Macromolecules

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Perspective

Block Copolymer Derived Porous Carbon Fiber: An Emerging Structural Functional Material

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Cite This: *Macromolecules* 2023, 56, 9939−9951

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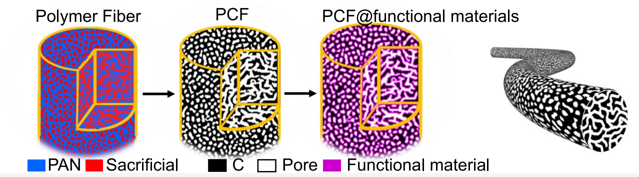


ABSTRACT: Since their inception over 60 years ago, block copolymers have ripened to a state that has extraordinary impacts on chemistry, physics, biology, materials science, and engineering. Meanwhile, the remarkable development of carbon fibers has reached a mature level that is believed to have little room for further improvement. Bridging the two seemingly unrelated materials, however, offers an uncharted landscape of opportunities for innovation. This Perspective parses the recent literature to provide a brief overview of the status of block copolymer derived structural functional porous carbon fibers, hoping to provoke more understandings and stimulate further development in this emerging class of materials.

■ INTRODUCTION

Since their discovery more than a century ago, polymers have gradually assumed an important role in modern society, as evidenced by their ubiquitous applications.[1,2] Block copolymers, as a special type of polymer, contain two or more blocks of polymers covalently bonded together, offering structures, properties, and functionalities that an individual polymer block cannot.[3−5] Because of the unique nanoscale behaviors, block copolymers have gained traction in fields ranging from lithography[6−9] to interface stabilization[10−13] and drug delivery,[14−16] to name a few.

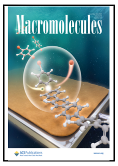
One area of interest is the fabrication of nanoscale porous structures, which hold great promise for catalysis, separation, filtration, and others.[17,18] Block copolymers, owing to the ability to self-assemble into nanoscale structures, can template the formation of porous structures. Via self-assembly and sometimes coupled with cross-linking,[19−21] block copolymers are useful for preparing porous polymers,[22−26] including porous engineering polymers.[27−30] Many reviews are readily available on this topic.[9,18,23,31−34] Upon integration with inorganic precursors, block copolymers are excellent “soft templates” for fabricating porous inorganic materials, such as metals, metal oxides, metal nitrides, and others.[9,35] One notable example is poloxamers, also known as Pluronics, which are nonionic surfactants initially used in biological science for reducing shear stress in cell culture[36] and later applied to templating the synthesis of mesoporous materials in materials science.[37] Conversely, the inorganic hard templates could be reversed to prepare porous polymers and carbons, often termed the “hard-template” approach. Considering the large number of reviews on porous polymers and porous carbons,[26,38−43] we will not focus on reviewing or summarizing reports on these topics.

Herein we mainly focus on an emerging material of porous carbon fiber derived from block copolymers. The author remarks that this work is not a comprehensive review of porous carbons or porous carbon fibers but a short summary of recent works on the direct utilization of block copolymers for preparing porous carbon materials, particularly fibers. We intend to provide a perspective on porous carbon fibers derived from block copolymers, and we wish to stimulate general interest and encourage further investigation into the material structures, properties, functionalities, and applications.

■ POROUS CARBONS AND OTHER POROUS MATERIALS

Depending on the pore size, the International Union of Pure and Applied Chemistry (IUPAC) has a standard definition for micropores (<2 nm), mesopores (2−50 nm), and macropores (>50 nm) in porous materials. The catalysis community widely adopts the pore size definition because the pore size has immediate implications for the catalytic properties, especially in terms of reactant/product transport[44,45] and catalytic confinement.[46] In catalysis, the porous materials can be either catalyst or catalyst support. Notable examples include zeolites and mesoporous oxides, which have found wide use in catalytic cracking and reforming.[46−48] The recent development of porous materials has flourished, and many porous materials, including

Received: July 31, 2023
Revised: December 3, 2023
Accepted: December 4, 2023
Published: December 13, 2023



ACS Publications

https://doi.org/10.1021/acs.macromol.3c01528

polymers of intrinsic microporosity (PIM),[49,50] metal−organic framework (MOF),[51] and covalent−organic framework (COF),[52,53] have emerged (Figure 1). Most of these materials, however, are insulative. Porous metals (e.g., porous Au[54]) and carbons are among the materials that possess both porosity and electrical conductivity.

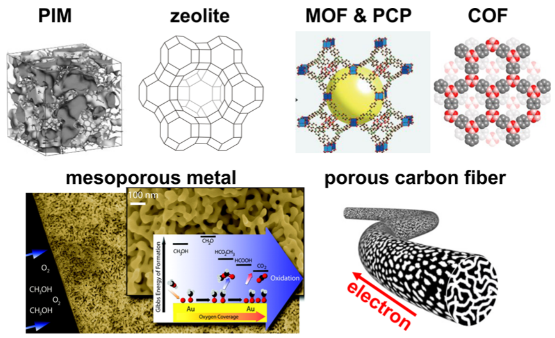


Figure 1. Representative porous materials, including insulative ones (e.g., PIM,[49,50] zeolite, MOF,[51] and COF[52,53]) and conductive ones (e.g., mesoporous metals such as Au[54] and porous carbon fiber).[55] Reproduced in part with permission from ref 49. Reproduced in part with permission from refs 51, 54, and 55. Copyright 2013, 2010, and 2019 AAAS.

Analogously, porous carbons can also be categorized into microporous, mesoporous, and macroporous. The boundary is somewhat blurry because porous carbons often contain more than one type of pore, and the pore size crosses a broad spectrum of length scales. One example is activated carbon. Depending on the processing condition, activated carbon contains pores of varying dimensions (i.e., micropores, mesopores, and macropores) and can satisfy the needs of many applications.[56,57] In addition, because of the low cost,[57] activated carbon is probably one of the most widely used forms of porous carbons. The drawback, however, is the need for improved control over pore size and distribution, hindering the use of activated carbon in specific applications that require precise pore sizes and uniform pore distributions. Precision and uniformity (or order)[58] are pivotal to rationally engineering valuable properties and functions of porous materials.

The "hard-template" approach,[59−61] which uses hard materials such as nanoparticles to template the formation of porous carbons, mitigates the issue of pore size control. The nanoparticle templates can be prepared in a controlled manner and usually have well-defined sizes, ensuring the formation of porous carbons with controlled pore sizes. However, using "hard templates" imparts additional material and processing costs. Direct preparation of porous carbons from the precursors without a template is thus attractive. To accomplish the direct preparation of porous carbons, the precursors must meet at least two requirements: (1) the precursors must have a high carbon yield, and (2) the precursors must have the capability of forming nanoscale structures, e.g., self-assembly.

■ PRECURSORS FOR POROUS CARBON

Elemental carbon is usually converted from some kinds of precursors (Figure 2). Coal is probably the most abundant form of natural elemental carbon. The theory says coal is reduced from dead plant matter under certain heat and pressure conditions over millions of years. Analogously, synthetic carbon is reduced from some organic materials, either biomass (e.g., natural plants) or synthetic organics (e.g., polymers), but under a controlled manner in a chemical laboratory in a relatively short time frame. Synthetic materials such as polymers must have a high carbon yield to produce porous carbon reliably and effectively. The synthesis of carbon fibers has tested many candidates, including biomass,[62,63] pitch,[64] polyethylene,[64−67] polypropylene,[68] polyaniline (PANI),[69] polyacrylonitrile (PAN),[70,71] phenolic resins,[72−74] and others.[75,76] Among them, PAN produces carbon fibers with the highest mechanical performances owing to the ability to form highly oriented crystalline carbon.

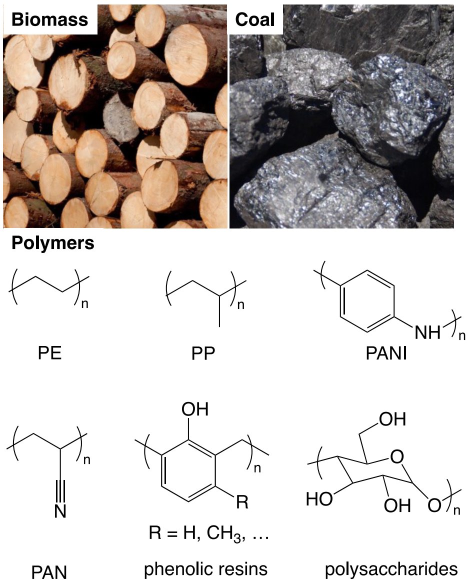


Figure 2. Representative precursors for carbon production, including biomass, coal, and polymers.

Despite the great success in preparing carbon fibers from PAN homopolymers,[77] much of the production of porous carbon fibers has overlooked the use of PAN-based block copolymer precursors. Initially, researchers utilized polymer blends to prepare porous carbon fibers.[78−80] Polymer precursors are usually mixed with inorganic nanoparticles[78] or polymer additives,[80] which template the formation of porous structures within the carbon fibers. These approaches introduce pores to the fibers, but the porous structures need to be well-controlled. Unlike the "polymer blend" approach, block copolymers offer significantly improved control over the porosity. Zhao and co-workers used Pluronics to template the synthesis of mesoporous carbon from phenolic resins.[81] Dai and co-workers used polystyrene-*block*-poly(4-vinylpyridine) to aid the synthesis of large-area highly ordered porous carbon film from resorcinol−formaldehyde resin.[82] In addition, Vogt and co-workers studied extensively the porous carbon materials using phenolic resins and poly(ethylene oxide)-*block*-poly(ethyl acrylate)-*block*-polystyrene.[73,74] These block copolymer templates are sacrificial, and a carbon precursor (e.g., phenolic resin) is embedded in one of the blocks. Direct use of block copolymers as a carbon precursor can simplify the porous carbon preparation. Matyjaszewski and co-workers synthesized PAN-based block copolymers, which produced porous carbons with nanoscale structures well-defined by the block copolymer self-assembly.[83−87] Similar strategies are practiced by many in the preparation of porous carbon particles, thin films, and monolith.[88−90]

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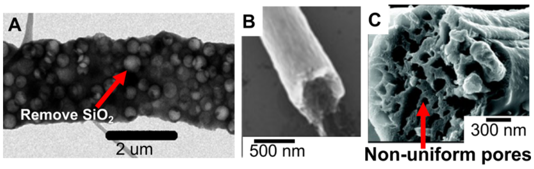

Figure 3. Representative synthesis of porous carbon fibers from (A) SiO_2@PAN,[78] (B) the cryogenic method,[79] and (C) polymer blends.[80] Reproduced in part with permission from refs 78−80.

Inspired by carbon fiber synthesis and block copolymer self-assembly, the author's group has designed the direct synthesis of block copolymer based porous carbon fibers.[55] The selection of block copolymers, however, is crucial. The polymer precursors must meet the rheological requirements for spinning yarns to ensure the reliable processing of polymer precursors into fibers to produce carbon fibers further. Otherwise, the production of polymer fibers and the subsequent carbon fibers is difficult. Typically, the polymer precursors must be made into solutions or be melted to a state with appropriate viscosities so that the polymers can be spun into fibers. For electrospinning, fibers cannot form if the viscosity is too low. Or if the viscosity is too high, beads form in the fibers, resulting in nonuniform fibers. Besides rheological properties, the sacrificial pore-generation ("pore-gen") block in the block copolymers must have a reasonably high glass transition temperature to ensure fiber intactness. If tension is required during pyrolysis to produce high-mechanical-strength carbon fibers, the fibers must remain intact upon tension and cannot be overly elastic.

As a proof of concept, Zhou et al. have reported the synthesis of porous carbon fibers from polyacrylonitrile-*block*-poly(methyl methacrylate) (PAN-*b*-PMMA),[55] where PMMA is chosen as the sacrificial pore-gen block due to its ability to decompose via multiple mechanisms, such as pyrolysis, dry etching, and wet etching (e.g., UV treatment and acetic acid rinsing).[91] PAN-*b*-PMMA can self-assemble upon thermal treatment during a relatively low-temperature heating step.[92] In classical PAN-based carbon fiber synthesis, the low-temperature heating step stabilizes the polymer. PAN undergoes oxidation and cross-linking to ensure a high carbon yield.[85] Therefore, the process is often called "stabilization" and "oxidation". In synthesizing porous carbon fibers from PAN-*b*-PMMA, the method advantageously uses the stabilization/oxidation step, allowing the block copolymer to self-assemble and form nanoscale structures. After the self-assembly, PAN-*b*-PMMA can be pyrolyzed to produce porous carbon fibers with nanoscale pores. The block copolymer self-assembly defines the porous structures governed by molecular weight and composition. The porosity control, both pore size uniformity and pore distribution, is significantly better than those from polymer blends (Figure 4). By controlling the block copolymer molecular weight and composition,[93] the porous carbon fibers have tunable uniform pore sizes in the 10−20 nm range. Fiber spinning conditions and thermal processing also play essential roles in controlling the pore size and fiber properties.[94,95]

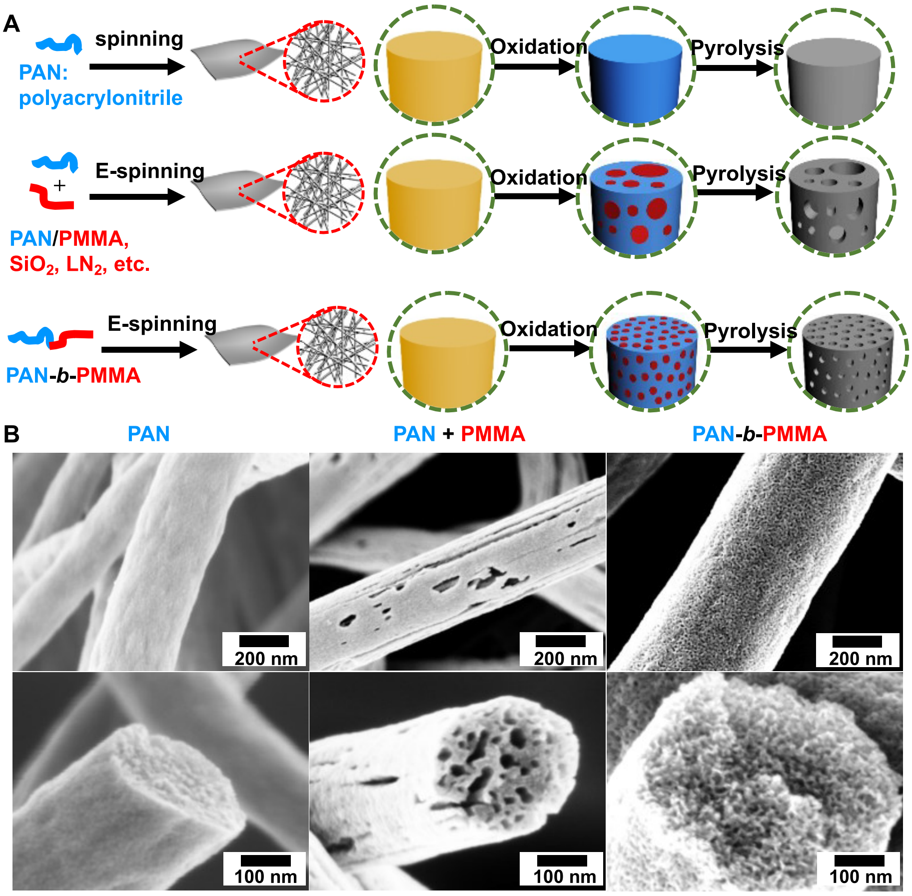

Figure 4. (A) Schematic illustration the synthesis process and (B) scanning electron micrographs of porous carbon fibers from block copolymers, in comparison with those from homopolymers and polymer blends. Reproduced in part with permission from ref 55. Copyright 2019 AAAS.

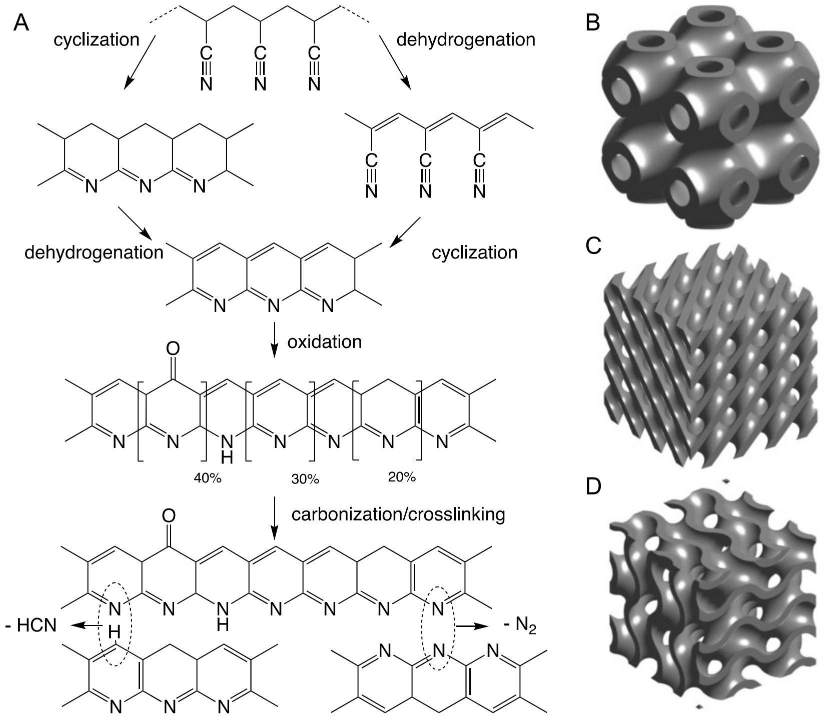

Figure 5. (A) PAN reactions upon heating and oxidation. Interchain reactions induce chain cross-linking. (B−D) Representative bicontinuous structures including (B) primitive, (C) diamond, and (D) gyroid. The interchain cross-linking reactions prevent the block copolymer from forming classical ordered mesoporous structures, resulting in kinetically trapped metastable bicontinuous structures.

■ ATTRIBUTES OF BLOCK COPOLYMER DERIVED POROUS CARBON FIBERS

PAN-Based Block Copolymers Exhibit Different Phase Behaviors from Typical Block Copolymers. The porous structure formation mechanism of PAN-based block copolymers differs from that of classical block copolymers. Depending on the Flory−Huggins interaction parameter (χ), the molecular weight or the degree of polymerization (N), and the volume fraction of the constituent blocks (ϕ), the classical block copolymers undergo microphase separation to form nanostructures such as lamellae, cylinder, sphere, and gyroid.[96] For a classical diblock copolymer, the phase diagram can be defined by the product of the Flory−Huggins interaction parameter and the degree of polymerization (χN) as a function of the volume fraction of blocks (ϕ).[4,5] The general shape of the phase diagram almost universally applies to most block copolymers that have no physical or chemical interchain cross-linking behaviors. Because the chains are only subject to non-cross-linking physical interactions (e.g., van der Waals forces), once above certain temperatures but below the order−disorder transition temperatures, the chains have sufficient mobility to form thermodynamically equilibrated structures. However, for PAN-based block copolymers such as PAN-*b*-PMMA, introducing the PAN block changes the phase behavior. The PAN block undergoes chemical cross-linking due to PAN oxidation/stabilization reactions (Figure 5). This cross-linking behavior drastically changes the phase behavior of PAN-containing block copolymers. The classical lamellar, cylindrical, spherical, and gyroid structures disappear, and the generic phase diagram becomes inapplicable to PAN-containing block copolymers. PAN cross-links regardless of the block copolymer composition, and if the PAN volume fraction is sufficiently high, it forms a continuous skeleton in the self-assembled block copolymer domains. This behavior can be advantageous to prepare interconnected porous structures, allowing for a continuous carbon framework and, thus, a continuous porous network. Such behaviors can be found in other cross-linkable block copolymers, which can be used to prepare porous polymers and porous carbons.

The phase behaviors and phase diagrams of cross-linkable block copolymers have been experimentally investigated using model systems such as poly(styrene-*block*-isoprene), which shows that the cross-linking density plays a significant role in the block copolymer morphologies.[97] Recently, theoretical investigation further reveals the morphological dependence on the polymer incompatibility (χN), the cross-linking density, and the incompatibility ($\chi_p N$) during the preparation state.[98] The cross-linking of PAN-containing block copolymers, however, is a dynamic process, where PAN is subject to oxidation during cross-linking, and thus the incompatibility may vary as cross-linking proceeds. Thus, systematic studies of cross-linkable PAN-containing block copolymers are yet to be performed both experimentally and computationally. Interesting parameters to be considered include but are not limited to cross-linking density, homo-cross-linking or hetero-cross-linking (i.e., cross-linking to the monomers of the same or different chemistries, respectively), and polymer- or agent-induced cross-linking. The agent-induced cross-linking may also have implications for plastic recycling,[99] especially for mixed wastes, the phase behavior of which is yet completely unknown. If the cross-linking agents are designed judiciously to enable dynamic cross-linking and de-cross-linking, the materials can gain recyclability. However, if the cross-linking agents induce permanent cross-linking (e.g., epoxy composites in wind turbines), the recyclability could be much hindered. In addition, if material reprocessing causes cross-linking, recyclability reduces. An example is the cross-linking of polyethylene (PE) during extrusion. Regardless, such cross-linking behavior changes the morphological behaviors of the polymers and may induce complex and interesting structures not seen in typical non-cross-linkable polymers.

Besides cross-linking, the fibrous structure can also cause block copolymer morphological alternations. It is well-known that due to one-dimensional confinement, block copolymers form exotic structures inside elongated fibrous structures.[100−103] The shear force during the fiber spinning process can potentially induce alignment, similar to the zone casting and shear flow processes where block copolymers show preferential domain orientation.[84,104,105] However, it is unclear whether these behaviors appear in PAN-containing block copolymer fibers, and further investigations are necessary.

Fibrous versus Nonfibrous Porous Carbons. In addition to the phase behaviors, block copolymer derived porous carbon fibers have significantly different properties from discrete particulate, monolithic, and thin film porous carbons (Figure 6), including hierarchical porous networks, mechanical strength, flexibility, and charge (ion and electron) transport properties.

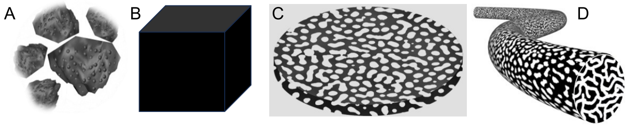

Figure 6. Different formats of porous materials: (A) particles, (B) monolith, (C) thin film, and (D) fibers.

Foremost, block copolymer-based porous carbon fibers contain hierarchical porous structures. These fibers have macropores because the fiber mesh creates a network during the fiber spinning process. Owing to the block copolymer microphase separation to form domains of 2−50 nm,[4,5] mesopores are introduced, and the polymer molecular weight and composition define the mesopore sizes. Under typical polymer processing conditions, PAN-produced crystalline carbon may contain misalignment and produce micropores (Figure 7).[106−108] Therefore, the porous carbon fibers derived from PAN-based block copolymers show multimodal pore size distributions. The pore size distribution can be advantageous for applications such as capacitive energy storage (Figures 8A,B).

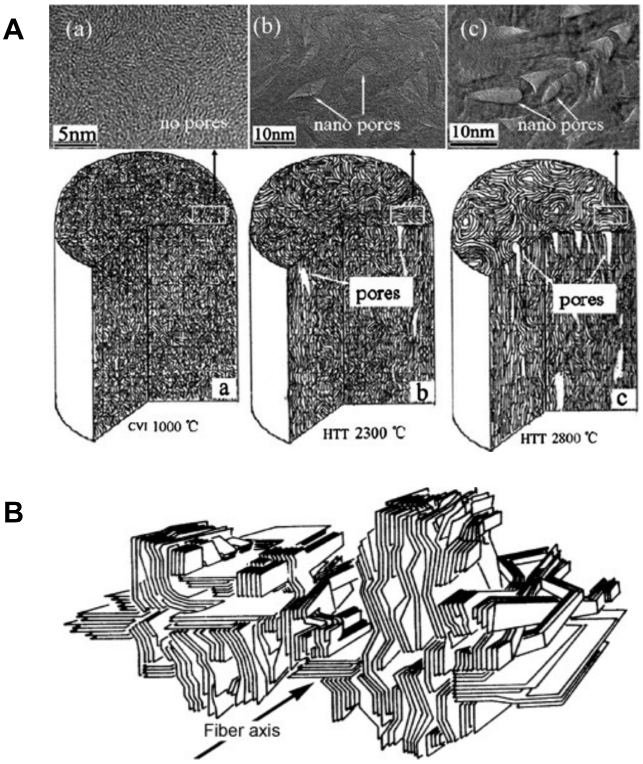

Figure 7. (A) High-resolution transmission electron micrographs and structural models of the turbostratic structure in carbon fiber after heating at (a) 1000, (b) 2300, and (c) 2800 °C.[106] Reproduced with permission from ref 106. Copyright 2011 Elsevier. (B) 3D model of a carbon structure in a high-modulus CF with interlinked crystallinity.[107] Reproduced with permission from ref 107. Copyright 1971 John Wiley and Sons.

Second, because of the PAN-associated cross-linking and block copolymer-associated microphase separation, the mesopores are in a continuous network amenable to fast mass transport. This bicontinuous network (continuous carbon skeleton and continuous pores) offers excellent transport of molecules, ions, and other species in and out of the porous structures, facilitating superb mass transport properties. The efficient charge transport is a highly attractive feature, particularly for ion-related applications. Compared with classical block copolymers, the cross-linkable PAN-based block copolymers can easily access the bicontinuous structures without deliberate control over the molecular weight and compositions. Electrochemical analysis coupled with quasi-elastic neutron scattering (QENS) measurements suggests a high ion diffusion coefficient (5.1×10^{-10} m^2/s) of room-temperature ionic liquid within the porous carbon fibers (Figures 8C,D), surpassing many other porous materials and about seven times faster than the ion diffusion in bulk.[109] The fibrous structure with a controllable fiber diameter also shortens the transverse distance for mass transport. If tuned to be electrically conductive along the axial direction, the continuous fibers ensure efficient electron transport and become an effective electrode material for electrochemical applications.

Third, a critical feature of fibers is mechanical flexibility. Fibers can be bent to any shape and geometry, allowing for knitting and weaving into complex structures.[111,112] Using carbon fibers as a flexible energy storage platform[113,114] can innovate the future of structural−functional materials.[115] One concern of the porous carbon fibers is the potentially weakened overall mechanical strength. With judicious material and structural engineering, the strength−mass ratio, however, does not necessarily reduce, analogous to the "truss-bridge" structure. Innovative designs of carbon fibers with controlled structures are attempted to couple the mechanical strength of typical carbon fibers and the structural properties of porous carbon fibers. Besides the simple blending and coextrusion process in a recent report,[116] other designs of carbon fibers with a porous skin layer can be advantageous to combine mechanical strength with structural complexity. In addition, the spinning of PAN fibers for producing carbon fibers requires careful control over the draw ratio during the spinning process. The introduction of additional polymer components in PAN-containing block copolymers likely changes the required draw ratio to produce high-mechanical-strength carbon fibers. Thus, additional investigation into the processing conditions of block copolymer precursors is needed.

Another great opportunity lies in the functionality of porous carbon fibers. Porous carbon fibers derived from PAN-based block copolymers have specific surface chemistries and properties dictated by the precursors. PAN is intrinsically doped with

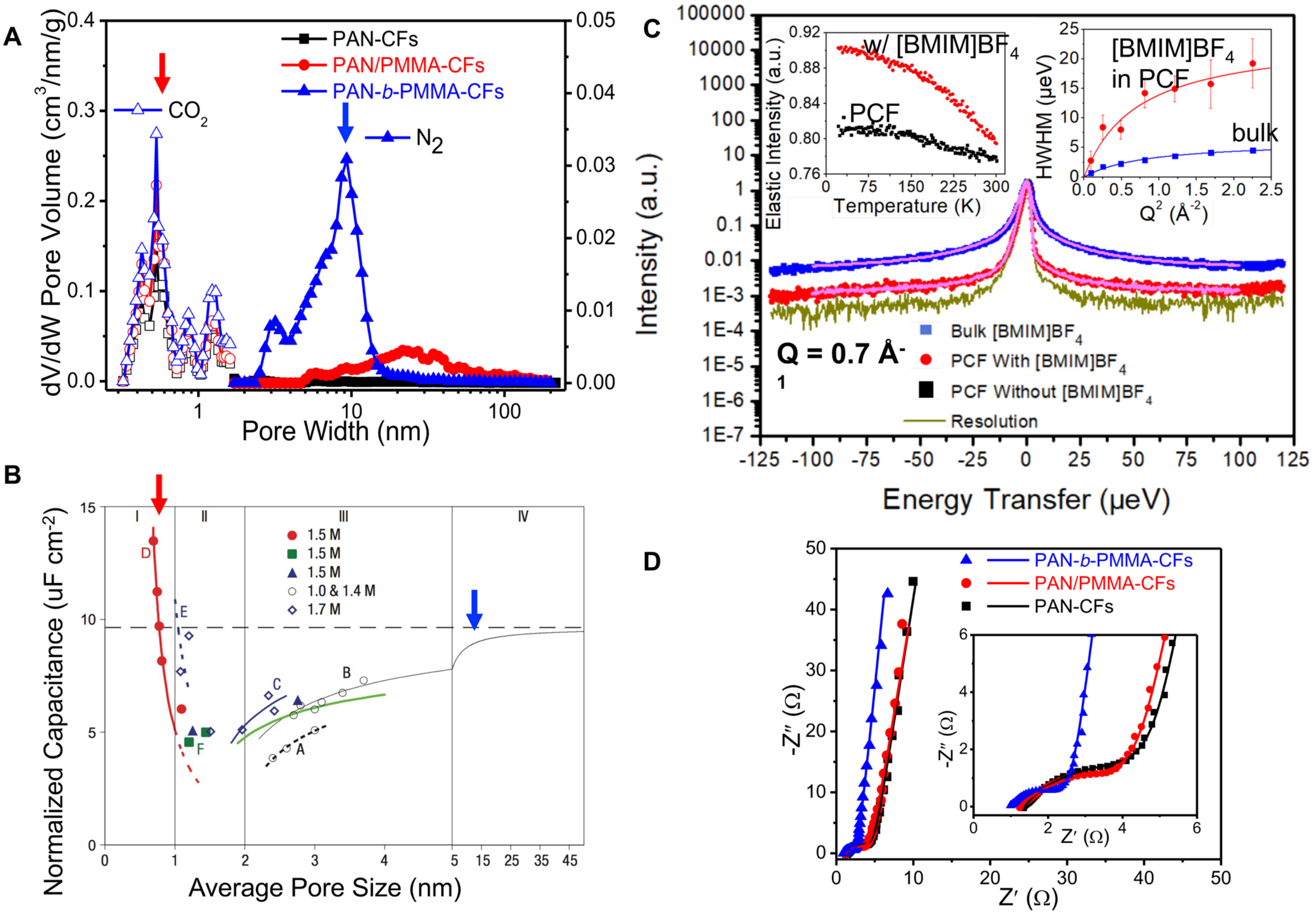

Figure 8. (A) Bimodal pore size distributions of block copolymer-based porous carbon fibers (PAN-*b*-PMMA-CFs) compared with those from PAN and PAN/PMMA blends (PAN-CFs and PAN/PMMA-CFs, respectively).[55] (B) Specific areal capacitance of porous materials as a function of pore size.[110] Bimodal pore size distributions are advantageous for energy storage to achieve high specific areal capacitances. Reproduced in part with permission from ref 110. Copyright 2008 Springer Nature. (C) QENS measurements to determine the ion diffusion coefficient in porous carbon fibers. (insets) 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) in porous carbon fibers shows no cooling/heating-induced phase changes and a significantly higher diffusion coefficient in porous carbon fibers than in bulk.[109] Reproduced in part with permission from ref 109. (D) Electrochemical impedance spectroscopy (EIS) measurements to determine the ion diffusion resistance in carbon fibers produced from PAN, PAN/PMMA blends, and PAN-*b*-PMMA block copolymers.[55] Reproduced in part with permission from ref 55. Copyright 2019 AAAS.

nitrogen, and the oxidation/stabilization process brings oxygen (Figures 5 and 9). The nitrogen and oxygen content can be modulated via the fiber synthesis process, resulting in porous carbon fibers with tunable levels of nitrogen and oxygen heteroatoms.[95] The heteroatoms affect the surface energy, hydrophobicity, ion/surface interactions, and electrochemical properties. The processing conditions, including solvents, temperature, pressure, and even humidity,[94] can affect porous carbon fibers' structure, properties, and functionality.

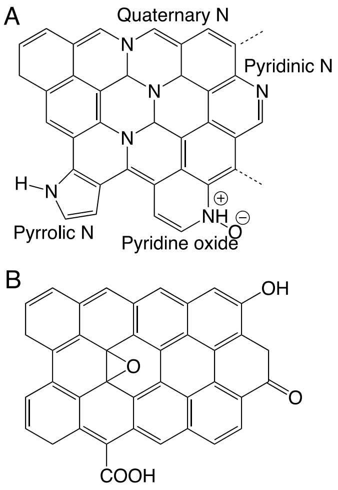

Figure 9. Possible (A) nitrogen and (B) oxygen species in porous carbons.

■ CASE STUDIES OF APPLICATIONS

Structural Energy Storage. Conductive porous materials are readily useful for capacitive energy storage.[39,110,117] The high surface areas of conductive porous materials interact with ions and induce the formation of an electrosorption layer to store energy electrochemically. Porous carbons have been widely used in capacitive energy storage, and the use of fibrous carbons significantly expands the form factor of capacitive energy storage electrodes.[113] The continuous fibers offer features that discrete carbon particles (e.g., activated carbon) cannot. First, because the fibers are structurally continuous and electrically conductive, polymer binders such as poly(vinylidene fluoride) (PVDF), polytetrafluoroethylene (PTFE), and Nafion[118] are no longer necessary (Figure 10). Polymer binders increase unnecessary

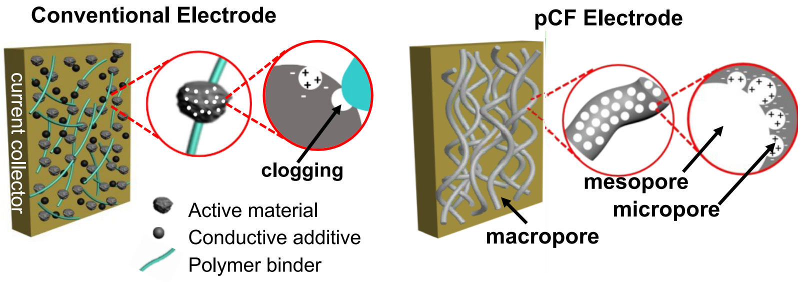

Figure 10. Comparison of conventional electrode and porous carbon fiber electrode designs. Conventional electrodes require insulating binders, thus giving poor electron transport and sluggish ion diffusion. Inactive conductive additives are introduced to mitigate the conductivity issue but add parasitic mass to the electrode. Porous carbon fiber electrodes have continuous diffusion channels and are flexible, binder-free, and conductive additive-free.

electrode weight, and worse, they induce sluggish ion and electron transport due to their insulative behavior. Bypassing the polymer binders also removes the need for additional conductive additives often used in capacitive electrode slurries. Owing to these reasons, fibrous carbon has attracted much interest in use as electrodes in electrochemical energy storage. Zhou et al.[55] have tested the direct use of PAN-*b*-PMMA derived porous carbon fibers, and the high specific surface area (>500 m^2 g^{-1}) provides a capacitive energy density of 66 μF cm^{-2}. Interestingly, after compiling many reported energy densities as a function of surface area for various fibrous materials, the authors found that high surface area often leads to a high energy capacity but not always a high energy density.[55] The porous structures and surface properties likely play an essential role in the energy density. Simply seeking a high surface area material does not warrant a desirable outcome of high energy density.

The total surface area and the specific areal energy density determine the total amount of electrochemical double-layer capacitive energy storage. A given ion has a given size; thus, a theoretical limit of specific areal energy density exists. To overcome this limit, an alternative method is to introduce electrochemical redox reactions and thus boost the energy density of capacitors, called supercapacitors or pseudocapacitors. The name pseudocapacitor stems from the characteristics that it resembles both capacitors and batteries, whereas the energy storage mechanism of batteries is predominantly electrochemical redox reactions. Porous carbon fibers derived from block copolymers have uniform mesopores. The mesopore uniformity provides a platform to load with a uniform layer of redox-active materials for pseudocapacitive energy storage. Redox-active materials, such as inorganic metal oxides, are often insulative by nature. Thick layers of redox-active materials render the entire electrode insulating, and electrons cannot effectively be conducted (Figure 11). Therefore, a uniform thinner layer of redox-active materials is beneficiary and allows for effective and efficient ion and electron transport.[119] The high surface area of mesoporous carbon fibers also provides high mass loading of active materials to reach practicality for potential use in the industry.

Porous carbon loaded with active materials, if at a sufficiently high loading, will become relevant for use in batteries. A simple demonstration of porous carbon fibers with an active material of MnO_2 allows for the testing of aqueous batteries for long-duration energy storage.[120] The concept, in principle, should be applicable to other batteries, including but not limited to lithium-, sodium-, and sulfur-based batteries.

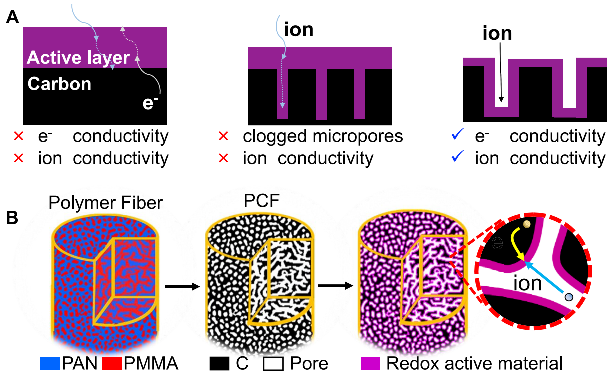

Figure 11. (A) Schematic illustration of loading a nanometer thick layer of active materials on top of (left to right) nonporous carbon, microporous carbon, and mesoporous carbon. To ensure the same level of loading, nonporous and microporous carbons result in a relatively thick layer of active material, which is often electrically insulating. (B) Mesoporous carbon fibers from block copolymer-derived porous carbon fibers enable the loading of a uniformly thin layer of active material to ensure high electrically conductivity and ion conductivity. Reproduced in part with permission from ref 119. Copyright 2019 Springer Nature.

Water Treatment and Contaminant Removal. Porous carbons are commonly used for water treatment. Most built-in refrigerator filters use activated carbon as the active material for removing contaminants. The porous structure and high surface area in activated carbon are responsible for trapping unwanted particles and adsorbing molecules and ions. The major drawback of activated carbon filters is that they cannot be easily regenerated and must be replaced once reaching the sorption capacity. Similarly, porous carbon fibers can also be used for water filtration based on size trapping and surface sorption mechanisms. The conductive nature of fibrous carbon is an additional attractive feature that allows for the electrosorption of ions from contaminated water, also known as capacitive deionization (CDI). The CDI process utilizes an externally applied voltage to control ion sorption on the porous carbon surfaces. Through active voltage control, deactivated porous carbon fibers can be regenerated for continuous use, bypassing the need for replacing filter cartridges. The most impressive feature of the block copolymer-derived porous carbon fibers is that they offer substantially fast ion transport and thus allow for swift ion removal from water,[121] a highly attractive feature for instant water filtration (Figure 12). The fast ion transport is attributed to the hierarchical porous structures, the interconnected porous networks, and the exceptional ion diffusion

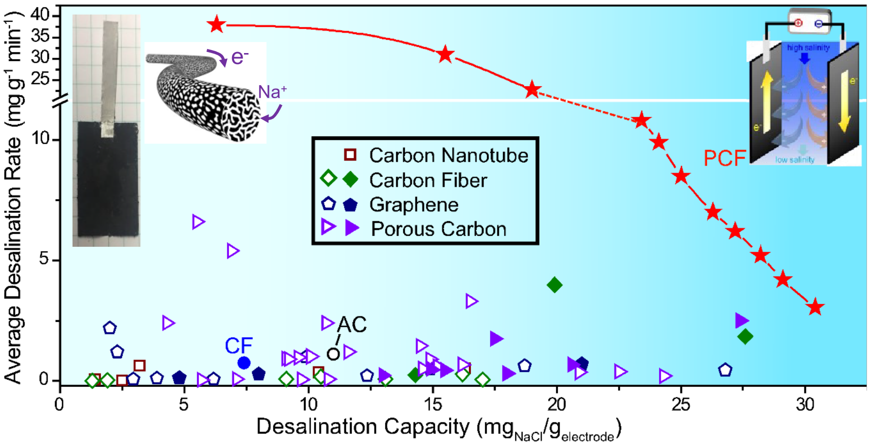

Figure 12. Block copolymer derived porous carbon fibers show exceptionally fast rate and high capacity of ion intake for desalination.[121] Reproduced with permission from ref 121. Copyright 2020 AAAS.

properties within the porous networks. It is found that the ion sorption on porous carbon fibers follows pseudo-second-order kinetics, and the analysis using the Weber−Morris model confirms that ion diffusion is not a limiting step in the ion sorption and removal process.[122] The same concept applies to treating other contaminants such as dyes,[122] volatile organic chemicals (VOCs), heavy metals, rare earth elements, and toxins.[123−125] The unique light-absorption capability of porous carbon fibers can potentially enable solar energy for water treatment and contaminant removal.[126] The evaporation of water molecules within the interconnected mesopores shows reduced evaporation enthalpy[126] and likely changes the evaporation behaviors of other molecules.

■ OUTLOOK

Some of the outlook perspectives have been pointed out in the above sections. The author will summarize a few key outlooks and provide representative research opportunities and challenges.

On the one hand, carbon fibers are well-known and well-developed materials that have relatively mature synthesis methods, processing conditions, and applications. Carbon fibers are mostly for high-end applications due to their high cost. Reducing the production cost or increasing the usage value of carbon fibers is critical for broad adoption in civilian uses. Some industries (e.g., Ford Motor Company) have heavily invested in introducing carbon fibers to the automotive industry, but the endeavors are paused due to many technical and economic considerations. The revitalization of carbon fibers, especially the development of porous carbon fibers with advanced structures, properties, and functionalization, increases the value and may incentivize the industry for further deployment of porous carbon fibers. For PAN-containing block copolymers to produce high-mechanical-strength carbon fibers, the molecular weight must be increased to a level comparable to industrially used PAN precursors. Alternatively, PAN-containing block copolymers can be a surface coating material to enrich the morphological properties of existing PAN-based carbon fibers. On the other hand, porous carbons are also well-developed, and a large body of knowledge has accumulated over the years.[26,38−43] Integrating fundamental knowledge and technical developments of carbon fibers and porous carbons is a great opportunity and will likely spark new inspiration and technological advancement.

Introducing block copolymer as a precursor for porous carbon fiber synthesis innovates both fields of block copolymers and carbon fibers. In research laboratories, block copolymers are often considered expensive specialty polymers for niche applications such as block copolymer lithography[6−9] and drug delivery.[14,15] In the industry, some of the most widely used block copolymers are thermoplastic elastomers, sometimes termed thermoplastic rubbers.[21] Common examples include styrene−butadiene rubber (SBR) and styrene−isoprene−styrene (SIS). The bottleneck for the general use of block copolymer derived porous carbon fibers is the current production scale of the precursor polymers. If PAN-*b*-PMMA or PAN-based block copolymers (e.g., polyacrylonitrile-*block*-polystyrene or PAN-*b*-PS[90]) can reach large-scale production, the synthesis of block copolymer-based porous carbon fibers will become scalable for commercialization. As we write this Perspective, some research laboratories are working with industrial partners to scale up the synthesis of PAN-based block copolymers. We welcome additional developers in this realm to capitalize on the materials for commercial success. Another approach is to utilize block copolymer as a functional material for existing carbon fibers via various structural designs, such as core−sheath, half−half compounding, interweaving, etc.

PAN-based block copolymers have the unique characteristics of PAN cross-linking upon oxidative annealing. Oxidative annealing is required to stabilize PAN and ensure a high carbon yield. Consequently, the PAN cross-linking complicates the microphase separation behavior of PAN-based block copolymers. Once PAN cross-links, part of the block copolymer chains are locked at kinetically trapped states. The block copolymers can no longer reach thermodynamic equilibrium, as classical non-cross-linkable block copolymers can. The cross-linking mechanism, rate, density, and type of cross-linking agents all play essential roles. Systematic determination of the kinetics and dynamics of such cross-linkable block copolymers presents significant challenges and opportunities. Cross-linking also changes the thermal, mechanical, and rheological properties of PAN-based block copolymers, which should differ from classical block copolymers.

Porous carbon fibers derived from PAN-based block copolymers have tunable levels of nitrogen and oxygen contents. Other heteroatoms can also be introduced before, during, and after the synthesis processes. The rich literature on doping porous carbons with heteroatoms can serve as a basis for controlling the surface properties of porous carbon fibers. PAN-based block copolymers provide an extra tunability during the synthesis process of porous carbon fibers. The intrinsically high level of nitrogen content in the polymer precursor (N/C ratio = 1/3) can be rarely found in other precursors. The resulting nitrogen species (e.g., pyrrolic N, pyridinic N, quaternary N, and pyridine oxide[85]) and oxygen species (e.g., hydroxyl, carboxylic, epoxy, aldehyde, etc.) (Figure 9) can further modulate the functionalization of porous carbon fibers. Porous carbon fibers functionalized with surface ligands, polymer molecules, and other surface groups enable sophisticated interaction with the surroundings.

The uniqueness of porous carbon fibers compared to other porous materials, such as porous silica, is electrical conductivity. In addition, the porous network allows for fast ion transport. Therefore, porous carbon fibers are an excellent material platform for electrochemical catalysis, energy storage, and others. Ion transport within the porous network differs from that in the bulk due to the interactions of ions with the surface functional groups. The fibrous electrode configuration provides additional attributes, such as flexibility, allowing interaction with biomolecules[127] and soft tissues. The softness, flexibility, and electrical conductivity enable porous carbon fibers to serve as a material for the brain−robot interface, connecting machines with human bodies. In addition, the ion conductivity in the porous network allows porous carbon fibers to convert ionic signals to electrical current, a feature not possessed by other electrode materials such as silicon nanowires used in existing biointerface systems.

The most common use of carbon fibers is polymer composites, in which carbon fibers are integrated with polymers such as epoxy and engineering plastics. Developing porous carbon fibers can potentially add features to the carbon fiber composites. The carbon fibers' porous network introduces surface interactions with the polymer matrices via mechanical, physical, or chemical interactions.[128] Integrating porous polymer precursor and carbon fibers with other polymers and ceramics[129] offers an opportunity to construct advanced materials with controllable thermal, mechanical, and other properties. However, the structural control of porous carbon fibers requires further design and engineering. Simply blending block copolymers with homopolymers requires additional tuning of the rheological properties and consideration of the fiber-spinning-induced complicated phase separation behaviors.[116]

Carbon fibers are intrinsically structural materials with exceptional flexibility, lightweight, and high mechanical strength. Porous carbon fibers offer high surface areas and diverse functionalities, allowing for loading additional active materials to provide multiple functionalities such as energy storage, gas sorption, and sensing. Functionalization of porous carbon fibers with multivalent ionic species can enable the use in critical element extraction (e.g., rare earth metals). Integrating porous carbon fibers for mechanical reinforcement and energy storage opens the avenue to structural energy storage, where the materials serve dual functions of mechanical support and energy supply. This feature is desirable in the electrification of the automotive industry. The lightweight carbon fibers add another feature of reduced weight, which can be highly appealing in the aviation industry.

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Notes

The author declares no competing financial interest.

Biography

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ACKNOWLEDGMENTS

G.L. acknowledges support from the Department of Chemistry at Virginia Tech. This material is based on the work supported by NSF Award DMR-1752611 through the CAREER award.

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