A facile and scalable approach to fabricating free-standing polymer—Carbon nanotube composite electrodes

Margarita R. Arcila-Velez[a,1], Robert K. Emmett[a,1], Mehmet Karakaya[b,c], Ramakrishna Podila[b,c], Kryssia P. Díaz-Orellana[a], Apparao M. Rao[b,c], Mark E. Roberts[a,c,*]

[a] Department of Chemical & Biomolecular Engineering, Clemson University, Clemson, SC 29634, United States
[b] Department of Physics & Astronomy, COMSET, Clemson University, Clemson, SC 29634, United States
[c] Clemson Nanomaterials Center, Clemson University, Clemson, SC 29634, United States

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ABSTRACT

Nanoporous carbon materials are widely utilized in high-power supercapacitors due to their structural properties, chemical stability and conductivity, despite their limited energy density and charge storage capacity. Conducting polymers, on the other hand, possess high charge capacities; however, their application in commercial devices is hindered by degradation arising from their poor chemical and physical stability. Composites of carbon nanomaterials and conducting polymers have synergistic properties beneficial to supercapacitors, such as high capacitance and stability, but the limitations in scalable synthesis and polymer aggregation prevent widespread utilization. In this work, robust free-standing carbon nanotube (CNT)/electrically conducting polymer (ECP) electrodes are prepared using a simple dispersion filtration method, which can easily be scaled up. This process eliminates the use of binder, substrate or additional inactive weight. Composite CNT/ECP electrodes showed enhanced capacitance and charge capacity, achieving values up to 448 F/g and 84 mAh/g compared to 27 F/g and 10 mAh/g for pure CNT electrodes in aqueous electrolyte. Resulting symmetric cells exhibited energy and power densities of ~5 Wh/kg and ~283 W/kg, respectively, in aqueous electrolytes; and ~12 Wh/kg and ~744 W/kg, respectively, in organic electrolytes when using PEDOT/CNT electrodes. Given the process simplicity, relatively low cost and high throughput, the present composites have great potential for large-scale manufacturing of CP/CNTs supercapacitor electrodes.

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1. Introduction

Rapid growth in the demand for electrical energy storage continues to encourage the development of new materials and devices. With their ability to improve the performance of batteries or provide high-power, a recyclable and safe alternative such as supercapacitors have experienced tremendous growth in this industry. Supercapacitors, which typically comprise high-surface area, inert carbonaceous electrode materials, offer the benefits of high power density, rapid charge/discharge, and long lifetime. Even with these important advantages, carbon materials (e.g., activated carbon, carbon nanotubes, graphene) are limited by relatively low energy density as a consequence of their physical charge storage mechanism, electrical double layer capacitance (EDLC), which is related to ion adsorption at the electrode surface. As we approach the maximum theoretical surface area in carbons, further increases in energy density are no longer attainable. On the other hand, electroactive materials such as metal oxides and electroactive conducting polymers (ECPs) can be prepared with relatively high surface areas, but are also able to store charge through Faradaic charge transfer in addition to EDLC. Metal oxides exhibit high Faradaic capacitance in aqueous solutions with good redox stability, but are limited by material cost, low operating voltage ranges, and the lack of scalable synthetic methods [1,2].

ECPs, such as polypyrrole (PPY), polyaniline (PANI), and poly (3,4-ethylenedioxythiophene) (PEDOT), provide a low-cost, large specific capacitance alternative to carbon materials and metal oxides [3–6] and can be easily prepared through various routes [7] from cheap monomers in large quantities. However, ECPs often suffer from poor cycle stability due to polymer over-oxidation stresses caused by volumetric changes that accompany the charge-discharge processes associated with ion insertion and removal [8]. To improve their performance and stability, significant efforts have

focused on creating micro or nanostructured ECP electrodes by modifying the synthesis processes, which enhances their mechanical and electrochemical properties [8–10]. Another approach to the same goal involves integrating a complementary material to reinforce and support the polymeric structure [11,12]. Carbon nanotubes (CNTs) are attractive for this purpose due to their excellent structural properties, electronic conductivity and chemical stability. CNTs improve the cycle life and mechanical properties of ECPs since CNTs adapt easily to changes in volume [13], and also introduce new electronic properties based on interactions between the two materials. Furthermore, the adaptation of such compositions helps overcome the low conductivity of ECPs in the neutral (or reduced) state and also increase electronic transport in thick electrodes [14]. Of equal importance, the addition of ECPs decreases CNT bundling and enhances the charge storage capacity compared to CNTs electrodes.

In-situ chemical polymerization is the prevalent method for preparing ECP/CNT composites, which consists of oxidative polymerization of ECPs in a CNT suspension and pressing the dry material into a pellet [15]. Through this approach, ECPs and CNTs are integrated on a molecular scale [16–20], increasing conductivity [21], although, homogeneity depends on the CNT dispersion and ECPs often prefer to grow on themselves rather than distributing homogeneously along the CNTs leading to polymer aggregation [17]. High specific capacitance values (500 F/g) [22] have been obtained by electrochemically polymerizing ECPs on CNTs due to strong interactions between the two materials [23]. Nevertheless, this method is limited to low amounts of polymer because as the film grows thicker it blocks electrolyte access to the CNTs. In melt compounding, CNTs are directly dispersed into a polymer melt; however, locally homogeneous states are difficult to achieve without breaking down the entangled CNTs [20]. A simple alternative to produce ECP/CNT composites involves mixing pre-synthesized ECP with CNTs [24,25], which is advantageous in terms of scalability and cost-effectivity [14]. Lota et al. [25] prepared composite electrodes by pressing a mixture of PEDOT and CNTs into pellets and obtained a single-electrode capacitance value of 95 F/g (at 2 mV/s), which possessed improved conductivity and cycle stability compared to PEDOT, albeit with significant diffusion limitations.

In this work, we present a simple, low-cost approach to fabricating free-standing ECP/CNT composite electrodes using a sequential dispersion-filtration process. After ECP synthesis, ECP/CNT dispersions (50/50 by wt.) are prepared in aqueous solutions containing sodium dodecyl sulfate (SDS) using ultrasonication, and then immediately filtered through a polyamide membrane with laboratory scale vacuum filtration. After electrodes are dried, robust, free-standing composite ECP/CNT paper electrodes are obtained, yielding high specific capacitance values up to 448 F/g (at 10 mV/s). In this process, no binder or pressure is needed to obtain efficient electrode performance. Considering the process simplicity, low cost and amenability to high throughput processing, our new approach to composite electrode fabrication provides a unique application to scalable, high power and energy supercapacitor electrode manufacturing.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes were purchased from Cheap-Tubes (dia.=30–50 nm, length=10–20 μm) and NanoTech Labs (dia.=70–80 nm, length=700–800 μm), and used as received. Polypyrrole (PPY), polyaniline (PANI), and Poly(3,4-ethylenedioxythiophene) (PEDOT) were synthesized using previously reported methods [26–28]. Briefly, PPY was synthesized by oxidative polymerization using $FeCl_3$ in methanol at 0 °C for 6 h. PANI was

synthesized by oxidative polymerization in aqueous HCl (1 M), using ammonium persulfate (APS) as an oxidant at 4 °C for 2 h. PEDOT was synthesized using $Fe(NO_3)_3$ in an aqueous solution containing sodium poly(4-styrene sulfonate) for 6 h.

2.2. Electrode fabrication

The ECP/CNT composites were prepared by dispersing CNTs with an ECPs in aqueous solutions containing 1 wt.% SDS using a tip sonicator probe with a power of 75 W for 15 min. Subsequently, the suspension was poured onto a polyamide filtration membrane (Whatman, 0.45 μm pore diameter) and filtered using a vacuum filtration setup. The filtrate on the supporting filter membrane was washed with distilled water several times, and then oven dried at 60 °C for 8 h. The resulting films were peeled off the membrane yielding free-standing ECP/CNT paper-like electrodes with good mechanical properties [28,29].

2.3. Electrode characterization

The physical properties of the composite electrodes were investigated using scanning electron microscopy (SEM, Hitachi SU-6600) and energy dispersive X-ray spectroscopy (EDAX).

Composite electrodes were electrochemically evaluated as single electrodes using a potentiostat (Princeton Applied Research VersaSTAT 4) in aqueous 3 M H_2SO_4 solutions and in 1.5 M tetraethylammonium tetrafluoroborate ($TEABF_4$) in acetonitrile (MeCN). A Pt mesh was used as counter electrode, Ag/AgCl (sat'd KCl) and Ag/Ag+ (0.1 M $AgNO_3$ in MeCN) electrodes were used as aqueous and non-aqueous pseudo-reference electrodes, respectively. Electrochemical characterization included cyclic voltammetry (CV) at scan rates of 10–300 mV s^{-1}, electrochemical impedance spectroscopy (EIS) (0.5 V DC bias, 0.1–10000 Hz, 20 mV RMS) and galvanostatic charge/discharge cycles (C/D) at a current such that the discharge time is equal to ~60 s. The reported specific capacitance values were calculated from CV at a scan rate of 10 mV/s using the complete electrode mass (ECP + CNT).

2.4. Capacitance, energy and power calculations

All the specific values of the electrodes are reported on a per mass basis (gravimetric) with respect to the total mass of the electrode (CNTs + ECP). The specific capacitance, C, of single electrodes measured in 3-electrode cells were determined by taking the average capacitance from CV measurements (current divided by scan rate and mass) over the full voltage range (at 10 mV s^{-1}). The capacitance of symmetric supercapacitors was calculated using the total mass of both electrodes (which were approximately equal) using two methods: first, by taking the average capacitance from CV measurements, as described for 3-electrode measurements; and second, from the inverse of the galvanostatic discharge slope (dV/dt) in the linear range, according to

$$C = \frac{I}{m}\left(\frac{dV}{dt}\right)^{-1} \tag{1}$$

where I is the discharge current and m is the electrode mass. Both calculations for capacitance are within 5%. Energy density, E, is calculated from

$$E = \frac{1}{2}C \times \Delta V^2 \tag{2}$$

where ΔV is the voltage difference from the charged to discharged state. The power density, P, is calculated from

$$P = \frac{\Delta E}{\Delta t} \tag{3}$$