

Controlling the Pore Size and Orientation in Block Copolymer Fibers and the Corresponding Porous Carbon Fibers

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Carbon is a widely used electrode material because of the high electrical conductivity, chemical stability, and structural versatility. Among various forms of carbon, carbon fibers are attractive because they offer continuous and rapid electron conduction. In addition to the high mechanical strength that enables their operation under extreme conditions, the self-standing nature eliminates the need for polymer binders which increases electrical resistance. Carbon fibers, similar to carbons in other formats, store electrical energy primarily by electrical double layers at electrode/electrolyte interfaces. Their surface areas, and pore size distributions are critical factors of ion-accessible surfaces and ion diffusion kinetics, both of which strongly influence capacitance and rate capability, the two figures-of-merit for supercapacitors.

Our group has developed a method for synthesizing porous carbon fibers (PCFs) with uniform mesopores and a narrow pore size distribution from poly(methyl methacrylate-*block*-acrylonitrile) (PMMA-*b*-PAN). The mesopore uniformity stems from the well-defined microphase separation of poly(methyl methacrylate) (PMMA) and poly(acrylonitrile) (PAN) into bicontinuous domains upon thermal annealing. The subsequent pyrolysis of PMMA-*b*-PAN decomposes PMMA and carbonizes PAN, resulting in uniform mesopores throughout each fiber. The method to some extent is similar to the direct use of block copolymers such as poly(acrylonitrile-*block*-butyl acrylate) (PAN-*b*-PBA) and poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) to generate carbon powders and films with porous structures. One expects that varying the molecular

weights of PMMA and PAN blocks alters the sizes of PMMA and PAN domains, and thus the mesopore size, pore volume, and surface area of PCFs after pyrolysis. However, all previous studies have focused on preparing porous carbons in the formats of powders, particles, and monoliths. The fibrous format of porous carbons requires drastically different polymer properties, and thus a systematic study of the block copolymer precursors is urgently needed to fully

Designation	PMMA M_n (kDa)	PAN M_n (kDa)	PDI	ϕ_{PAN}	Surface Area (N ₂) (m ² g ⁻¹)	Surface Area(CO ₂) (m ² g ⁻¹)	Mesopore Peak Size (nm)
PMMA 39	39	-	1.02	-	-	-	-
BCP 39-13	39	13	1.16	0.25	421	119	12.7
BCP 39-36	39	36	1.10	0.48	615	123	11.7
BCP 39-149	39	149	1.20	0.79	228	124	10.9
PMMA 62	62	-	1.06	-	-	-	-
BCP 62-20	62	20	1.15	0.25	605	126	15.7
BCP 62-56	62	56	1.14	0.48	918	208	13.7
BCP 62-200	62	200	1.10	0.77	391	118	12.1
PMMA 85	85	-	1.10	-	-	-	-
BCP 85-40	85	40	1.17	0.32	562	132	18.6
BCP 85-60	85	60	1.20	0.42	657	129	17.2
BCP 85-215	85	215	1.16	0.72	342	141	13.7

Table 1. Block copolymers and the resultant porous carbon fibers.

elucidate the conversion of block copolymers into porous carbon fibers. The foremost question is how to design block copolymer precursors of certain molecular weights and compositions to obtain specific structures and properties in porous carbon fibers.

In this annual report, we systematically study the interplays among the molecular weight and composition of PMMA-*b*-PAN, the porous structures of PCFs (surface areas, pore size distributions, and pore volumes), and the electrochemical performances of PCFs (impedance, gravimetric capacitance, and rate capability). To design block copolymers for PCFs with hierarchical porous structures, we have synthesized three series of PMMA-*b*-PAN by RAFT polymerization with different polymerization times (Table 1). The three series of PMMA-*b*-PAN have three number-average molecular weights (M_n) of PMMA ($M_n = 39, 62, \text{ and } 85 \text{ kDa}$)

are denoted as BCP 39-X, BCP 62-X, and BCP 85-X, with the numbers and X representing the number average molecular weight (M_n) of PMMA and PAN in kDa, respectively. The target PAN volume fractions (ϕ_{PAN}) of the three block copolymers in each series are approximately 25%, 50%, and 75%. The molecular weights of all polymers were determined using SEC with a light scattering detector. The SEC trace of each BCP showed a unimodal peak, indicating a relatively low polydispersity index ($\text{PDI} \leq 1.20$). As the PAN volume fraction was increased from ~ 0.25 , ~ 0.5 , to ~ 0.75 in each series, the retention time was reduced, and the molecular weight of PAN block increased. The SEC traces of the block copolymers with the highest ϕ_{PAN} showed small tails at long retention times, indicating the presence of some low-molecular-weight polymers resulted from premature termination during polymerization.

Electrospinning and pyrolysis of PMMA-*b*-PAN yielded PCFs. Depending on the molecular weight and composition, the mesopore size of PCFs varied between 10.9 and 18.6 nm, and increased with decreasing ϕ_{PAN} . In each of the three series, block copolymers with $\phi_{\text{PAN}} \sim 0.5$ showed the maximum surface areas (Figure 1). Block copolymer with an intermediate molecular weight ($M_n, \text{PMMA-}b\text{-PAN} = 62\text{-}b\text{-}56$ kDa) achieved the maximal surface area of $918 \text{ m}^2 \text{ g}^{-1}$.

We have also utilized the porous carbon fibers for depositing pseudocapacitive materials such as MnO_2 . Our judiciously designed mesopores have an average diameter of ~ 11 nm and are partially filled with a $< 2\text{-nm}$ -thick layer of MnO_2 (Figure 2). On the one hand, the mesopores provide continuous channels for efficient ion transport across the entire electrode, significantly reducing the ion diffusion resistance. On the other hand, the fibrous carbon network provides expressways for efficient electron transport without the need for any conductive additives. This contrasts with hard-templated mesoporous carbon particulates (*e.g.*, CMK-3), which have limited electrical conductivity and demand polymer binders to hold the discrete carbon particulates together. At high mass loadings approaching 7 mg cm^{-2} , the PCF-supported MnO_2 electrodes (PCF@ MnO_2) show superior electron/ion transport and outstanding charge-storage performances.

Thanks to this support, the PI contributed one article and two invited reviews (see publications below).

Publications:

Tianyu Liu, Zhengping Zhou, Yichen Guo, Dong Guo, Guoliang Liu,* “Block copolymer derived uniform mesopores enable ultrafast electron and ion transport at high mass loadings”, **Nature Communications**, **2019**, 10, 675. [DOI: [10.1038/s41467-019-08644-w](https://doi.org/10.1038/s41467-019-08644-w).]

Tianyu Liu, Guoliang Liu,* “Block Copolymer-Based Porous Carbons for Supercapacitors”, **Journal of Materials Chemistry A**, **2019**, DOI: [10.1039/C9TA07770G](https://doi.org/10.1039/C9TA07770G).

Tianyu Liu, Guoliang Liu,* “Block Copolymers for Supercapacitors, Dielectric Capacitors and Batteries”, **Journal of Physics: Condensed Matter**, **2019**, 31, 233001.

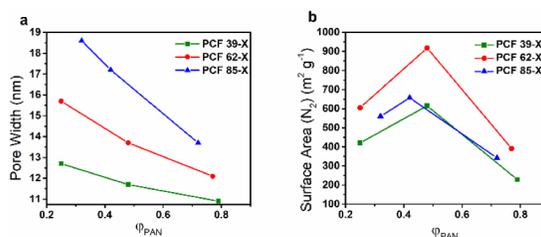


Figure 1. (a) Mesopore sizes and (b) surface areas of PCFs based on N_2 isotherms.

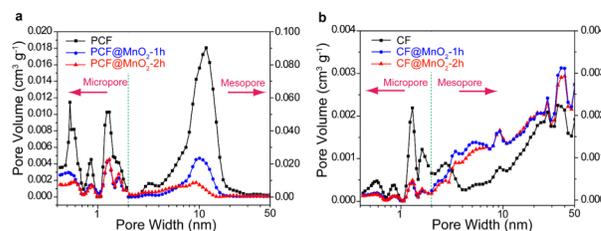


Figure 2. (a and b) Pore size distributions of (a) PCF, PCF@ $\text{MnO}_2\text{-1h}$, and PCF@ $\text{MnO}_2\text{-2h}$ and (b) CF, CF@ $\text{MnO}_2\text{-1h}$, and CF@ $\text{MnO}_2\text{-2h}$. The micropore and mesopore size distributions are measured by the physisorption of carbon dioxide (at 273 K) and nitrogen (at 77 K), respectively, and calculated using the density functional theory. Note the different scales in the micropore and mesopore ranges. Compared to PCFs, CFs contain one order of magnitude lower mesopore volume. The high mesopore volume of PCFs confirms that the mesopores are interconnected and thus are accessible to the adsorbates.