

Nanofiber-based Electrodes for High Power Supercapacitors

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We report a facile method for obtaining extremely high surface area and hierarchically- porous carbon nanofibers for supercapacitor application. First, blends of polyacrylonitrile (PAN) and sacrificial Nafion at different compositions in dimethyl formamide (DMF) have been electrospun into non-woven nanofiber mats with diameters in the range of 200-300 nm. Electrospun nanofiber mats are then subjected to stabilization and carbonization processes to obtain porous carbon nanofibers (CNFs) as PAN converts to carbon and the sacrificial Nafion decomposes out to create intra-fiber pores. Scanning and Transmission electron microscopy (SEM/TEM) images (figures 1, 2) of both longitudinal and cross sections of fibers show a remarkable interconnected pore network. Figure 1 shows the SEM images of three different porous carbon nanofibers fabricated via this process exhibiting hierarchical pore-structure; internal pores due to Nafion decomposition and external pores due to inter-fiber spacing. Please refer to the figure caption for detailed information about the material composition used. These images demonstrate the tunability of the pore sizes within CNFs by varying the amount of Nafion and the total solid concentration in the initial solution. In particular, we find that the pore size increases as the fraction of Nafion in Nafion/PAN blend increases, as expected. In addition, we found that for the same Nafion: PAN composition, the pore size increased on decreasing the solution concentration in DMF (compare figures 1b and 1c). This is possibly because the lower solution concentration decreases the relaxation time of the polymers, resulting in faster phase separation and larger domain size of Nafion within the electrospun nanofibers. This eventually leads to larger pore size after Nafion decomposition.

The samples were characterized via nitrogen physisorption (not shown); they exhibit specific surface area of up to 1600 m²/g with a large fraction of mesopores (2 – 4 nm). These samples were prepared using the single-step carbonization process, as described above without any chemical or physical activation processes. In particular, samples in figures 1a and 1b showed an average pore size of 1.3 nm and 4.7 nm respectively. For the sake of clarity, these fibers are referred to as CNF-1.3 nm and CNF-4.7 nm respectively.

The non-woven fiber mats of porous CNFs were tested as electrode materials for supercapacitors without the addition of polymeric binding agents using both aqueous and organic electrolytes. Figure 3 provides the cyclic voltammetry (CV) curves of CNF-4.7 nm sample at various scan rates. These electrodes exhibit near-ideal rectangular CV curve even at a high scan rate of 2V/s. This is attributed to the relatively larger pore size in these materials compared to most activated carbons, which

allows faster ion transport and charge/discharge. Note that activated carbons often deviate from ideal behavior even at a scan rate of 100 mV/s scan rate [1]. Figure 4 provides the capacitance of these materials vs. scan rate. These materials exhibit a specific capacitance of up to 220 F/g. 60% capacitance is retained even at a high scan rate of 2 V/s. In figure 5, we show the specific capacitance (measured via charge/discharge) vs. current density data of ‘CNF-4.7 nm’ sample in direct comparison with activated carbon [2]. 80% of capacitance is retained at 20 A/g, while only 40% is retained for activated carbon. These results indicate that the porous carbon nanofibers exhibit large power handling capability; this is attributed to the hierarchical pore-structure consisting of meso (internal) and macro-pores (external) optimizing both surface area and ion transport.

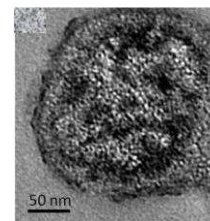


Figure 2. TEM image of microtomed porous carbon nanofiber section showing continuous pores (light region) inside the nanofiber.

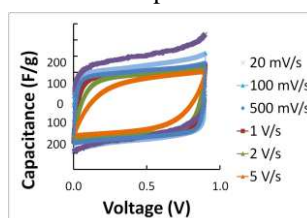


Figure 3. Cyclic voltammetry curve of porous carbon nanofibers (CNF-4.7 nm) at various scan rates in 1M H₂SO₄

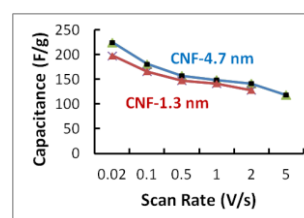


Figure 4. Specific capacitance vs. scan rate for two samples of porous carbon nanofibers with different average pore diameters in 1M H₂SO₄.

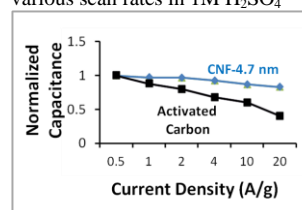


Figure 5. Capacitance (C) normalized using C at 20 mV/s as a function of current density for porous carbon nanofiber sample and activated carbon in 1M H₂SO₄.

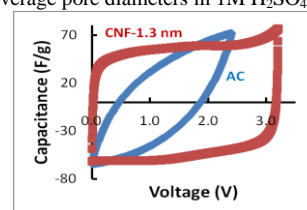


Figure 6. Cyclic voltammetry of porous carbon nanofiber and activated carbon at 100 mV/s in 1M TEABF₄/acetonitrile.

Finally, these porous carbon nanofibers were tested as electrodes in organic electrolyte (1M TEABF₄ in Acetonitrile). Figure 6 shows representative CV curves for our ‘CNF-1.3 nm’ sample and activated carbon (purchased commercially) at 100mV/s scan rate. As seen in the figure, the porous carbon nanofibers exhibit near-ideal CV behavior; however, the activated carbon shows a huge deviation from an ideal behavior, further corroborating that the hierarchical pore structure in our materials allow faster ion transport. In addition, the porous CNFs allow us to expand the voltage window to 3.2 V possibly due to absence of functional groups on the carbon surface.

References: [1] Journal of The Electrochemical Society, 156 (2009) A7. [2] Ra et al, Carbon, 47 (2009) 2984.

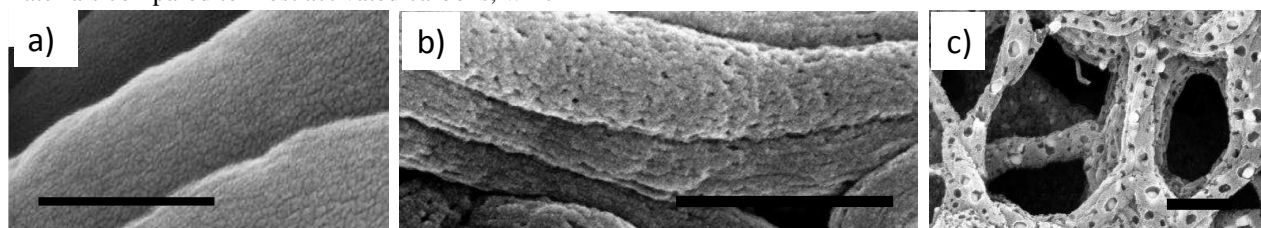


Figure 1: SEM images of mesoporous carbon nanofibers fabricated via high temperature calcination of the nanofibers electrospun using the following w/w compositions of PAN:Nafion, solid percent in DMF in initial solution a) 40:60, 15% b) 20:80, 25% c) 20:80, 20%. Scale bars = 500 nm. All samples exhibit >1500 m²/g specific surface area as measured using nitrogen physisorption (not shown).