

Superionic Conduction over a Wide Temperature Range in a Metal-Organic Framework Impregnated with Ionic Liquids

Yukihiro Yoshida,^{*,[a]} Kazuyuki Fujie,^[b] Dae-Woon Lim,^[a] Ryuichi Ikeda,^[a] and Hiroshi Kitagawa^{*,[a]}

Abstract: Most molecules in confined space show markedly different behaviors from those in bulk state. However, large pore is composed of two kinds of region; interface region in which liquid interacts with the pore surface and core region in which liquid behaves as bulk. Here we report the realization of highly mobile ionic liquid (IL) in a mesoporous metal-organic framework (MOF). The hybrid shows a high room-temperature conductivity ($4.4 \times 10^{-3} \text{ S cm}^{-1}$) and low activation energy (0.20 eV); both not only are among the best values reported for IL-incorporated MOFs but also are classified as a superionic conductor. The conductivity reaches over $10^{-2} \text{ S cm}^{-1}$ above 343 K and follows the Vogel-Fulcher-Tammann equation up to ca. 400 K. In particular, the hybrid is advantageous at low temperatures ($< 263 \text{ K}$), where the ionic conduction is superior to that of bulk IL, making it useful as solid-state electrolytes for electrochemical devices operating over a wide temperature range across room temperature.

Ionic liquids (ILs), which are composed entirely of ions and melt below room temperature (or 100°C), have high ion density even in liquid state. Therefore, their negligible vapor pressure (wide liquid temperature region and negligible flammability) and high ionic conductivity have been the subject of intensive research over recent years as potentially benign solvents for electrochemical devices such as electric double-layer capacitors,^[1–3] fuel cells,^[4,5] dye-sensitized solar cells,^[6,7] and lithium ion batteries.^[8,9] Most recently, hybrid materials, where ILs are incorporated into porous solids, have attracted huge interest because of their promising applications in “solvent-free” devices capable of preventing liquid leakage.^[10–16] However, the ionic conductivity (σ) of these hybrid materials has been lower than $10^{-3} \text{ S cm}^{-1}$, which is comparable to that of typical liquid electrolytes and is considered as a benchmark for electrochemical applications,^[17] mainly due to the Coulombic interactions between ions of ILs and frameworks.^[18–23] Theoretical studies predicted that ILs in porous materials preferentially construct an “interface region” with a thickness of ca. 1 nm on the framework surface (Figure 1).^[22] Diffusivity of ions in this region is greatly restricted by the interactions with the frameworks. On the other hand, if the materials contain sufficiently large pores to prevent the contact of the facing interface regions, additional ILs occupying the core of

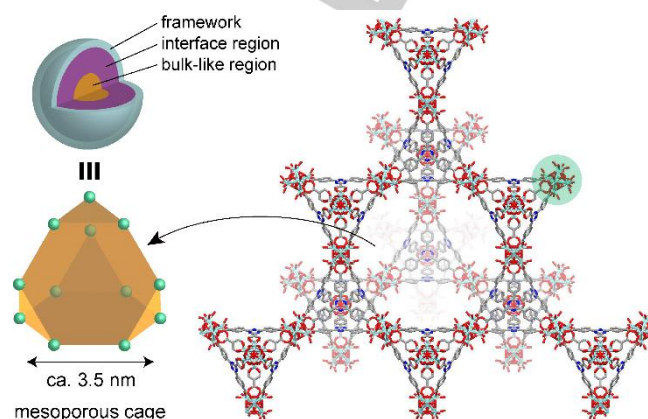


Figure 1. (upper left) Schematic of interface region (purple) and bulk-like region (orange) within a mesoporous cage. (right) Framework structure of PCN-777 viewed along the [111] direction (gray: C, blue: N, red: O, pale blue: Zr),^[28] where hydrogen atoms are omitted for clarity. A green circle shows the $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}]$ cluster unit. (lower left) Mesoporous cage with truncated tetrahedral geometry in PCN-777, where green circles indicate a $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}]$ cluster unit.

the pores (so-called “bulk-like region”) behave in the similar way as bulk ILs, which are expected to show high diffusivities even in a confined nanospace.

For porous materials, metal-organic frameworks (MOFs) are particularly attractive because of their designability by the vast number of combinations of metal-based building blocks and organic linkers that allow tailoring framework and pore structures, compositions, and functionalities.^[24–27] In this study, we chose a zirconium-based mesoporous MOF, PCN-777 with a formula of $[\text{Zr}_6\text{O}_4(\text{OH})_{10}(\text{H}_2\text{O})_6(\text{TATB})_2]$ (H_3TATB : 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid),^[28] to provide the bulk-like region in the pores. In the solid, four $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}]$ cluster units are connected by four tritopic TATB^{3-} ligands to form a microporous tetrahedron edge-shared to each other to construct a three-dimensional β -cristobalite-like network (Figure 1). The size of the mesoporous cage with truncated tetrahedral geometry is as large as ca. 3.5 nm, which is one of the largest cavities among existing MOFs. Despite its high porosity, PCN-777 has an excellent thermal durability with the framework decomposition occurring above 700 K. As the ion diffusivity of ILs confined in the pores is expected to be partly inherited from the bulk state, a highly ion-conducting $(\text{EMI})[\text{N}(\text{CN})_2]$ ($\sigma_{298\text{K}} = 2.8 \times 10^{-2} \text{ S cm}^{-1}$),^[29,30] composed of 1-ethyl-3-methylimidazolium (EMI^+) cations and dicyanamide ($\text{N}(\text{CN})_2^-$) anions, is an obvious target for ILs to be incorporated into PCN-777. We prepared a series of the hybrid materials with different filling levels of $(\text{EMI})[\text{N}(\text{CN})_2]$ to investigate how ions of $(\text{EMI})[\text{N}(\text{CN})_2]$ occupy the interface and bulk-like regions in the mesopores and behave in each region.

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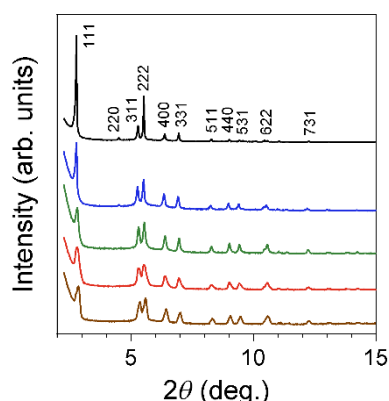


Figure 2. PXRD patterns of (EMI)[N(CN)₂]@PCN-777 hybrids with a filling level of 25% (blue), 50% (green), 75% (red), and 100% (brown) with pristine PCN-777 (black).

Hybrid materials, in which (EMI)[N(CN)₂] with an adequate volumetric filling level (f)^[31] at an interval of 12.5% ($f = 12.5, 25, 37.5, 50, 62.5, 75, 87.5$, and 100%) is impregnated into PCN-777, were prepared by grinding together in a mortar and annealed for capillary action^[32,33] (see Experimental Details in Supporting Information). The hybrids with $f < 75\%$ maintained the powder form, whereas the incorporation for $f > 87.5\%$ yielded gel-like hybrids. Figure 2 shows the powder X-ray diffraction (PXRD) patterns of hybrids with different f values. The framework structure is evidently well preserved throughout the impregnation process (Figure S1 in Supporting Information); the intensity of (111) reflection steadily decreases with increasing f , which is readily ascribed to the disordered or mobile ions of (EMI)[N(CN)₂] within the pores.^[32,33] Scanning electron microscopy (SEM) images of the hybrids show the absence of (EMI)[N(CN)₂] at the grain boundary (Figure S2).

Figure 3a displays the nitrogen gas adsorption isotherms of the hybrid materials measured at 77 K. For $f = 12.5\%$ hybrid, there is a pronounced uptake at around $P/P_0 = 0.35$ as indication of the presence of mesopores, in addition to a sharp uptake attributed to the micropore filling at low relative pressure. The maximum nitrogen uptake capacity was estimated to be $209 \text{ cm}^3 \text{ g}^{-1}$, which is significantly smaller than that of the parent PCN-777 ($1011 \text{ cm}^3 \text{ g}^{-1}$) despite only 12.5% occupied pores. As shown in Figure 3b, the nitrogen uptake rapidly decreases with increasing the filling level and eventually becomes negligible for $f \geq 50\%$, at which approximately 15 EMI–N(CN)₂ ion pairs are accommodated in a mesoporous cage.

To clarify the origin of the peculiar sorption behavior, a control group of hybrid materials was prepared by the incorporation of EMI-based ILs composed of bis(trifluoromethanesulfonyl)amide

(TFSA[−]) and bis(pentafluoroethanesulfonyl)amide (PFSA[−]) anions into PCN-777. We note that these anions have lower Lewis basicity compared with that of N(CN)₂[−] anion; Gutmann's donor numbers were estimated to be 41.8 for N(CN)₂[−],^[34,35] 15.7 for TFSA[−],^[35,36] and 14.0 for PFSA[−]^[35,36] based on the solvatochromic effect. In the nitrogen sorption isotherm at 77 K, the maximum nitrogen uptake capacity of (EMI)[N(CN)₂]@PCN-777 with $f = 25\%$ ($89 \text{ cm}^3 \text{ g}^{-1}$) is apparently smaller than those of (EMI)(TFSA)@PCN-777 ($247 \text{ cm}^3 \text{ g}^{-1}$) and (EMI)(PFSA)@PCN-777 ($270 \text{ cm}^3 \text{ g}^{-1}$) with the same f value (Figure S3). Considering the larger calculated interaction energy between EMI⁺ and N(CN)₂[−] ($82.4 \text{ kcal mol}^{-1}$; Figure S4) compared with that in (EMI)(TFSA) ($80.5 \text{ kcal mol}^{-1}$),^[37] it is possible that the formation of rigid ion clusters of (EMI)[N(CN)₂] near the framework in PCN-777 causes the suppressed penetration of nitrogen gas.

To examine the relationship between the filling level and radial distribution of ILs in the pores, the vibrational and thermal properties for hybrids with different f values were investigated. For $f = 12.5\%$ hybrid, an intense infrared (IR) band attributed to the C–N rocking mode of EMI⁺ cations (1562 cm^{-1} ; referred as to Band A)^[38] is shifted to a low frequency by 9 cm^{-1} relative to that

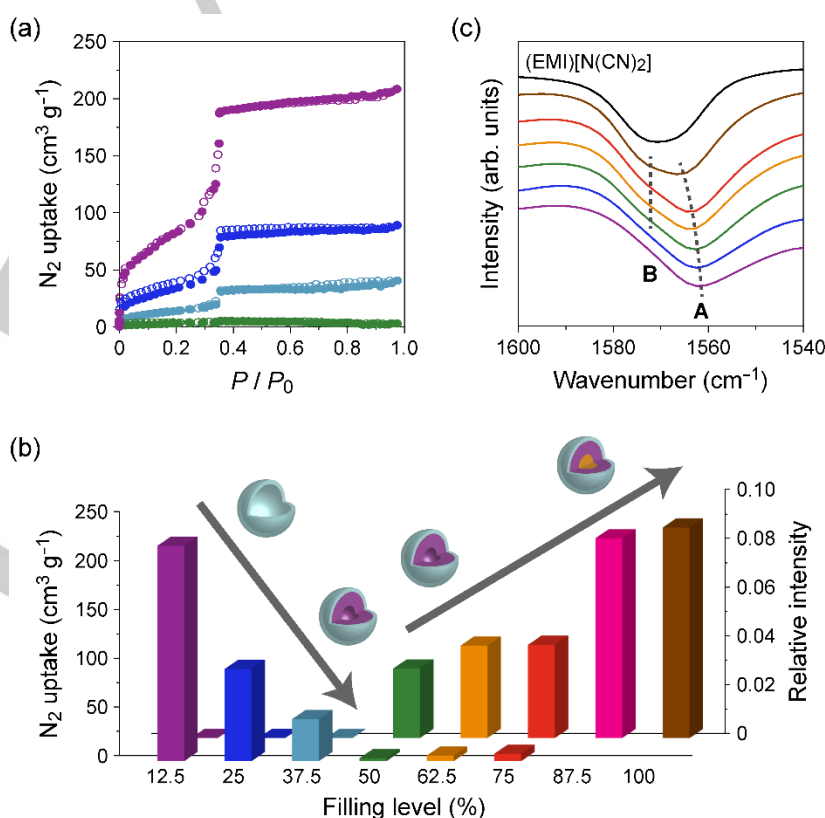


Figure 3. (a) Nitrogen gas adsorption (closed circles) and desorption (open circles) isotherms of hybrids measured at 77 K (volume of nitrogen adsorbed per mass of PCN-777). (b) Maximum nitrogen uptake (front line) and relative intensity of Band B to Band A assigned to the C–N rocking mode (rear line; see (c)) of hybrids as a function of filling level (f). See Figure 1 for schematic spheres. (c) IR spectra of hybrids and (EMI)[N(CN)₂]. Right (A) and left (B) dotted lines show Bands A and B, respectively (see text for details). Color code (purple: $f = 12.5\%$, blue: $f = 25\%$, pale blue: $f = 37.5\%$, green: $f = 50\%$, orange: $f = 62.5\%$, red: $f = 75\%$, pink: $f = 87.5\%$, brown: $f = 100\%$).

of the bulk (EMI)[N(CN)₂] (Figure 3c). The downshift is indicative of the ion-framework Coulombic interactions with negatively charged TATB³⁻ ligands in the interface region. Such significant interactions with frameworks are responsible for no crystallization exothermic and melting endothermic peaks in the differential scanning calorimetry profiles (Figure S5). An increase in *f* leads to a slight upshift of Band A accompanied by the appearance of a new band (Band B) at ca. 1572 cm⁻¹ for *f* ≥ 50% (see Figure 3b for the relative intensity of Band B to Band A). The new band is readily ascribed to the bulk-like (EMI)[N(CN)₂] occupying the bulk region. The impregnation of (EMI)[N(CN)₂] into PCN-777 also leads to an upshift of the C≡N stretching mode of N(CN)₂⁻ anions (2122 cm⁻¹ for (EMI)[N(CN)₂]) by 6 cm⁻¹ for *f* = 12.5% hybrid (Figure S6), possibly associated with the Coulombic interactions with the positively charged parts in the framework (i.e., Zr(IV) and onium). We note that such two distinct confinement states of (EMI)[N(CN)₂] were confirmed by the thermogravimetric measurements (Figure S7). These results provide strong experimental evidence that ions of (EMI)[N(CN)₂] are largely confined near the framework at the initial filling process, whereas additional (EMI)[N(CN)₂] occupy the core of the mesopores and behave in the similar to the bulk liquid.

As shown in Table 1, the room-temperature ionic conductivity (σ_{298K}) continues to rise with the incorporation of (EMI)[N(CN)₂] until *f* = 62.5%, i.e., from 2.8×10^{-5} S cm⁻¹ for *f* = 12.5% hybrid and 4.4×10^{-3} S cm⁻¹ for *f* = 62.5% hybrid.^[39] The latter value is among the highest in the existing IL-incorporated MOF hybrids.^[16] According to the Nernst-Einstein equation for the relationship between the ion diffusivity (*D*) and molar conductivity ($\Lambda = \sigma/M$, where *M* is the molar concentration), $D = \Lambda RT/z^2 F^2$ (*R*: universal gas constant, *z*: charge of ions, *F*: Faraday constant), the *D* value at 298 K (*D*_{298K}) for *f* = 62.5% hybrid was estimated to be 3.1×10^{-11} m² s⁻¹. It is noteworthy that the *D*_{298K} value is comparable to those of 13 typical bulk ILs tabulated in Ref. 36 ($1.6\text{--}9.9 \times 10^{-11}$ m² s⁻¹ at 303 K), which were estimated from pulse-field-gradient spin-echo NMR measurements. It is apparent that the increase in *D*_{298K} (Figure 4) with increasing *f* arises from the gradual filling of (EMI)[N(CN)₂] in the bulk-like region, in which ions are more mobile than those in the interface region.^[19,21] The diminished *D*_{298K} value from *f* = 62.5% to *f* = 75% hybrids is possibly caused by the denser packing of (EMI)[N(CN)₂] in the bulk-like region, which hampers the ion diffusion.^[19,20] Thus, the moderate filling of ILs in the bulk-like region appears to be a key to the increased molar conductivity.

Table 1: Typical diffusive properties of hybrids at 298 K.

<i>f</i> (%) ^[a]	σ (10 ⁻³ S cm ⁻¹) ^[b]	Λ (S cm ² mol ⁻¹) ^[c]	<i>D</i> (10 ⁻¹¹ m ² s ⁻¹) ^[d]
12.5	0.028	0.036	0.096
25	0.21	0.14	0.37
37.5	1.7	0.76	2.0
50	2.6	0.84	2.2
62.5	4.4	1.2	3.1
75	3.1	0.67	1.8

[a] Volumetric filling level; [b] Ionic conductivity; [c] Molar conductivity ($\Lambda = \sigma/M$; *M*: molar concentration); [d] Ion diffusivity estimated based on the Nernst-Einstein equation (see text).

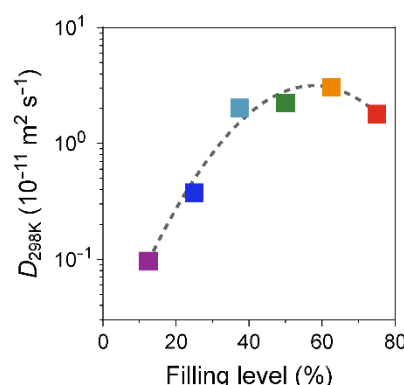


Figure 4. Room-temperature ion diffusivity (*D*_{298K}) of hybrids as a function of filling level (*f*). A dotted line is a guide to the eye. Color code (purple: *f* = 12.5%, blue: *f* = 25%, pale blue: *f* = 37.5%, green: *f* = 50%, orange: *f* = 62.5%, red: *f* = 75%).

Figure 5a shows the temperature dependence of σT for hybrids with different *f* values in the temperature range of 298–343 K. The conductivity of all hybrids follows the Arrhenius-type activated behavior given by the equation, $\sigma T = A \exp(-E_a/k_B T)$, where *E*_a is the activation energy, *A* is the pre-exponential factor, and *k*_B is the Boltzmann constant. It should be noted that the σ value at 343 K exceeds 10⁻² S cm⁻¹ for *f* = 62.5% hybrid (1.1×10^{-2} S cm⁻¹; Figure S8). The very low *E*_a value of 0.20 eV in addition to the high σ_{298K} value apparently falls in the range observed for superionic conductors.^[40,41]

It has been known that the freezing and volatilization of water causes a significant performance degradation of electrochemical devices using aqueous electrolytes; namely, a limited operation temperature between 273 and 373 K. Notably, the *f* = 62.5% hybrid shows no weight reduction up to a temperature as high as 444 K (Figure S7), providing a very wide temperature range (ca. 280 K) including the liquid-like state of (EMI)[N(CN)₂] in PCN-777. To assess the applicability of the hybrid as alternative electrolytes, we measured the ionic conductivity of the hybrid over a wider temperature range (248–433 K) on heating process. As shown in Figure 5b, the conductivity steadily increases with increasing temperature up to 403 K, above which the σ value rapidly drops due to the decomposition of (EMI)[N(CN)₂]. Provided the ideal glass transition temperature (*T*_g) is equal to the measured value (*T*_g = 164 K), the σT value at 248–403 K can be well fitted with the Vogel-Fulcher-Tammann equation,^[42–44] $\sigma T = A \exp[-B/(T - T_0)]$, where *A* and *B* are fitting parameters. It is particularly important that the conductivity of the hybrid is higher than that of the bulk (EMI)[N(CN)₂] below 263 K, as the parent IL shows a steep decrease in σ below ca. 268 K associated with the melting event (*T*_m = 261 K; see Figure S5). At 248 K, the σ value of the hybrid is more than one order higher than that of the bulk (EMI)[N(CN)₂] (Figure S9). Therefore, the present hybrid is a good candidate for solid-state electrolytes for diverse electrochemical devices operating over a wide temperature range.

In summary, by studying the relative properties of mesoporous MOFs incorporating ILs with various filling levels, we have gained an intuitive insight into the relationship between the radial distribution of ILs in the pores and ionic conduction of the hybrid systems. ILs become occupied the core of the mesopores after

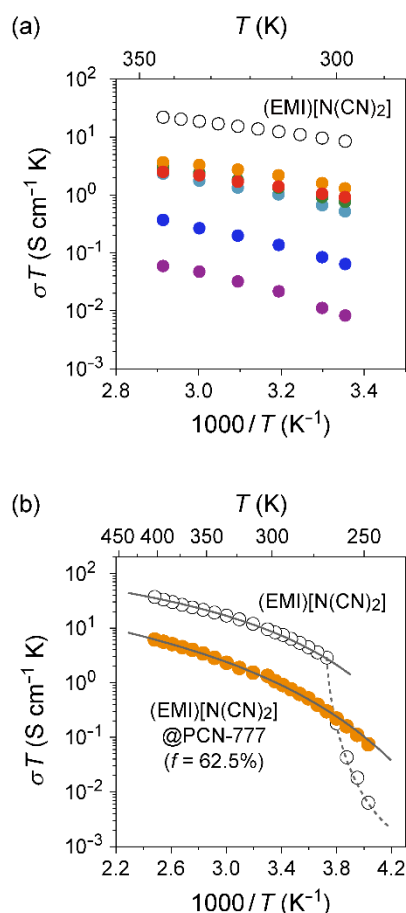


Figure 5. (a) Temperature dependence of σT for hybrids with various f values in the temperature range of 298–343 K on heating process. (b) Temperature dependence of σT for $f = 62.5\%$ hybrid in the temperature range of 248–403 K on heating process. Solid lines are fitted to the Vogel-Fulcher-Tammann equation (see text), whereas a dotted line is a guide to the eye. In both figures, the σT values of (EMI)[N(CN)₂] are shown for comparison.^[30] Color code (purple: $f = 12.5\%$, blue: $f = 25\%$, pale blue: $f = 37.5\%$, green: $f = 50\%$, orange: $f = 62.5\%$, red: $f = 75\%$).

they are deposited onto the framework, whereas further filling results in a denser packing in the pores. The key to the realization of superionic conduction is the construction of the bulk-like region in the pores. High mobility of ions occupying the bulk-like region leads to a new class of solid-state superionic conductors with the highest $\sigma_{298\text{K}}$ ($4.4 \times 10^{-3} \text{ S cm}^{-1}$) among the IL-incorporated MOF hybrids reported to date. Furthermore, the hybrid shows a notably excellent ionic conduction over a wide temperature range; the σ value steadily increases up to ca. 400 K ($> 10^{-2} \text{ S cm}^{-1}$ above 343 K) and exceeds that of the parent IL at low temperatures ($< 263 \text{ K}$). Such special features make it a promising green and versatile alternative to conventional aqueous electrolytes over a wide temperature range across room temperature.

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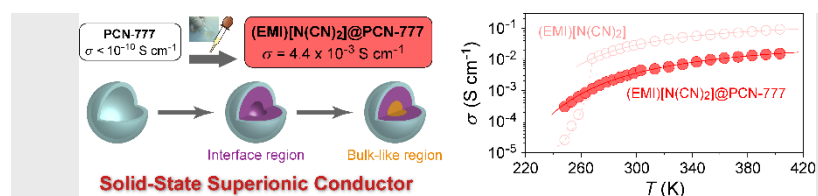
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COMMUNICATION



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Superionic Conduction over a Wide Temperature Range in a Metal-Organic Framework Impregnated with Ionic Liquids

An unprecedented solid-state superionic conductor was obtained by incorporating ionic liquid (IL) into mesoporous metal-organic framework (MOF). Because ILs occupying the core of mesopores behave as bulk, the hybrid shows the highest room-temperature conductivity ($4.4 \times 10^{-3} \text{ S cm}^{-1}$) among the IL-incorporated MOF hybrids reported to date.