

Supporting Information

Experimental Details

Fabrication of porous carbon nanofibers (P-CNF)

Porous CNFs (P-CNF) were obtained by carbonization of electrospun nanofibers of Nafion and polyacrylonitrile (PAN). We refer our reader to our previous publication for a detailed description of the fabrication procedure [1]. For this study in the ionic liquid electrolyte, the electrospun nanofibers were stabilized by heating to 280 °C at a rate of 5 °C min⁻¹ under air atmosphere and held at 280 °C for 5h, then carbonized by heating to 1000 °C at a rate of 5 °C min⁻¹ and held at 1000 °C for 1h under an inert atmosphere. This process converted PAN to carbon and decomposed out Nafion to generate intra-fiber pores.

Fabrication of activated porous carbon nanofibers (a-P-CNF)

To fabricate activated porous carbon nanofibers, the P-CNF mats were activated with potassium hydroxide (KOH, Amresco, reagent grade) with the aim to further enhance surface area, while retaining the through-connected meso and macropore structure of P-CNFs. For the activation treatment, the P-CNFs were soaked in 30 wt% KOH solution overnight, blotted with lint-free paper upon removal from the solution, and then heated to 800 °C at a rate of 5 °C min⁻¹ under nitrogen flow. They were held at 800 °C for 30 minutes and were intensively washed with distilled water to remove any remaining residue.

Fabrication of Control Samples

As control, we fabricated and tested two different control samples – non-porous carbon nanofibers (NP-CNF) and activated carbon nanofibers (a-CNF). The former was fabricated via stabilization and carbonization (using the same conditions as for P-CNF) of pure PAN electrospun nanofibers. The latter was fabricated via KOH activation (using the same method as used for a-P-CNF) of NP-CNF.

Nanofibers Characterization

The external morphology of electrospun nanofiber mats was characterized using scanning electron microscopy (Zeiss Supra 50VP). To characterize internal assembly, nanofibers were embedded in epoxy matrix (purchased from Electron Microscopy Science) and then microtomed into thin longitudinal and cross sections using a Leica EM UC6 ultramicrotome equipped with a diamond knife. The sections were picked up on lacey carbon copper grids (purchased from Electron Microscopy Science) and characterized using transmission electron microscopy (JEOL JEM2100) operated at 200 kV. The specific surface area (SSA) of CNFs was measured using nitrogen sorption isotherms at 77K (Autosorb-1, Quantachrome). Prior to the adsorption-desorption measurement, all samples were degassed at 200⁰C under vacuum for 24h to remove impurities. The pore size distribution (PSD) of CNFs was calculated based on adsorption-desorption curves using the quenched solid density functional theory (QSDFT) with assuming slit-shaped pores.

Electrochemical testing

A Swagelok cell (PFA-820-6, purchased from Swagelok) setup (Figure S1) with 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMIMTFSI, purchased from Io-li-tec) ionic liquid electrolyte was used for the electrochemical testing. Two freestanding carbon nanofiber mats (electrodes)

with a loading density of 3 mg cm^{-2} and a thickness of $150 \text{ }\mu\text{m}$ per electrode were placed on either side of a Celgard 3501 separator, and sandwiched between two stainless steel rods ($1/2''$ diameter) (current collectors). The cell was hand-tightened upon completion. All cells were assembled in a glove box (MBraun) with water content below 1 ppm and were connected to the potentiostat (Gamry Reference 3000) through electrical feedthroughs for electrochemical measurements. Cyclic voltammetry (CV) was performed with various scan rates from 20 mV s^{-1} to 5 V s^{-1} in the voltage window from 0-3.5 V. The specific capacitance, C , and energy density, E , were evaluated using the following equations:

$$C = \frac{\int I dV}{m \times \nu} \quad (1)$$

$$E = \frac{1}{8} CV^2 \quad (2)$$

where I is current response, m is mass of one electrode, ν is scan rate. Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range from 100 kHz to 10 mHz with an alternating current amplitude of 10 mV at open circuit voltage. Note C is calculated using weight of one electrode and E is calculated for the device using weight of both electrodes.



Figure S1: Picture of a Swagelok cell setup used for electrochemical testing.

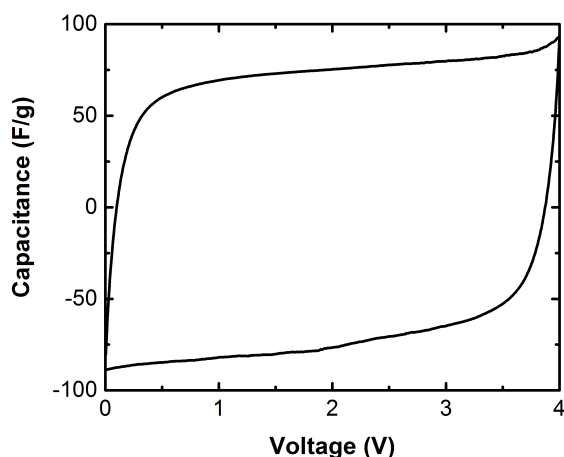


Figure S2: CV showing a 4V window of P-CNF samples in EMIMTFSI

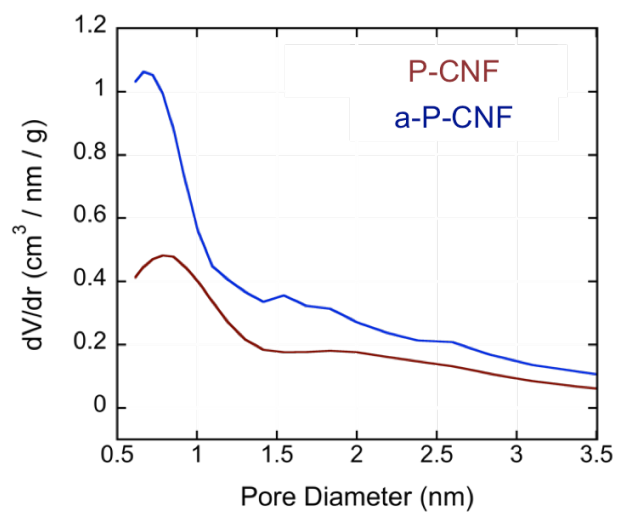


Figure S3: BET pore size distribution of porous carbon nanofibers (P-CNF) and activated porous carbon nanofibers (a-P-CNF).

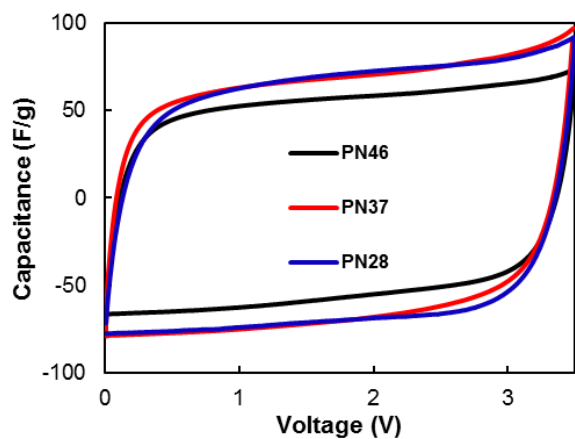


Figure S4: CVs of various compositions of porous carbon nanofibers - carbonized 40:60 PAN:Nafion (PN46), carbonized 30:70 PAN:Nafion (PN37), and carbonized 20:80 PAN:Nafion (PN28) at 100 mV s⁻¹.

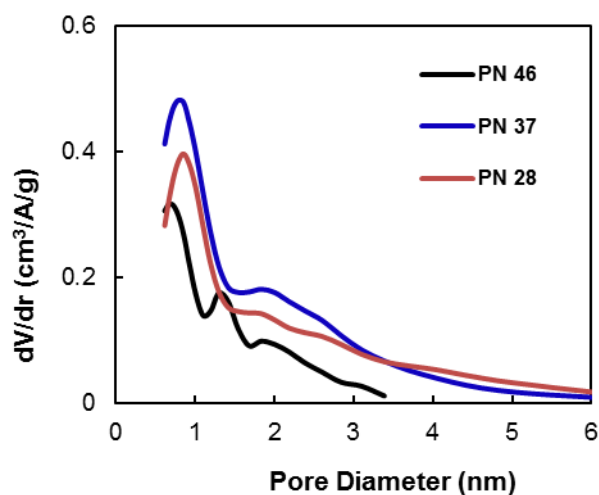


Figure S5: Pore size distribution of PN 46, PN37, and PN 28.

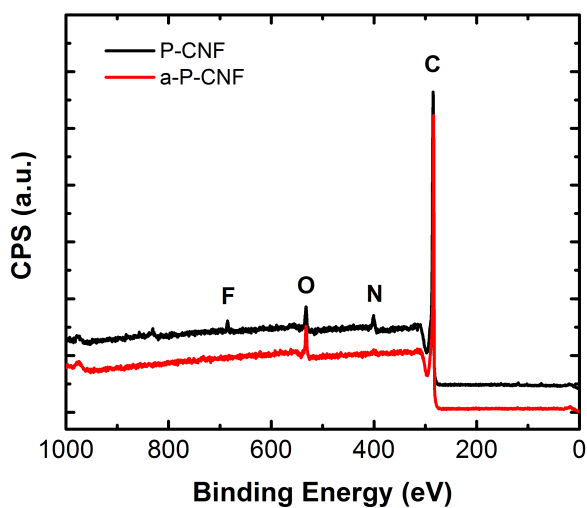


Figure S6: X-ray photoelectron spectroscopy of P-CNF and a-P-CNF.

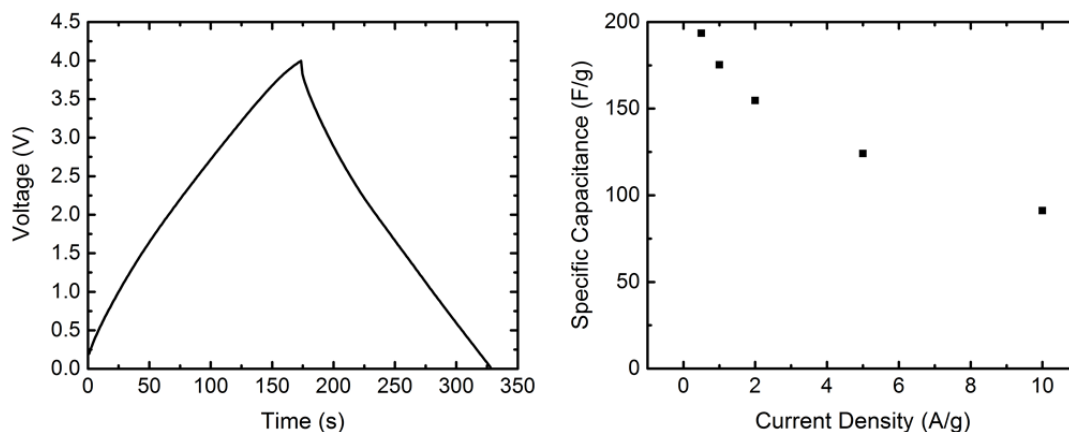


Figure S7. Charge-discharge curve at current density of 1 A g⁻¹ (left) and the specific capacitance at various current densities (right) of a-P-CNF. A linear response in the voltage versus time indicates a solely electrochemical double layer capacitance of a-P-CNF as expected. Moreover, the voltage drop at the beginning of the discharge curve is small corresponding suggesting low equivalent series resistance.

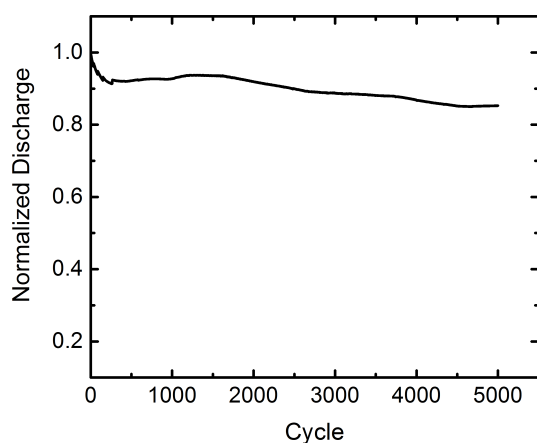


Figure S8: Cyclic stability of a-P-CNF for 5000 cycles using charge-discharge measurement at a current density of 5 A g⁻¹. The capacitance was normalized to the first cycle. There was a 10% drop in capacitance in the first 1000 cycles followed by a steady and slow decrease for the next 4000 cycles. The sample still retained 83% of its initial capacitance after 5000 cycles.

Table S1. Summarized elemental analysis from X-ray photoelectron spectroscopy results.

Samples	C	N	O	F
P-CNF	92.5	3.8	2.9	0.8
a-P-CNF	94.3	0.8	4.9	0

1. Tran, C.; Kalra, V. *Journal of Power Sources* **2013**, 235, (0), 289-296.