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Polyaniline and carbon nanotube coated pineapple-polyester blended fabric composites as electrodes for supercapacitors

Felicidad Christina R. Ramirez[a,b,c], Prakash Ramakrishnan[d,1], Zailla P. Flores-Payag[e], Sangaraju Shanmugam[d], Christina A. Binag[a,b,c,*]

[a] The Graduate School, University of Santo Tomas, España, Manila 1015, Philippines
[b] Department of Chemistry, College of Science, University of Santo Tomas, España, Manila 1015, Philippines
[c] Advanced and Nano Materials Laboratory, Research Center for the Natural and Applied Sciences, University of Santo Tomas, España, Manila 1015, Philippines
[d] Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 333, Techno Jungang Daero, Hyeonpung-myeon, Dalseong-gun, Daegu, 42988, Republic of Korea
[e] Research and Development Division, Philippine Textile Research Institute, Department of Science and Technology, Taguig City 1631, Philippines

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ABSTRACT

Conducting and electroactive fabrics suitable for supercapacitor electrodes were successfully prepared by combining carbon nanotubes (CNT) and polyaniline (PANi) with pineapple-polyester blended woven fabrics (PPWF) via dip-and-dry process and *in situ* chemical polymerization. The conductivity and capacitive behavior were studied using four-point probe technique, electrochemical impedance spectroscopy, cyclic voltammetry, and galvanostatic charge discharge experiments. PANi/CNT/PPWF composites produced higher conductivity (0.3877 S cm^{-1}) and areal capacitance values (386 mF cm^{-2} at 1 mA cm^{-2}) compared to the binary composites, PANi/PPWF (0.00685 S cm^{-1}, 14.3 mF cm^{-2}), and CNT/PPWF (0.2615 S cm^{-1}, 8.52 mF cm^{-2}). Combining the high conductivity of CNT and the pseudocapacitive behavior of PANi greatly enhanced the charge storage capability of the composites. The PPWF composites also produced higher areal capacitance values compared to pure polyester composites. The incorporation of hydrophilic pineapple fibers led to lower charge transfer resistance and better electrolyte transport within the composite. Based on these characteristics, PANi/CNT/PPWF is a promising electrode material for supercapacitors.

1. Introduction

Fast advancement of technology and world economic growth has led to an ever-increasing demand for energy. Due to this high-energy requirement, new and efficient energy storage devices, such as batteries and supercapacitors, must be developed. Supercapacitors store energy by separating charge on the surface of its electrode material. They can be charged and discharged many times (1,000,000 cycles) without losing its energy storage capability [1]. Its charge-discharge cycles occur very quickly, in less than a minute, leading to high power densities (1000–10,000 W kg^{-1}) however, its energy density is quite low (~5 Wh kg^{-1}) [1,2]. Because of this, supercapacitors can be used to store or supply quick, and large surges of energy.

Improved supercapacitor performance is mainly achieved by modification and/or development of new electrode materials. Ideal supercapacitor electrodes must have high surface area, high conductivity, and electroactivity. The use of nanomaterials and composites of carbon, conducting polymers, and metal oxides has proven to produce significant progress [1]. In this digital mobile age, however, energy storage devices must not only store large amounts of energy, but must also be lightweight, flexible, and environment-friendly. This multi-objective design can be achieved through the use of composite materials [3].

The use of textiles in energy storage devices is seen beneficial due to its flexibility, lightweight, low cost, high mechanical strength, and high surface area. Textiles are considered as three-dimensional (3-D) materials because of their series of overlapping fibers, which compared to flat surfaces, can be used to hold on to larger amounts of electroactive materials. Various textiles have already been used in energy storage, namely, cotton [4–10], cotton-lycra [11], polyester [6,7], viscose [7,12], nylon lycra [13] and linen [7]. Textiles, however, are mainly insulators and must be made conducting for them to find application as supercapacitor electrodes. This can be achieved by the addition of

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[*] Corresponding author at: Department of Chemistry, College of Science, University of Santo Tomas, España, Manila 1015, Philippines
E-mail addresses: christina.binag@ust.edu.ph, cabinag@yahoo.com (C.A. Binag).

[1] affiliated with -Division of Nano and Energy Convergence Research, Daegu Gyeongbuk Institute of Science and Technology (DGIST), 333, Techno Jungang Daero, Hyeonpung-myeon, Dalseong-gun, Daegu, 42988, Republic of Korea

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conductive carbon materials, such as carbon nanotubes [12,14,15], activated carbon [6,16], and graphene [4].

Carbon materials also store charge by electrostatic means and are mainly used in electric double layer capacitors (EDLC). EDLCs exhibit moderate capacitance values (10 to 100 times lower), compared to pseudocapacitors [1]. Pseudocapacitors store charge via faradaic reactions and employ conducting polymers, such as polyaniline (PANi) [12,17,18], polypyrrole (PPy) [7,11,15,19] and metal oxides, such as MnO_2 [8,14], and $NiCo_2O_4$ [20], as electroactive materials. Pseudocapacitive materials exhibit high capacitance values but suffer from poor cycling stability [1,21,22]. To further enhance the charge storage properties of each material and address their drawbacks, we fabricated a conducting polymer-carbon-fabric composite.

Polyaniline (PANi) and multiwalled carbon nanotubes (CNT) were combined with pineapple-polyester blended woven fabrics (PPWF) to make conducting, and electroactive composites for supercapacitor electrodes. CNT was incorporated onto PPWF via dip-and-dry technique, while PANI was added using *in situ* chemical polymerization. The PPWF composites were compared with their polyester (PWF) counterparts to observe the effect of the pineapple fibers. All composites were then characterized using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), four-point probe technique for conductivity, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge discharge tests (GCD).

2. Experimental

2.1. Materials

Multiwalled carbon nanotubes (CNT) (99% purity, diameter: 10 nm, length: 10um) were obtained from Carbon Nano-material Technology Co., LTD, Korea, and were washed with 5 M HNO_3 at 50 °C before use. An aqueous dispersion of CNT was prepared by mixing 25 mg of MWCNT (25 mg) and 75 mg sodium dodecyl sulfate (SDS) in 5 mL H_2O [23]. The suspension was sonicated to ensure proper dispersion.

Pineapple (*Ananas comosus*) blended polyester fabric (PPWF, 80:20 polyester/natural fabric ratio,ρ = 0.403 g cm^{-3}) was provided by the Philippine Textile Research Institute of the Department of Science and Technology (PTRI-DOST). Pure polyester woven fabric (PWF, ρ = 0.547 g cm^{-3}) was used as a comparison. All fabrics were washed with 2% liquid detergent for 1 h, rinsed twice with water, and dried.

2.2. Preparation of fabric composites

To prepare the CNT/fabric composites, PPWF (1 cm × 2 cm × 0.0267 cm) or PWF (1 cm × 2 cm × 0.0233 cm) swatches were immersed in the CNT dispersion for 30 min and dried in an oven (Binder) for 30 min at 70 °C. The fabrics were then immersed in D.I. H_2O to remove excess surfactant and dried once more. The entire cycle was repeated until 0.5 mg cm^{-2} of CNT was added.

PANi was polymerized on the fabrics via *in situ* chemical polymerization. PPWF or PWF (1 cm x 2 cm) was immersed in a diffusion bath containing 1 mL of 0.1 M aniline (Sigma Aldrich) mixed with 0.2 M HCl for 2 h. Polymerization was initiated using 1 mL of 0.125 M $(NH_4)_2S_2O_8$ in 0.2 M HCl. The polymerization was allowed to continue for 1 h at 0–4 °C. The composites were then washed with 0.2 M HCl and ethanol, and dried in a desiccator overnight.

To prepare the ternary composites, PANi/CNT/fabrics, PANi was polymerized on previously prepared CNT/fabrics via *in situ* chemical polymerization following the same parameters used to prepare PANI/fabric composites.

2.3. Characterization

The water absorbency of pristine PPWF and PWF was measured by PTRI-DOST using AATCC Test Method 79-2014 [24]. Briefly, one drop of water was placed at the surface of the fabric and the amount of time for it to be absorbed was measured. The surface morphology of the pristine fabrics and composites were analyzed using SEM (Hitachi TM3000) and FESEM (Hitachi S4800), respectively. Prior to FESEM measurement, samples were coated with Pt using a Hitachi E-1045 ion sputter coater. A Shimadzu IR-Prestige21 with a DRS-8000 Diffuse Reflectance Accessory was used to measure the FTIR spectra of the samples from 4000 cm^{-1} to 400 cm^{-1}. TGA was performed using a Perkin Elmer TGA4000 with a temperature range of 50–700 °C, at a 10 °C min^{-1} temperature ramp, and under a 20 mL min^{-1} N_2 gas flow. The conductivity of the fabric composites was measured using the four-point probe technique. Conductivity was calculated based on Eqs. (1) and (2):

$$\rho = \frac{\pi}{ln2}\frac{V}{I}t \tag{1}$$

$$\sigma = \frac{1}{\rho} \tag{2}$$

where ρ is resistivity (Ω cm), V is the voltage difference between the two inner probes (V), I is the current applied on the two outer probes (A), t is sample thickness (cm), and σ is the calculated conductivity of the composite (S cm^{-1}) [25].

All electrochemical experiments were carried out using a Biologic VSP-300 using a three-electrode system with the textile composite, Pt coil, and Ag/AgCl electrode as the working, counter, and reference electrodes, respectively, with 1.0 M H_2SO_4 as the electrolyte. EIS was performed from 200 kHz to 10mHz with a sinusoidal signal of 10 mV at open circuit potential (OCV). Cyclic voltammetry (CV) and Galvanostatic Charge Discharge (GCD) measurements were done using a potential range of -0.20 V to 0.80 V. Areal capacitance was computed using equations 3 and 4 for CV and GCD, respectively:

$$C_a = \frac{1}{2A\nu\Delta V}\int idV \tag{3}$$

$$C_a = \frac{i\Delta t}{A\Delta V} \tag{4}$$

where C_a is areal capacitance (mF cm^{-2}), i is current (mA), ΔV is the potential window (V), A is the area of the composite (cm^2), ν is scan rate (mV s^{-1}), and Δt is time of discharge (s).

3. Results and discussion

The pristine fabrics, PPWF and PWF, were both white in color and had similar thickness and density. Water absorbency tests show that PPWF is more hydrophilic than PWF, as PPWF only took 83 s to absorb a water droplet as compared to PWF with 2076 s. Upon addition of CNT and PANi, the fabrics turned black and dark green, respectively, indicative of the presence of the electroactive materials and formation of the conducting emeraldine salt state of PANi. The electroactive materials adhered well to the fabric, as it was stable to washing in dilute acids and solvents, and bending (Fig. 1).

3.1. Surface morphology

Closer inspection of the materials using SEM (Fig. 2) shows that pineapple threads are composed of thin, rough, and striated ribbon-like fibers bundled together. Pineapple threads are mainly found along the warp, and a few fibers are mixed with the weft. The weft is mainly composed of polyester fibers. Compared to pineapple, polyester fibers are smooth, thicker, and cylindrical. CNT/PPWF images (Fig. 2c-d) show that both pineapple and polyester fibers are completely covered with a web-like layer of intertwined CNT tubes. High magnification FESEM images of PANi-containing fabrics (Fig. 2e-f) show that PANi completely covers the fibers of the fabric and forms cauliflower-like

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