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Hybrid-Capacitors with Polyaniline/Carbon Electrodes Fabricated *via* Simultaneous Electrospinning/Electrospraying

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ABSTRACT

Hybrid-capacitors have the potential to synergistically combine the benefits of both electrochemical double layer capacitors (EDLCs) (long cycle life) and Faradaic-capacitors (high capacitance). However, new processes that intimately combine the two primary materials from each capacitor (carbon and conductive polymer, respectively) within the electrodes in an ordered fashion on the nanoscale are needed to realize this potential. In this study, we report on a novel method (simultaneous electrospinning/electrospraying (E/E)) for fabricating hybrid-capacitors with high surface area electrodes consisting of polyaniline (PANI) and carbon nanoparticles (referred to as E/E electrodes). E/E produces a unique nanofiber/particle network of PANI and carbon. The hybrid-capacitor with E/E electrodes exhibits an excellent specific capacitance of 235 $F g^{-1}$ (*vs.* 138 Fg^{-1} for capacitor with state-of-the art hybrid electrodes) at a current density of 1 $A g^{-1}$. Moreover, the hybrid-capacitor with E/E electrodes retains approximately 84% capacitance after 1000 charge-discharge cycles (*vs.* 67% for capacitor with state-of-the art hybrid electrodes). These results indicate the feasibility of producing E/E electrodes and their promise as future materials in hybrid-capacitors.

1. Introduction

Supercapacitors (also known as ultracapacitors) have attracted significant attention as an electrical storage device that have the potential bridge the divide between high energy density batteries and high power density traditional capacitors [1]. With fast charge-discharge capabilities and intermediate energy densities, applications for supercapacitors range from portable mobile electronics to electric vehicles [2]. Typically, supercapacitors can be divided into two primary classes: electrochemical double layer capacitors (EDLCs) and Faradaic-capacitors, which differ based on their charge storage mechanisms. EDLCs store charge in an electric double layer close to the electrode/solution interface [1,3]. EDLCs exhibit rapid charge-discharge cycles due to the fast kinetics of ion adsorption/desorption on the surface of the electrode materials. The performance of EDLCs is mainly dependent on the porosity and surface area of the active electrode materials, where various carbon materials (*e.g.*, activated carbon, carbon nanotubes, graphene) have been extensively investigated and widely used as EDLC electrodes [4,5]. Contrastingly, Faradaic-capacitors store charge from a Faradic redox reaction, which occurs throughout the bulk of the material (*e.g.*, oxides, conductive polymers, *e.g.*, polyaniline (PANI)) [6,7]. Typically, Faradaic-capacitors store more charge compared to EDLCs, but EDLCs typically have longer lifetimes (retain more charge after many charge-discharge cycles) [1,8]. Combining materials from EDLCs and Faradaic-capacitors (*e.g.*, carbon materials and PANI, respectively) into a hybrid-capacitor using various nanostructures and processing methods has attracted significant interest in regards to attaining a capacitor with the synergistic properties of EDLCs (long lifetime) and Faradaic-capacitors (high capacitance) [9–13]. Wang *et al.* [11] demonstrated a high specific capacitance of 240 $F g^{-1}$ and 83% capacitance retention after 500 cycles with a hybrid-capacitor with activated carbon and PANI in the electrodes prepared by a electrochemical deposition method. This is just one example of a hybrid-capacitor with a combination of improved capacitance and cycling ability. Other hybrid-capacitor examples include combining conductive polymer and microstructured carbons using the following fabrication methods: vapor deposition [14], electro-deposition [15,16], electrochemical polymerizations [17,18]. The variance in results and morphological characterization suggests that the morphology of the electrodes in hybrid-capacitors can play a significant role on the overall charge storage and retention.

Another method to fabricate polymer-based electrodes is electrospinning. Electrospinning is a versatile method in which

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polymer fibers on the order of less than 100 nm in diameter can be produced by ejecting a polymer solution from a syringe needle under an electric field gradient [19]. Electrodes have been produced with electrospinning for various energy devices, such as batteries, capacitors, and fuel cells [20–22]. Previous studies show that carbon fibers produced from the pyrolysis of electrospun polymer fibers can improve capacitor performance [23–26]. The micro-and meso-porous structure of a polymer nanofiber array provides high porosity and large total surface area thereby improving ion absorption and transport (*i.e.*, higher capacitance and higher ion conductivity) [24,27]. Additionally, electrospinning can be combined with other electrode fabrication methods. Several studies combined electrospun materials with polymerization methods [10,13] or with carbonization process [24,28,29]. One example of the use of electrospinning to produce capacitor electrodes includes work by Yan *et al.* [10], where a flexible carbon nanofiber-PANI composite was fabricated using rapid-mixture polymerization of aniline in electrospun carbon nanofiber (CNF) paper. The hybrid-capacitor with these electrodes resulted in high capacitance ($638\,F\,g^{-1}$ at $2\,A\,g^{-1}$) and good stability (90% capacitance retention after 1000 cycles). This is just one example of how electrospinning has become a facile and versatile method to produce nanofibers and can be combined with other processing techniques for a variety of applications where nanostructure can impact performance [30,31].

In this study, we combine electrospinning and electrospraying (E/E) in a simultaneous process to produce PANI/carbon nanofiber/particle network electrodes for hybrid-capacitors. The E/E process has been employed previously in our laboratory to produce electrodes for fuel cells [32,33] and reactive membranes for water filtration [34]. Fig. 1 illustrates the E/E process to produce hybrid electrodes, where this E/E method differs from electrospinning or electrospraying alone, where nanofibers and particles can form interconnected morphologies simultaneously. This technique provides a facile path to combine fibers/particles in a composite material with tunable particle size, fiber diameter, and material loadings. The electrochemical performance of a hybrid-capacitor with E/E electrodes was evaluated and compared to control capacitors produced with conventional electrode fabrication methods. Morphologies of E/E electrodes before and after capacitor testing were also investigated and compared with conventional electrodes. For the first time, this work demonstrates the fabrication of PANI/carbon nanofiber/particle network electrodes fabricated *via* simultaneous E/E and the two-electrode capacitor performance of these electrodes.

2. Experimental

2.1. Materials

Aniline (ACS reagent), chloroform (contains 100–200 ppm amylenes as stabilizer, ≥99.5%), ammonium peroxydisulfate (≥98%), and sulfuric acid (ACS reagent, 95.0-98.0%) were purchased from Sigma-Aldrich and used as received. Polyethylene oxide (PEO, M_w = 8,000,000 g/mol, Polysciences, Inc.), a mixture of activated carbon and carbon nanotubes (activated carbon: APS: 80 nm; carbon nanotube: o.d. = 30–100 nm, length = 5–30 μm, US4898, US Research Nanomaterials), porous separator (25 μm microporous monolayer membrane (PP), 3501, Celgard), and untreated carbon fiber paper (165 μm measured by ultra meter caliper, EC-AC-Paper, FuelCell.com) were used as received. All solutions used in this study were made using deionized water obtained from a NANOPure water purification system (Barnstead) with resistivity greater than 18 MΩ cm.

2.2. Synthesis of polyaniline

Polyaniline (PANI) was synthesized by interfacial polymerization using a procedure similar to one previously reported in literature [35]. The procedure is as follows. 3.2 mmol of aniline was dissolved in chloroform. 0.8 mmol of ammonium peroxydisulfate (oxidant) was dissolved in 20 ml of 1 M sulfuric acid. These two solutions were then quickly poured together and formed a two-phase insoluble mixture, where PANI formed at the organic/aqueous interface and diffused into the water phase over a 12 h period at room temperature. No mechanical stirring was used in

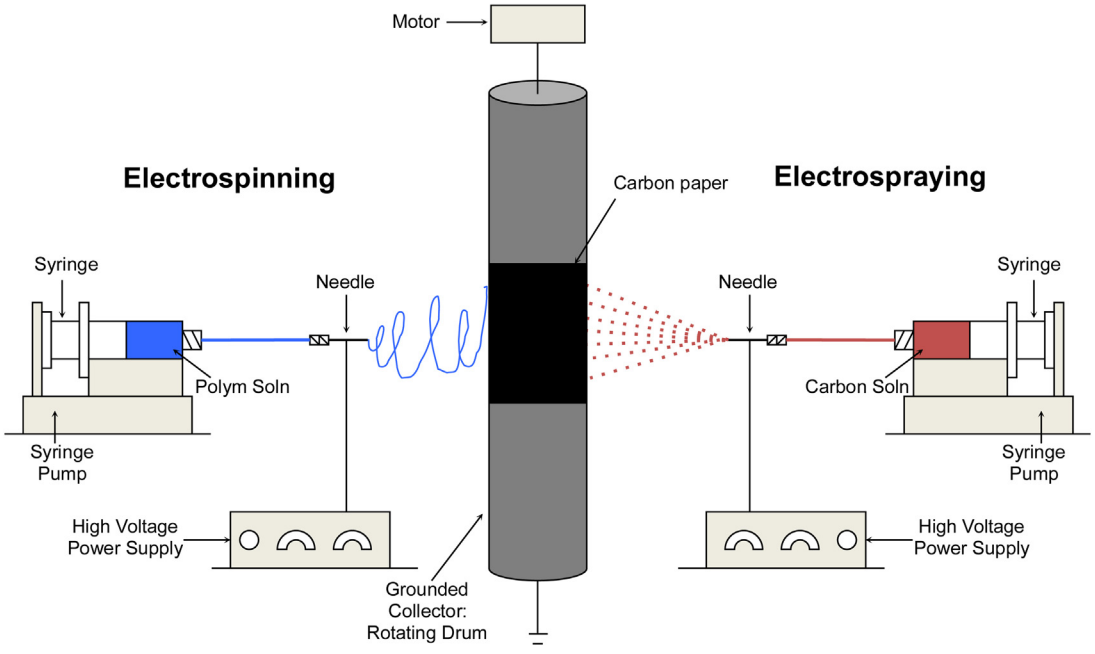

Fig. 1. Schematic of simultaneous electrospinning/electrospraying (E/E) apparatus.