

Supporting Information

Fig. S1 shows that at least 4% of pure PAN in DMF is necessary for the solution to be electrospinnable. Bead-on-string morphology is formed at this concentration.

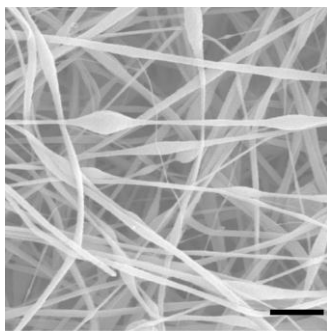


Fig. S1 SEM image of 4% pure PAN in DMF. The scale bar is 1 micron.

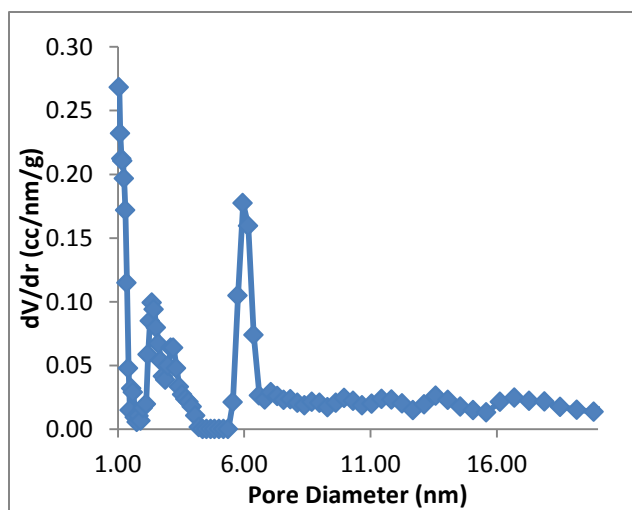


Fig. S2 Pore distribution data for porous carbon nanofibers shown in **Fig. 5a** measured via Nitrogen physisorption. Total surface area=1541m²g⁻¹.

The specific surface area (SSA) of carbon nanofibers (CNFs) was measured using nitrogen adsorption isotherm at 77K (Autosorb-1, Quantachrome). Prior to the adsorption-desorption measurement, all samples was degassed at 200^oC 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) assuming slit-shaped pores. Carbonized 80:20 Nafion: PAN electrospun nanofibers exhibit a cumulative volume of 1.336 cc g⁻¹, a total specific surface area (SSA) of 1541 m² g⁻¹, and an average pore size of 4.6 nm. Note that this pore volume does not include the macropores formed due to inter-fiber spacing. It only includes the micro and meso pores within the nanofibers. A typical carbonized electrospun pure PAN nanofibers has a SSA of about 200 m² g⁻¹. The additional surface area in our porous carbon nanofibers comes from the micro/meso pores formed due to decomposition of Nafion.

Fig. S3 shows the SEM image of calcined 60:40 Nafion: PAN nanofibers electrospun using only 10wt% total solution concentration in DMF. Bead-on-string morphology was formed due to the relatively lower solution concentration. This image demonstrates that uniform pore-structure is formed after calcination even for beaded nanofibers. Note that the pore sizes in these nanofibers are much larger than those shown

in fig. 6, which shows calcined nanofibers electrospun using higher solution concentration. This is possibly due to the faster kinetics of polymers in a lower concentration solution that leads to enhanced phase separation during the electrospinning timescale, thereby forming larger Nafion domains.

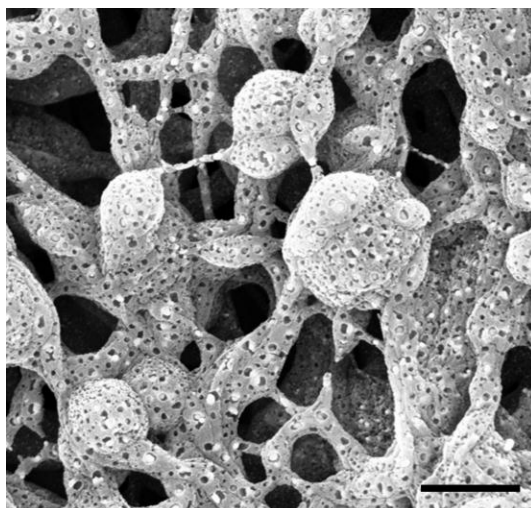


Fig. S3 SEM image of electrospun 60:40 Nafion: PAN at 10 % total solution concentration after carbonizing. The scale bar is 1 micron.

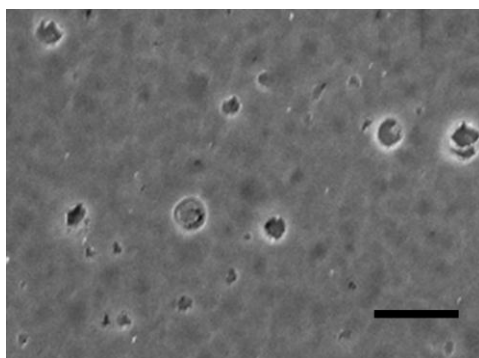


Fig. S4 SEM images of casted film 50:50 Nafion: PAN after carbonizing. The scale bar is 2 micron.

Fig. S.4 shows the SEM image of the calcined film made from 50:50 Nafion: PAN solution. As shown in the image, the carbonized film consists of pores with sizes in the range from 1-2 μm . The difference in the pore size between the porous carbon nanofibers and the porous carbon film represents the difference in the domain sizes of PAN and Nafion in the two materials. This further corroborates the benefit of electrospinning that results in kinetically-trapped desired structures with phase separation only at the nanoscale.

Table. S1 Electrical conductivity of different carbonized samples

Nafion: PAN (wt/wt)	Electrical conductivity (S cm^{-1})
0:100	0.15
60:40	0.13
80:20	0.12

The conductivity of CNFs was measured using a two-point method with stainless steel current collectors. Toray carbon paper with a known conductivity of 11 S cm^{-1} was used to determine the contact and circuit resistance. All samples exhibit similar values indicating the presence of a percolating carbon network within the porous carbon.