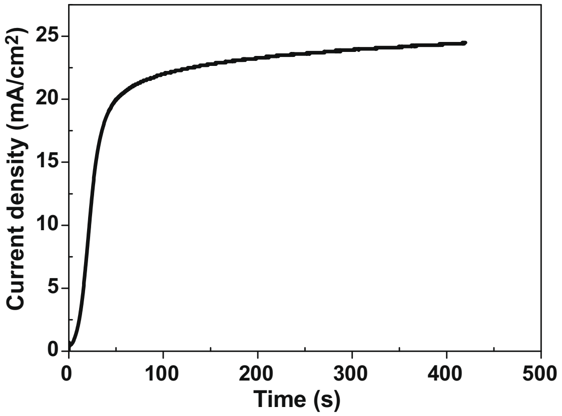


Fig. 1. Potentiostatic deposition of polyaniline film.