

Hybrid supercapacitor materials from poly(3,4-ethylenedioxythiophene) conformally coated aligned carbon nanotubes



Mehdi Ghaffari^{a,b}, Suppanat Kosolwattana^{a,b}, Yue Zhou^{b,c}, Noa Lachman^d, Minren Lin^b, Dhiman Bhattacharya^e, Karen K. Gleason^e, Brian L. Wardle^d, Q.M. Zhang^{a,b,c,*}

^a Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

^b Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

^c Department of Electrical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

^d Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

^e Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

Conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) conformally coated aligned carbon nanotubes (PEDOT/A-CNTs) were developed and investigated as the active material for supercapacitor electrode applications and the results were compared to those of non-coated CNTs as well as that of PEDOT coated randomly packed CNTs. The electrochemical performance of the electrodes was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS). The results revealed that the PEDOT conformally coated and densified (5% volume fraction, V_f) A-CNTs exhibit a specific volumetric capacitance of 84.0 F/cm³, much higher compared to the non-coated and non-densified A-CNTs (1% V_f) that had a specific capacitance of only 3.9 F/cm³. Ion insertion/de-insertion processes in the PEDOT coating layers are observed in impedance spectra for the PEDOT-coated A-CNT electrodes at rates that are not limiting to cell performance relative to ion transport through the channels formed by the PEDOT/A-CNTs. Specific energy and power densities of 11.8 Wh/l and 34.0 kW/l, respectively, were obtained for these nano-tailored electrodes, with high capacitance retention compared with those of PEDOT coated random CNTs.

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1. Introduction

Electrochemical capacitors or supercapacitors have prompted renewed interest in portable devices and electric vehicles where high power delivery in short term pulses is necessary [1–3]. Due to their high surface area and conductivity, carbon based materials such as activated carbon (AC) and carbon nanotubes (CNTs) have been extensively investigated as active electrode materials for supercapacitors. CNTs are especially attractive for their superior electronic and structural properties compared to other materials [4–9]. Nevertheless, like activated carbon, CNTs suffer from the fact that the charge accumulation takes place only on the surface, limiting specific capacitance [1]. To address this limitation, conducting polymers (CPs) such as polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been

used to coat mixtures of carbon nanotubes since in CPs the entire mass and volume of the polymer is involved in the charge storage process, resulting in enhanced capacitance [1,10–19].

Despite this improved charge storage capability, the traditionally CP-coated randomly packed CNTs are not ideal electrode materials for supercapacitors. For example, the ion transport path in these electrodes is tortuous which results in high time constants for mobile ion transport in these porous electrodes (Fig. 1a) and hence reduced power density [20,21]. In addition, the mechanical failure of CPs, caused by the large volume change during the charge/discharge process of the CP, which fills the gaps between CNTs, causes capacitance loss at long cycle operation [15–19]. Perhaps the most effective approach to address these problems is the alignment of the CNTs where the ordered nano-morphology facilitates ion transport by providing highly aligned pathways between the current collectors and the capacitor separator (Fig. 1a and b), resulting in higher power density [20–25]. Such continuous ionic conduction pathways also significantly reduce the effect of the large volume changes of CPs during charge cycles (Fig. 1b) and thereby improves the cycle life of the capacitors, as will be shown in this paper.

* Corresponding author at: Department of Electrical Engineering, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 814 863 8994; fax: +1 814 863 7846.

E-mail address: qxz1@psu.edu (Q.M. Zhang).

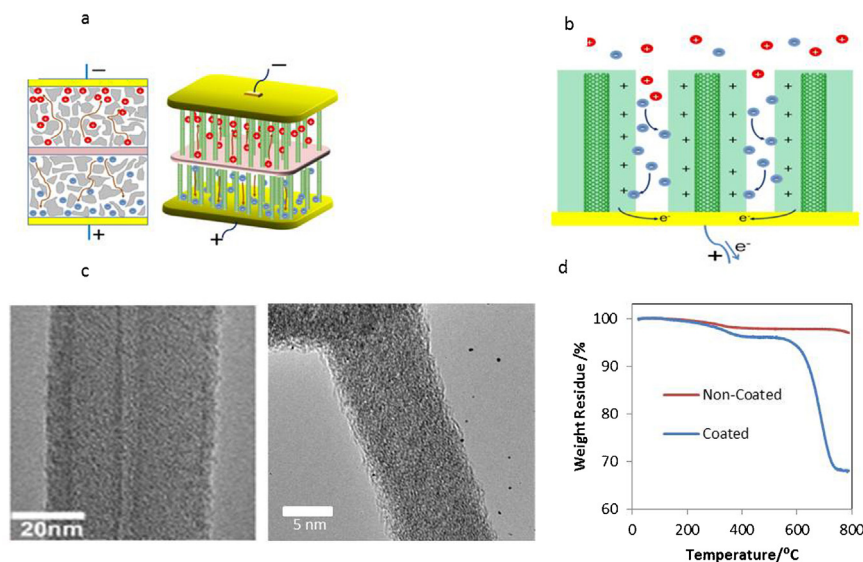


Fig. 1. (a) Schematic comparison of the tortuous ion transport paths in nanoporous electrodes formed, for example, from activated carbons (left), and parallel ion pathways in the A-CNTs (right). (b) Schematic representation of CP-coated A-CNT used as supercapacitor electrode. Cations and anions along with electrons and holes are shown in the figure. (c) TEM images of A-CNT conformally coated with PEDOT. The contrast in the image on the right shows the uniform coating of PEDOT on A-CNT [27], in consistency with the image on the left, showing the detailed morphology of CNT used in this work. (d) TGA plots for the coated and non-coated samples.

In this study, we investigate ion transport and storage mechanisms in a newly developed electrode material for supercapacitor applications composed of mechanically densified PEDOT conformally coated A-CNT forests that preserves the nano-morphology of the A-CNTs to maintain efficient ion transport [26,27]. The reason for the selection of PEDOT lies on the fact that it is very operable in acidic, alkaline and organic electrolytes that make it a good candidate for practical applications [12–14]. Additionally, PEDOT has higher electrochemical window compared to other CPs. Synergistic effects between the two components (A-CNT and PEDOT) with complementary properties leads to a dramatic increase in capacitive performance for the PEDOT/A-CNT electrodes relative to non-coated A-CNTs, with specific capacitance values exceeding those in the literature. The PEDOT/A-CNT electrodes were assembled in a three layer supercapacitor configuration (two electrodes separated by a 20 μm porous separator) using 3 M 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄) in propylene carbonate (PC) as electrolyte and were characterized in a two electrode configuration for the electrochemical performance.

2. Experimental

2.1. Synthesis of A-CNT 'Forests'

Aligned multi-walled carbon nanotubes (A-CNTs) were synthesized *via* thermal catalytic chemical vapor deposition with a thin catalyst layer of Fe/Al₂O₃ at 750 °C [26]. The A-CNTs arrays growth rate was approximately 2 $\mu\text{m}/\text{s}$. The as-grown CNT forests had a 1% volume fraction (V_f) with densities of 10⁹–10¹⁰ CNTs/cm². The A-CNTs (with 2–3 walls) have average diameter of 8 nm and the spacing between aligned CNTs (center to center) are \sim 80 nm.

2.2. Conformal PEDOT coating

The as grown A-CNT forests were coated with poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer *via* an oxidative chemical vapor deposition process (oCVD) [27]. Iron (III) chloride was used as an oxidant and heated *in situ* at 300 °C to sublime. Liquid EDOT monomer was heated in a monomer jar outside the chamber to 150 °C and flowed into the vacuum chamber

simultaneously. A conformal PEDOT coating was obtained over the A-CNT samples placed inside the oCVD vacuum chambers. Substrate temperature of 70 °C for the A-CNTs and reaction pressure of 50 mTorr were maintained during this conformal deposition process. As deposited PEDOT films were electrically conductive since they were already doped with the chloride ions from the oxidant iron (III) chloride and needed no further doping steps. The dopant, chloride ion, is associated with the sulfur in the thiophene ring, which bears a positive charge in the doped state.

2.3. Device fabrication

The PEDOT-coated A-CNT arrays of 200 μm thick were utilized for symmetric supercapacitor electrodes fabrication. For high volume fraction PEDOT/A-CNTs electrode fabrication, a mechanical biaxial densification in two orthogonal directions was applied to reduce the inter-tube spacing of the CNT forests from that of the as synthesized A-CNTs [26]. The 1% and 5% volume fraction of PEDOT conformally coated and non-coated A-CNTs were fabricated into electrodes and their electrochemical performances were compared in this study. For electrochemical characterization, the electrodes were filled with the solution of 3 M EMI-BF₄ (from Iolitec) in propylene carbonate (PC, from Aldrich) and a three-layer capacitor composed of PEDOT/A-CNT electrode//polypropylene separator (Celgard 3501)//PEDOT/A-CNT electrode was prepared. This capacitor was then sandwiched between two gold current collectors (from Alfa Aesar, 10 μm thick) and finally two stainless steel plates as electrodes. The resulting symmetric supercapacitor cell had dimensions of 2 mm by 2 mm (in-plane dimensions) and 0.5 mm thick.

2.4. Characterizations

Morphology of the coated and non-coated A-CNTs was studied using scanning electron microscopy and transmission electron microscopy. Cyclic voltammetry was characterized by a potentiostat (Princeton Applied Research; PARSTAT 2273) at 100 mV/s scan rate and maximum voltage of 2.0 V. Galvanostatic charge-discharge behavior was also investigated by a potentiostat (Princeton Applied Research; Versastat 4) at different discharge rates (0.5, 1, 2.5, 5

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