

EXCEPTIONALLY FAST ION DIFFUSION IN BLOCK COPOLYMER-BASED POROUS CARBON FIBERS

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ABSTRACT: Confined ionic liquids in hydrophilic porous media have disrupted lattices and can be divided into two layers. An immobile ion layer adheres to the pore surfaces, and an inner layer exhibits potentially faster mobility than the bulk. In this work, we report a new porous medium of block copolymer-based porous carbon fibers (PCF) synthesized from polyacrylonitrile-*block*-polymethyl methacrylate (PAN-*b*-PMMA). The PCF contain a network of unimodal mesopores of 13.6 nm in diameter. Elastic neutron scattering shows no freezing point for 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) confined in PCF down to 20 K. Quasi-elastic neutron scattering (QENS) is used to measure the diffusion of [BMIM]BF₄ confined in PCF, which surprisingly is seven-fold faster than that in the bulk. The unprecedentedly high ion diffusion remarks that PCF hold exceptional potential for use in electrochemical catalysis, energy conversion, and storage.

Fast diffusion is crucial for ions, molecules, and other chemical species to transport in materials such as polymer,¹ metal organic framework,² and covalent organic framework³ and to participate in fast-kinetics electrochemical processes (e.g., electrochemical reactions). Room temperature ionic liquids (RTIL) are attractive electrolytes because of the high stability.⁴⁻⁵ Their strongly attractive intermolecular forces, however, reduce their diffusion and limit their use in diffusion-controlled processes.

Frustrated by mismatched cation and anion sizes, RTIL form a weak lattice structure, allowing the ions to exist as liquids and diffuse at room temperature.⁶ Nevertheless, compared with aqueous systems, the diffusion of RTIL is orders-of-magnitude slower. If the lattice structure is disrupted, the ion diffusion properties improve.⁷ Therefore, nanopore-induced confinement is an effective method to increase ion mobility because it further weakens the lattice structure.⁸ To this end, both pore size and interfacial interactions play a significant role. Too strong interactions between the ions and micropore surfaces lead to immobility of the former, forming a fixed surface ion layer that fills the whole pore. Given slightly larger pores, which accommodate more ion layers, the ions towards the center move independently of the fixed surface ion layer, decoupling them from the typical ionic liquid lattice. In general, pores of larger sizes can fit more ion layers in the centers, extending the effect of the disrupted ion lattice to improve the ion mobility. But, if the pore size is too large, the confinement effect diminishes, and the ion diffusion behavior approximates to that in

the bulk. Therefore, the pore size must be small enough to disrupt the lattice structure, but large enough to hold as many ions as possible to get the most benefit from confinement of the ions. Moreover, the pores should be as uniform and interconnected as possible to facilitate ion transport.

Block copolymer-based porous carbon fibers (PCF) are emerging materials with unique hierarchical structures that allow easy accessibility to their large internal surface areas through their interconnected pores.⁹⁻¹¹ Similar to nonporous carbon fibers, the interwoven fibers form a mat with abundant inter-fiber spaces as macropores, as well as micropores intrinsically defined by the inter-layer distances of graphitic carbon. Unique to PCF, however, is a unimodal interconnected mesoporous network in each individual fiber, which acts as a network of channels to deliver ions to the internal micropores. While ion mobility in micropores is limited due to the lack of space for ions to occupy, the mesoporous network has significant space away from the pore walls that allows for uninhibited ion diffusion.¹² The extra pore space is especially important for electrochemical applications, where ions in the fixed surface layer are mostly immobile and the space away from the pore walls prevents clogging of the pores with the immobile ion layer. Moreover, defined by the block copolymer molecular weight, the tunable mesopores offer sufficient space to hold non-surface layer ions, but are tight enough to disrupt the ionic lattice structure. Therefore, we hypothesize that the block copolymer-defined mesoporous structures will provide an exceptional porous network for enhanced ion diffusion.

To test this hypothesis, we synthesized block copolymer-based porous carbon fibers from polyacrylonitrile-*block*-polymethyl methacrylate (PAN-*b*-PMMA) and investigated the diffusion within. To quantify the ultimate capability of porous carbon fibers for ion diffusion, we chose a RTIL system of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄). Self-diffusion of the [BMIM] cation both in the bulk and confined in porous carbon fibers was measured using quasi-elastic neutron scattering (QENS). Diffusion coefficients were compared to the literature for [BMIM] confined in porous media, and the block copolymer-based porous carbon fibers showed seven-fold faster ion diffusion than that in the bulk.

Porous carbon fibers were synthesized according to an established method in our previous report (Figure 1a).⁹ Briefly, PMMA was synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization using cumyl dithiobenzoate (CDB) as the chain-transfer agent. The purified PMMA (65.7 kDa, Đ = 1.08) was characterized by size exclusion chromatography (SEC) with both dynamic light scattering and refractive index detectors (Figure S1). Then, block copolymer was synthesized by chain extension of CDB-terminated PMMA using acrylonitrile. The resulting PAN-*b*-PMMA (136.7 kDa, Đ = 1.12) was purified and characterized by SEC (Figure S1) and ¹H NMR (Figure S2). Thermogravimetric analysis (TGA) in nitrogen showed a char yield of 32% at 600 °C (Figure S3). PAN-*b*-PMMA was electrospun into polymer fibers, which were oxidized at 280 °C for 8 h and then pyrolyzed at 800 °C for 1 h into porous carbon fibers. X-ray photoelectron spectroscopy (XPS) revealed the composition of the carbon fibers, which included 10.2% N and 4.1% O (Figure S4). Scanning electron microscopy (SEM) showed the block copolymer-based porous carbon fiber mat possessed abundant macropores in between the fibers (Figure 1b). Within each fiber were interconnected mesopores, as evidenced by the cross-sectional SEM (Figure 1c) and TEM (Figure 1d).

The porosity and general interconnectivity of the pores (Figure 1d) suggested a large easily accessible internal pore volume in PCF.

It is well known that ionic liquids behave differently in confined environments and QENS is incapable of differentiating between the confined and unconfined ion liquids. In other words, when a porous material is fully immersed in an ionic

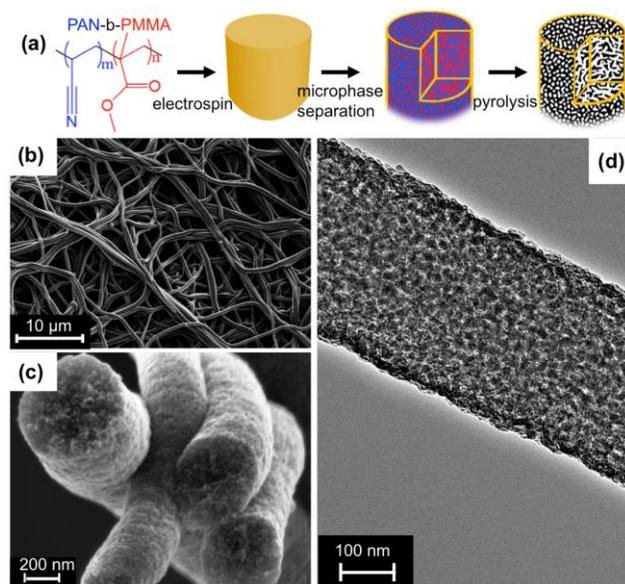


Figure 1. (a) Schematic illustration of the synthesis of PCF from PAN-*b*-PMMA. (b) SEM image of a porous carbon fiber mat. (c) Cross-sectional SEM shows the uniform mesopores within each fiber. (d) TEM images illustrate internal porosity and interconnectivity of the porous network inside the fibers.

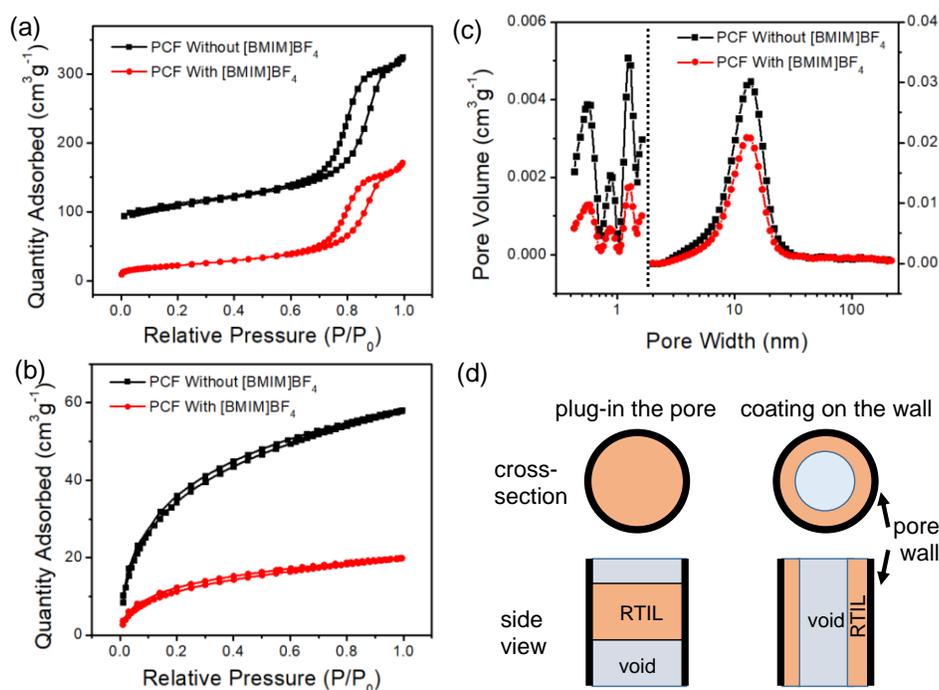


Figure 2. (a) N₂ and (b) CO₂ physisorption isotherms before and after loading [BMIM]BF₄ into the porous carbon fibers. The reduced adsorbed quantities confirm the loading of the ionic liquid in the fibers. (c) Pore size distributions show that the ionic liquid occupied the pore volumes but did not change the pore sizes. (d) Physisorption suggests that [BMIM]BF₄ filled the pores as plugs (left) rather than coating on the walls (right).

liquid, diffusion-controlled processes are measured as a combination of diffusion outside the material (non-confined) and inside the internal pores (confined). Therefore, a high volume of confined ionic liquid is required to maximize the signal of confined ion diffusion. Porous carbon fibers have high internal volumes within their mesoporous networks, and thus are ideal for QENS measurement of ion diffusion under confinement. However, it is crucial to leave macropores void and fill only the mesopores and micropores with ions, properly confining the ionic liquid. Because macropores are generally too large to significantly disrupt the lattice structure of an ionic liquid, any ions in the macropores behave as if they are in the bulk. To prepare for QENS measurement, we filled only the meso- and micro-pores with the ionic liquid by suspending PCF in a solution of [BMIM]BF₄ in acetonitrile (0.015 mg/mL). The suspension was stirred for 3 h at room temperature. Afterwards, acetonitrile was removed by heating PCF in an oven at 80 °C under vacuum for 12 h.

Physisorption tests of both N₂ at 77.4 K and CO₂ at 273.2 K (**Figure 2a and 2b**) were performed before and after loading with [BMIM]BF₄ to confirm the occupation of the meso- and micropores. After loading [BMIM]BF₄, the N₂-sorbed surface area decreased from 404 to 76 m²/g, as determined using the Brunauer-Emmett-Teller (BET) method. Based on non-local density functional theory (DFT), pore size distributions exhibited predominant micropore sizes of 0.55, 0.86, and 1.23 nm, as well as a mesopore peak at ~13.6 nm (**Figure 2c**). Notably, all meso- and micropore sizes remained unchanged but the total volumes decreased by ~48.5%. Physisorption relies on the accessibility of gas molecules to the pore surfaces. The reduced surface area and pore volume, in combination with the unchanged pore size, suggest that the ionic liquid blocked some

sorption sites. The ionic liquid likely formed plugs in the pore rather than coatings on the wall (**Figure 2d**), which would lead to a reduction in the pore sizes. If the adsorbate (i.e., N₂ and CO₂) is soluble in the ionic liquid, the physisorption will give a falsely large surface area because the adsorbate is dissolved in the liquid rather than adsorbed on the pore surfaces. Considering the low solubility of N₂ in [BMIM]BF₄, similar to that in [BMIM]PF₆,¹³ the gas dissolution effect is unlikely to affect the N₂ results. Physisorption of CO₂ showed the same trend, and thus the effect of CO₂ solubility was also negligible. Regardless, the physisorption serves as a qualitative means for confirming the presence of the ionic liquid in the fibers.

Relying on the high incoherent scattering cross-section of hydrogen atoms,¹⁴ quasi-elastic neutron scattering (QENS) is the technique of choice to explore the dynamics in systems that contain hydrogen atoms.¹⁵⁻¹⁶ Since the cation of [BMIM]BF₄ is rich in hydrogen atoms, the dynamics of the bulk and PCF-confined BMIM ions could be measured using QENS. First, temperature-dependent energy-resolved elastic scans were conducted using high flux backscattering spectrometer¹⁷ on the confined [BMIM]BF₄ (**Figure 3a**). The elastic intensity of the confined ionic liquid was significantly higher at 10 K compared to the bare PCF matrix, suggesting the presence of the ionic liquid in the pores (in agreement with the physisorption data). [BMIM]BF₄ melts at 265 K, and at this temperature the elastic intensity would show a step corresponding to a thermal phase transition.¹⁸⁻¹⁹ The absence of a step in all elastic scattering spectra collected for [BMIM]BF₄ in the fibers, however, confirmed the confinement of [BMIM]BF₄ within the pores and the disruption of the ionic liquid's lattice structure.²⁰ **Figure 3 (main panel)** shows representative quasi-elastic spectra meas-

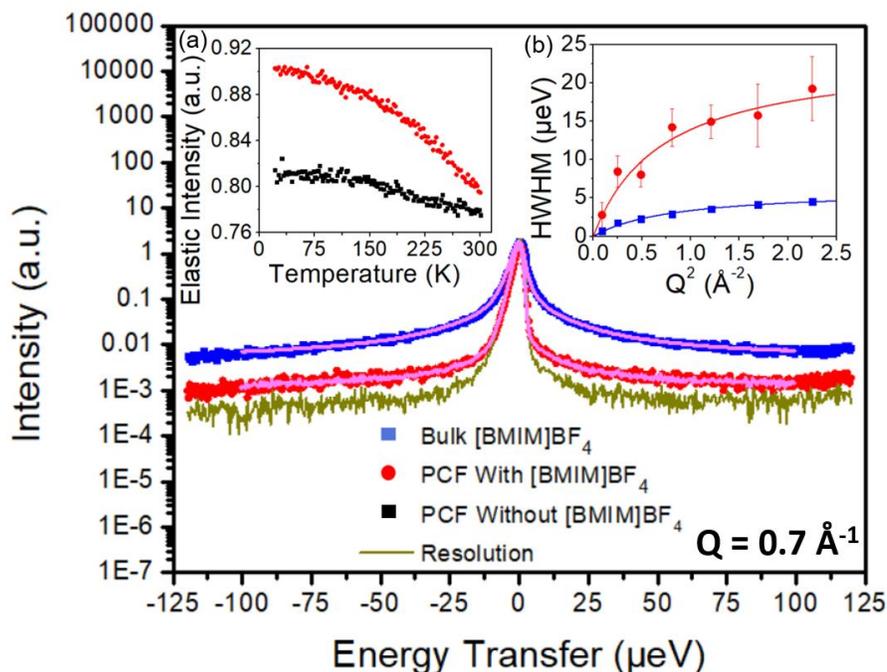


Figure 3. Representative QENS spectra of [BMIM]BF₄ in the bulk and confined within the porous carbon fibers at $Q = 0.7 \text{ \AA}^{-1}$ with normalized maximum intensity. (inset a) Elastic scattering spectra of porous carbon fibers with and without [BMIM]BF₄. The enhanced elastic scattering intensity confirms that [BMIM]BF₄ was loaded into the pores. The lack of a thermal transition corresponding to the melting of [BMIM]BF₄ suggests the confinement of the ionic liquid in the pores. (inset b) The extraction of HWHM at each Q allows for determination of the Q dependence of HWHM. The Q -dependence of HWHM allows for calculation of the diffusion coefficient of the [BMIM] cation.

ured using backscattering silicon spectrometer²¹ and the corresponding model fits (See SI for details) of the bulk and confined [BMIM]BF₄, together with the instrument resolution. Even though the spectrum collected from the bulk [BMIM]BF₄ appeared to exhibit more pronounced QENS broadening than that for the confined [BMIM]BF₄, the data analysis (using Eq. 1, SI) demonstrates that the mobile ions in the confined ionic liquid (those that contributed to the QENS signal rather than the elastic line) gave rise to a relatively broader signal. In other words, while the overall QENS intensity for the PCF with [BMIM]BF₄ was lower due to immobilized ions that contributed only to the elastic scattering, those that remained mobile exhibited higher diffusivity than the ions in the bulk [BMIM]BF₄ despite its overall higher QENS intensity. The half-width at half-maximum (HWHM) of the slow components of the bulk and confined [BMIM]BF₄ (**Figure 3b**) showed a non-linear dependence on Q², which corresponded to a long-range translational mobility of the ions.²²⁻²³ Therefore, the translational diffusion coefficient (*D*) of the cation in the bulk liquid was determined using a jump diffusion model (diffusion with a relaxation time), giving a value of $(0.73 \pm 0.06) \times 10^{-10} \text{ m}^2\text{s}^{-1}$, in agreement with similar systems in a previous report.²² The diffusion dynamics of the confined cation were found to be non-homogeneous, i.e., non-exponential, requiring the introduction of an exponent $\alpha(Q) = 0.5$ (a typical value used for other small molecule glass formers)²⁴⁻²⁵ to fit the data using a Cole-Cole distribution function (see SI for detail). This functional form has been employed successfully in many confined systems.²⁶⁻²⁷ For the confined [BMIM] cation, the diffusion coefficient value was determined to be $(5.1 \pm 1.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, about ~ 7 times greater than that of the unconfined bulk.

Although this enhanced diffusion behavior of the confined fluid has been witnessed in other materials,¹⁴ the amount of enhancement is unprecedented. Compared to all available materials to date, the porous carbon fibers show the largest increase in diffusion coefficient for the [BMIM] cation (**Table 1**), likely owing to a few features of PCF.²⁸ First, our porous carbon fibers are hydrophilic due to the high content of surface N and O heteroatoms, similar to our previous reports.²⁹⁻³⁰ Strong interactions between the carbon surface and the adsorbed surface-layer

Table 1. Diffusion coefficient of [BMIM] cations in porous carbon fibers in comparison with those in other materials.

	D_{BMIM} ($10^{-10} \text{ m}^2\text{s}^{-1}$)	Pore diameter (nm)	Method
Carbide-derived carbon ¹⁵	0.52	0.8 / 3.1	QENS
Mesoporous carbon ¹⁷	2.55	8.8	QENS
Vertically-aligned CNT ²³	0.31	4	PFG-NMR
Silicon carbide-carbide derived carbon ²⁶	2.32	0.8	QENS
CNT(20,20) ²⁷	2.86	1.3	MD
CNT(40,40) ²⁷	0.43	2.7	MD
CNT(34,0) ²⁷	0.41	1.3	MD
Graphene Sheets ²⁷	0.01	2.7	MD
Porous carbon fibers*	5.1	13.6	QENS

All diffusion coefficients are based on long-range diffusion at 298/300 K. CNT, carbon nanotubes; PFG-NMR, pulse field gradient nuclear magnetic resonance; and MD, molecular dynamics modelling.

ions disrupt the ion lattice structure in the diffuse layer, while reducing friction between the adsorbed surface-layer ions and the diffuse-layer ions. Second, the mesopore size allowed for a

significant amount of confined ionic liquid to exist in the diffuse-layer rather than the adsorbed-layer. The lack of a transition in the elastic scan (**Figure 3a**) indicated that the disruption in the lattice structure extends across the whole pore, frustrating the packing so that the diffuse-layer ions do not freeze between 10 K and 300 K. The disruption of the lattice, in combination with the reduced friction between the adsorbed ions and the confined diffuse-layer ions, leads to the exceptionally high diffusion coefficient. Our results match the observations of Dyatkin *et al.*,³¹ where the ions inside 0.8-nm micropores were immobile and the high diffusion coefficient was attributed to the inner ion layers inside mesopores. Ghoufi *et al.* also found a large increase in diffusion of the [BMIM] cation in 1.3 nm diameter pores of (20,20) carbon nanotubes (CNTs), owing to a small friction.³² With mesopore sizes of 13.6 nm in PCF herein, the favorable larger pore size and surface interactions resulting from heteroatoms further improved the ion diffusion characteristics.

In summary, advanced QENS measurements show that the block copolymer based porous carbon fibers have exceptional ion diffusion properties. The confined ions exhibit a seven-fold increase in the diffusion coefficient. Attachment of the cations to the pore wall (which are not mobile within the sensitivity of the instrument) contributes to the elastic incoherent scattering fraction, which, in turn, can be related to the electrochemical capacitance of porous materials. The fast diffusivity of the cations away from the wall could contribute to high rate capability of the porous carbon fibers for use in supercapacitors, as well as fast charging/discharging in batteries. The exceptional ion diffusion also holds great promise for fast mass transport in electrochemical catalysis. Lastly, tunability in PCF properties based on the initial block copolymer offers opportunities to control hydrophilicity, pore size, and other characteristics to further adjust the confinement effect. Therefore, the block copolymer-based porous carbon fibers represent an outstanding platform material for electrochemical applications.

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