

Beyond the Paddle-Wheel Mechanism: Hop Function Analysis of Ion Transport in Organic Ionic Plastic Crystals

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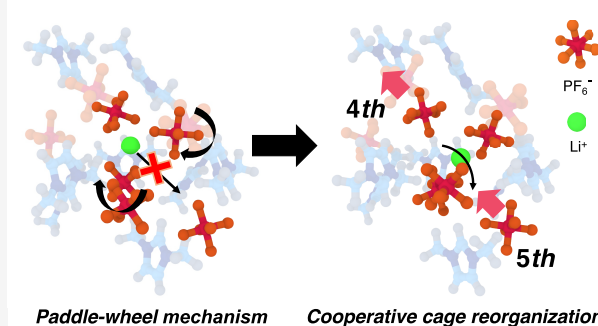
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ABSTRACT: The paddle-wheel mechanism has long been invoked to explain ion transport in organic ionic plastic crystals (OIPCs), wherein rotational motion of matrix ions is assumed to facilitate ion hopping. Here, we critically examine the paddle-wheel mechanism using molecular dynamics (MD) simulations combined with hop function analysis for a representative OIPC, Li-doped 1,3-dimethylimidazolium hexafluorophosphate ([MMIM][PF₆]). While matrix ions ([MMIM]⁺ and PF₆[−]) exhibit translation-rotation coupling consistent with the paddle-wheel mechanism, Li⁺ ion transport, central to the ion conductivity of solid-state electrolytes (SSEs), is decoupled from the rotational dynamics of neighbor ions. Instead, the hop function analysis reveals that the collective rearrangement of the third, fourth, and fifth nearest PF₆[−] anions around Li⁺ forms the transition-state configuration governing Li⁺ hopping. This process constitutes the primary Li⁺ ion transport mechanism, replacing the conventional paddle-wheel mechanism. Our results establish the hop function analysis as a robust framework for disentangling ion transport mechanisms in complex solid-state electrolytes and call for a reassessment of long-standing mechanistic assumptions in OIPCs.

From paddle-wheel to cooperative cage reorganization



INTRODUCTION

Solid-state electrolytes (SSEs) are central to the development of safe and high-energy-density electrochemical devices, where the microscopic mechanism of ion transport determines their macroscopic performance. Among diverse classes of solid electrolytes, organic ionic plastic crystals (OIPCs), consisting of molecular ions, have attracted considerable attention due to their unique combination of translational crystalline order and rotational disorder of matrix molecular ions.^{1–9} This combination enables relatively high ion conductivity of OIPCs on the order of 10^{−5}–10^{−2} S/cm^{6,10–15} at room temperature while retaining the system in mechanically stable crystalline solid states, as confirmed by experiments^{4,12,16–21} and simulations.^{22–31} However, a molecular-level understanding of the ion transport mechanism in OIPCs, especially how the transport of Li⁺ ions relates to the motions of neighbor matrix ions, remains incomplete due to a lack of direct molecular-level evidence.

The paddle-wheel mechanism has long been considered the dominant microscopic ion transport mechanism of OIPCs.^{3,21,32–38} The paddle-wheel mechanism suggests that the rotational motions of neighbor matrix molecular ions should modulate the free energy barrier for an ion to hop between neighbor sites,^{32,37} thus facilitating the ion conduction in OIPCs. This mechanism is motivated by seminal experimental observations^{1–3,18,20,29,32,39} that multiple phase transitions between solid rotator phases exist for OIPCs,

rotational modes of matrix ions are liberated across each phase transition, and the ion conductivity increases discontinuously at the phase transition. For instance, single-pulse NMR studies on diethyl(methyl)(isobutyl)phosphonium hexafluorophosphate ([P¹²²⁴][PF₆]) have shown that the activation of [P¹²²⁴]⁺ rotation at the phase transition between rotator phases coincides with an increase in ion conductivity by nearly 2 orders of magnitude.² In addition, broadband impedance spectroscopy and conductometry measurements on Li⁺-doped plastic crystalline systems have revealed power-law scaling relations between rotational relaxation times and dc ionic conductivity, suggesting a coupling between molecular rotation and ion transport.^{41,42} These observations have reinforced the paddle-wheel mechanism as a plausible ion transport mechanism in OIPCs.

Despite the widespread acceptance of the paddle-wheel mechanism, direct molecular-level evidence establishing a causal link between the rotational dynamics of matrix ions and individual ion hopping events remains limited.³⁷ Most

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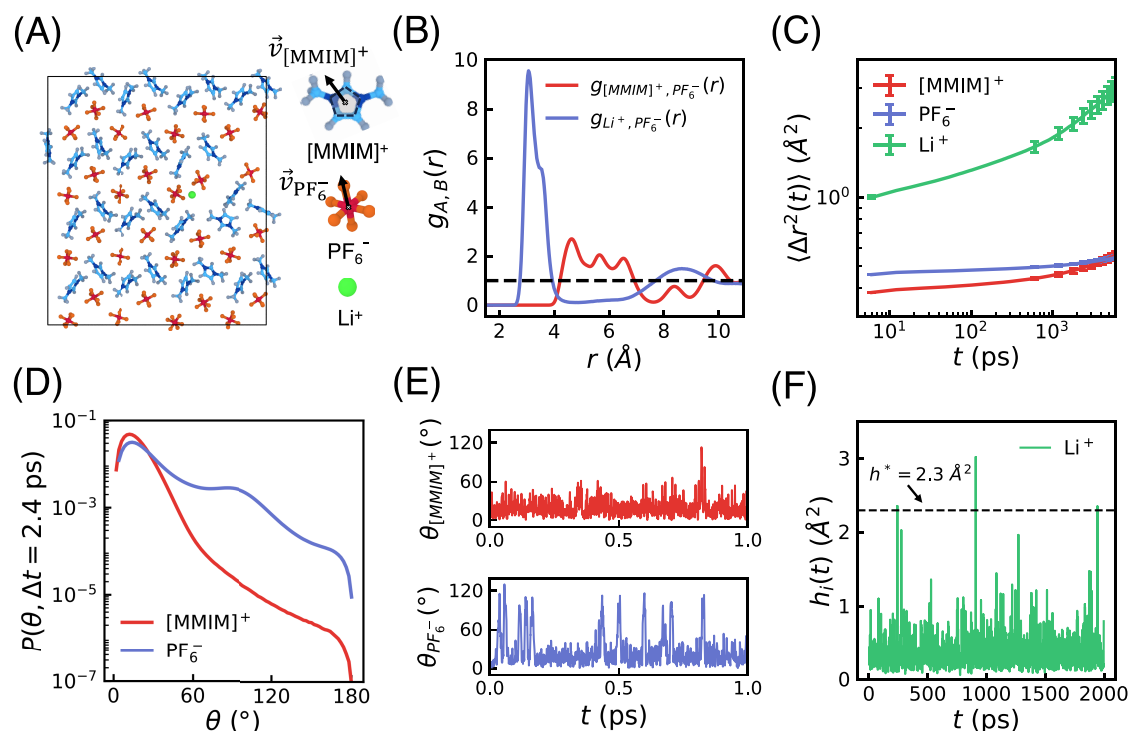


Figure 1. (A) Representative simulation snapshot of the [MMIM][PF₆], viewed along a direction perpendicular to the *c*-axis. [MMIM]⁺ and PF₆[−] matrix ions are displayed with their characteristic vectors to evaluate their rotational motions. (B) Radial distribution functions ($g_{[\text{MMIM}]^+, \text{PF}_6^-}(r)$ and $g_{\text{Li}^+, \text{PF}_6^-}(r)$) between [MMIM]⁺ and PF₆[−] matrix ions and between Li⁺ and PF₆[−] ions, respectively at *T* = 300 K. (C) Mean-square displacements ($\langle \Delta r^2(t) \rangle$'s) of Li⁺, [MMIM]⁺, and PF₆[−] ions. (D) Probability distribution functions ($P(\theta, \Delta t = 2.4 \text{ ps})$) of the rotational displacement (θ) during $t = 2.4 \text{ ps}$ for [MMIM]⁺ and PF₆[−] matrix ions. (E) Representative time traces of the transient rotational displacement ($\theta_{[\text{MMIM}]^+}$ and $\theta_{\text{PF}_6^-}$) of a particular pair of [MMIM]⁺ and PF₆[−] ions during 1 ps. (F) Hop function ($h_i(t)$) of a particular Li⁺ ion as a function of time *t* during 2 ns. The dashed line corresponds to $h_i(t) = h^*$.

experimental studies relied on ensemble-averaged transport properties or indirect correlations, such as changes in ionic conductivity across phase transitions or scaling relations between rotational relaxation times and macroscopic conductivity,^{20,44} rather than on direct observation of individual ion hopping events and their associated transition states.^{45–47} Particularly for Li⁺ transport in OIPCs, where strong electrostatic interactions and heterogeneous coordination environments^{4,9,23,30,48–56} may lead to complex transport pathways, resolving Li⁺ ion hopping events at the molecular level and clarifying their relation to neighbor matrix ions are essential to understanding the microscopic ion transport mechanism.

In this study, we address this challenge by combining molecular dynamics (MD) simulations with hop function analysis to directly resolve individual hopping events in OIPCs and identify the slow variable (or reaction coordinate) governing the ion hopping kinetics. In heterogeneous environments where local fluctuations evolve slowly compared to the ion hopping, event statistics deviate from Poisson behavior, reflecting the emergence of multiple slow variables and significantly complicating the identification of microscopic ion transport pathways.^{57–59} Hop function analysis provides a framework for identifying the microscopic reaction coordinate underlying non-Poisson hopping dynamics and has been successfully applied to granular materials,⁶⁰ supercooled water,^{58,61–63} and amorphous solids.^{46,64–69} By applying this framework to a well-characterized model Li-doped OIPC

system, we obtain an event-resolved description of ion transport that goes beyond phenomenological correlations.

We perform extensive atomistic MD simulations for Li-doped 1,3-dimethylimidazolium hexafluorophosphate ([MMIM][PF₆]). We find from the hop function analysis that the hopping motions of matrix ions ([MMIM]⁺ and PF₆[−]) are coupled to the rotational motion of neighbor matrix ions, consistent with the paddle-wheel mechanism. On the other hand, the hopping motions of Li⁺ ions are decoupled from the rotation of neighbor matrix ions, inconsistent with the paddle-wheel picture. In addition, the hopping event statistics of Li⁺ ions deviates significantly from Poisson behavior, indicating that the Li⁺ ion transport is dynamically disordered. We also find that Li⁺ ion hopping is associated with collective rearrangement of the third, fourth, and fifth nearest PF₆[−] anions, which opens the old cage around Li⁺ and forms a new cage that confines Li⁺. This defines the transition-state configuration for Li⁺ with a transient coordination number of 2, which accelerates the Li⁺ hopping rate by 4 orders of magnitude compared to equilibrium caged states. These results point to a Li⁺ transport mechanism beyond the conventional paddle-wheel description and underscore the utility of hop function analysis as a powerful framework for disentangling ion transport mechanisms in complex solid-state electrolytes.

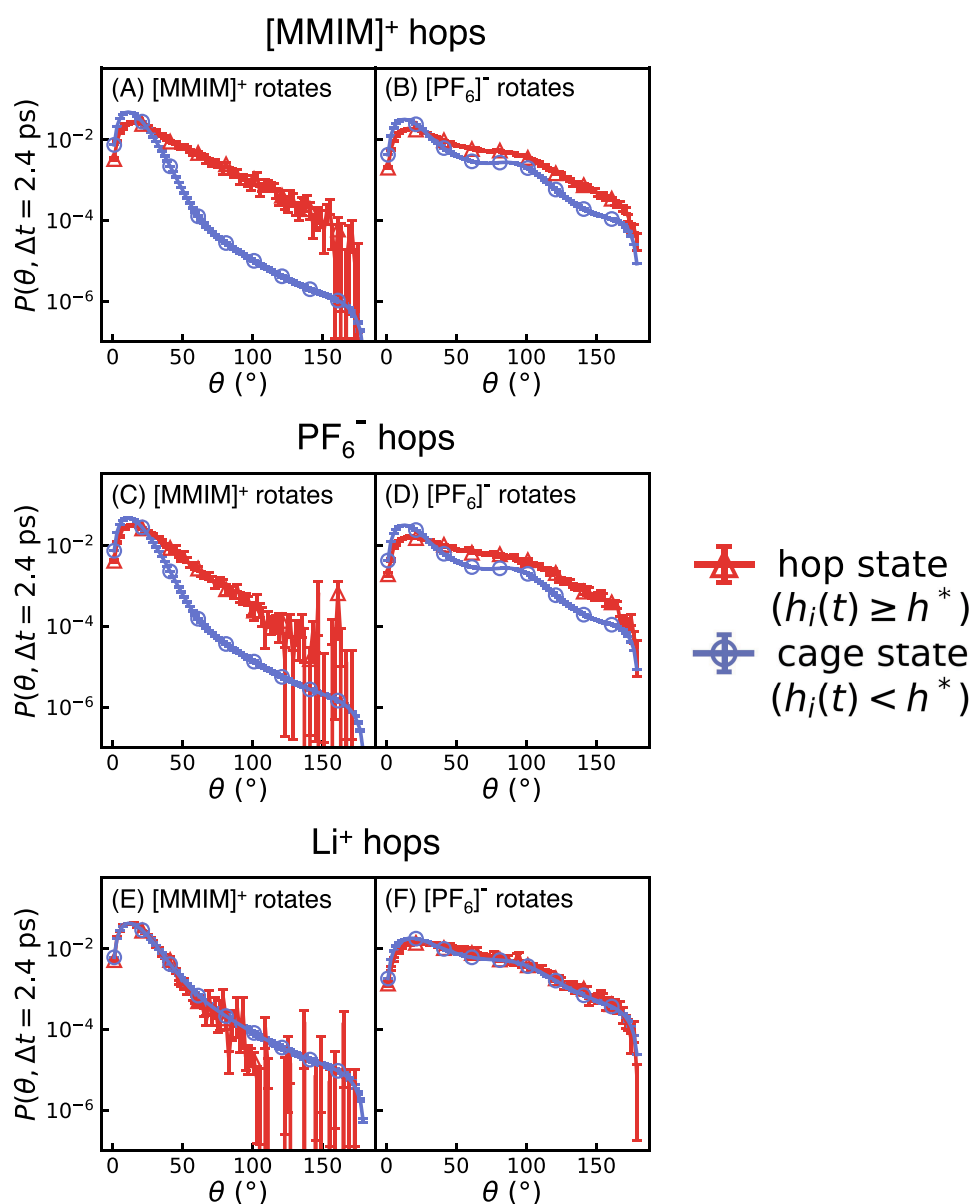


Figure 2. Probability distribution functions ($P(\theta, \Delta t = 2.4 \text{ ps})$) of the angular displacement (θ) of the first-shell neighbor ions around a target ion when the target ion is either in the cage state (blue, $h_i(t) < h^*$) or in the hop state (red, $h_i(t) \geq h^*$). The first shell for the target ion is identified based on the radial distribution functions (Supporting Information). In our study, three ionic species (Li^+ , $[\text{MMIM}]^+$, and PF_6^-) may hop and two matrix ions ($[\text{MMIM}]^+$ and PF_6^-) may rotate such that there are six possible combinations of the rotation-hopping correlations. (A, B) Rotations of neighbor $[\text{MMIM}]^+$ and PF_6^- are estimated, respectively, when $[\text{MMIM}]^+$ ions hop (red) or rattle (blue). (C, D) Rotations of neighbor $[\text{MMIM}]^+$ and PF_6^- are estimated, respectively, when PF_6^- ions hop (red) or rattle (blue). (E, F) Rotations of neighbor $[\text{MMIM}]^+$ and PF_6^- are estimated, respectively, when Li^+ ions hop (red) or rattle (blue).

RESULTS AND DISCUSSION

Structural and Dynamical Characteristics of Li-Doped $[\text{MMIM}][\text{PF}_6]$

We examine Li-doped 1,3-dimethylimidazolium hexafluorophosphate ($[\text{MMIM}][\text{PF}_6]$) as a well-characterized model OIPC for the mechanistic interrogation of ion transport. This system, consisting of imidazolium cations^{12,18,19,70–73} and hexafluorophosphate anions,^{2,5,74–76} exhibits key structural and dynamical characteristics common to many plastic crystalline ionic materials, including long-range translational order with rotational disorder of matrix ions and measurable ionic conductivity in the solid state. Figure 1A depicts a representative simulation snapshot of Li-doped $[\text{MMIM}]$ -

$[\text{PF}_6]$, where matrix ions of $[\text{MMIM}]^+$ and PF_6^- occupy lattice sites with rotational disorder. The radial distribution function ($g_{[\text{MMIM}]^+, \text{PF}_6^-}(r)$) between $[\text{MMIM}]^+$ and PF_6^- exhibits multiple peaks extending to long distances, which is a characteristic feature of crystalline solids (Figure 1B and Supporting Information). Li^+ ions are coordinated by neighbor PF_6^- anions such that $g_{\text{Li}^+, \text{PF}_6^-}(r)$ shows a high peak around $r \approx 3 \text{ \AA}$ (Figure 1B) and the average coordination number of PF_6^- anions around Li^+ is about 3.4. Such a relatively simple coordination environment arising from the combination of an imidazolium-based cation and PF_6^- anion provides a suitable platform for resolving microscopic ion hopping events without strong competing specific interactions.

Li^+ ions dominate the ion conductivity of the OIPC, whereas $[\text{MMIM}]^+$ and PF_6^- matrix ions maintain the system in the solid phase. Figure 1C shows the mean-square displacements ($\langle \Delta \vec{r}(t)^2 \rangle$'s) of all ion species at multiple time scales. Li^+ ions diffuse readily at $t \geq 10^3$ ps, while matrix ions rattle mostly at their corresponding lattice sites even at long times. This shows that the Li^+ ion transport is central to the ion conductivity of OIPC in the solid phase.

Matrix ions in $[\text{MMIM}][\text{PF}_6]$ exhibit substantial rotational mobility even at short time scales. We consider the rotations of two characteristic unit vectors, $\vec{v}_{[\text{MMIM}]^+}$ and $\vec{v}_{\text{PF}_6^-}$ (Figure 1A). $\vec{v}_{[\text{MMIM}]^+}$, the unit vector normal to an imidazolium ring, corresponds to the slowest rotational mode of $[\text{MMIM}]^+$. On the other hand, $\vec{v}_{\text{PF}_6^-}$ is a bond vector between P and F atoms of PF_6^- . Figure 1D shows the probability distribution functions ($P(\theta, \Delta t = 2.4 \text{ ps})$) of how much $[\text{MMIM}]^+$ and PF_6^- rotate during $t = 2.4$ ps. We select the short time of $t = 2.4$ ps because we identify the individual Li^+ hopping events with a time resolution of $t = 2.4$ ps (see the Methods section). $P(\theta, \Delta t = 2.4 \text{ ps})$ of PF_6^- anions shows two peaks around $\theta \approx 30$ and 90° . The first peak around $\theta \approx 30^\circ$ indicates that most PF_6^- anions rotationally rattle during 2.4 ps. On the other hand, the second peak around $\theta \approx 90^\circ$ implies that some PF_6^- anions undergo rotational hopping motions during 2.4 ps. While $[\text{MMIM}]^+$ cations are relatively less rotationally active compared to PF_6^- anions, $[\text{MMIM}]^+$ sometimes do undergo rotational hopping motions. Figure 1E depicts the representative temporal series of the transient rotational displacements ($\theta_{[\text{MMIM}]^+}$ and $\theta_{\text{PF}_6^-}$) of a pair of $[\text{MMIM}]^+$ and PF_6^- . Both PF_6^- and $[\text{MMIM}]^+$ undergo rotational hopping motions within 1 ps.

Li^+ ions in $[\text{MMIM}][\text{PF}_6]$ undergo hopping motions readily, and the hop function $h_i(t)$ captures the individual hopping event successfully. Figure 1F shows $h_i(t)$ of a particular Li^+ ion during 2 ns. In most cases, Li^+ ion rattles within a cage of neighbor PF_6^- anions with a small value of $h_i(t)$. However, the Li^+ ion sometimes hops out of an old cage to a new one, to which $h_i(t)$ responds sensitively with a peak. We determine the criterion value of h^* (see the Methods section for details) to assign the Li^+ ion to either a cage state ($h_i(t) < h^*$) or a hop state ($h_i(t) \geq h^*$). According to this criterion, the particular Li^+ ion in Figure 1F undergoes the hopping motion three times during 2 ns. We also calculate the hop functions ($h_i(t)$'s) for matrix ions. Even though matrix ions hardly diffuse, as shown for their $\langle \Delta \vec{r}(t)^2 \rangle$'s in Figure 1C, the hop function analysis further enables detection of the very rare translational hopping motion of $[\text{MMIM}]^+$ and PF_6^- matrix ions during our simulations (Supporting Information).

Testing the Paddle-Wheel Mechanism through Rotation-Hopping Correlations

Having established the ability to detect individual hopping events of all ionic species (Li^+ , $[\text{MMIM}]^+$, and PF_6^-), we investigate whether and how neighbor ions around a target ion relate to its hopping motion. We define the neighbor ions as the ions located within the first shell from the target ion. The shells are determined based on the radial distribution function ($g_{A,B}(r)$) between the target ion A and neighboring species B (Supporting Information). For example, if the distance between PF_6^- and Li^+ ions is less than 4.8 Å, the PF_6^- ion is considered a first-shell neighbor ion for the Li^+ ion.

In order to test the paddle-wheel mechanism, we examine the direct correlation between the individual hopping event of

a target ion and the rotation of its first-shell neighbor ions. Because the matrix ions exhibit substantial rotational mobility in OIPCs (Figure 1D), it is essential to compare the rotational motions of neighbor matrix ions in the cage and hop states of the target ion, instead of counting the total number of hopping and rotation events. There are six possible combinations of correlations among Li^+ , $[\text{MMIM}]^+$, and PF_6^- ions. Figure 2 depicts all six probability distribution functions ($P(\theta, \Delta t = 2.4 \text{ ps})$) of the rotational displacement (θ) of neighbor ions in the first shell during $\Delta t = 2.4$ ps. Red lines correspond to how much the first-shell neighbor ions rotate when the target ion undergoes hopping motions with $h_i(t) \geq h^*$ and the target ion is in the hop state. On the other hand, blue lines correspond to $P(\theta, \Delta t = 2.4 \text{ ps})$ when the target ion just rattles and is in the cage state with $h_i(t) < h^*$. Note that the time window $\Delta t = 2.4$ ps is chosen to capture rotational motions on the time scale relevant to hopping events (see the Methods section).

When the matrix ions ($[\text{MMIM}]^+$ and PF_6^-) undergo hopping motions, the rotational motion of their neighbor ions is active compared to when those matrix ions do not hop but remain confined within their cages, consistent with the paddle-wheel mechanism. Figure 2A,B depicts $P(\theta, \Delta t = 2.4 \text{ ps})$ of neighbor $[\text{MMIM}]^+$ and PF_6^- matrix ions when a target $[\text{MMIM}]^+$ hops. $P(\theta, \Delta t = 2.4 \text{ ps})$ at large θ is much larger for the target $[\text{MMIM}]^+$ in the hop state (red) than in the cage state (blue). The rotation of neighbor $[\text{MMIM}]^+$ ions is activated more significantly than that of PF_6^- ions, which may be attributed to the bulkier size of $[\text{MMIM}]^+$. Similarly, when a target PF_6^- ion hops and is in the hop state, $P(\theta, \Delta t = 2.4 \text{ ps})$ of neighbor $[\text{MMIM}]^+$ and PF_6^- ions is much larger at large θ than when the target PF_6^- ion is in the cage state (Figure 2C,D).

The rotation of neighbor ions around a Li^+ ion is hardly associated with whether the Li^+ ion hops or not, unlike what has been suggested by the paddle-wheel mechanism. Figure 2E,F depicts $P(\theta, \Delta t = 2.4 \text{ ps})$'s of neighbor $[\text{MMIM}]^+$ and PF_6^- ions around Li^+ ions in both cage and hop states. There is little difference within statistical errors in $P(\theta, \Delta t = 2.4 \text{ ps})$ between hop and cage states of Li^+ ion. This indicates that, despite the presence of rotational motion of neighbor matrix ions, Li^+ hopping events are not directly correlated with neighbor ion rotations.

The ion-specific dichotomy of transport behaviors remains consistent across different time scales. We further examine the direct correlation between the individual hopping event and the rotation of neighbor ions at $\Delta t = 10$ and 100 ps (Supporting Information), and observe the same trend: the hopping of matrix ions aligns with the paddle-wheel picture while the Li^+ hopping decouples from the rotation of neighbor ions.

We also employ the quaternion-based rotational analysis⁷⁷ to track the rotational matrix ions, which provides a smooth and numerically stable representation to capture three-dimensional rotational events on any arbitrary axis. We estimate the three-dimensional rotation angle (θ_q) of matrix ions and the probability distribution function ($P(\theta_q, \Delta t = 2.4 \text{ ps})$) from the quaternion-based rotational analysis as shown in the Supporting Information. $P(\theta_q, \Delta t = 2.4 \text{ ps})$'s from the quaternion-based rotational analysis exhibit the same trends with $P(\theta, \Delta t = 2.4 \text{ ps})$'s in Figure 2.

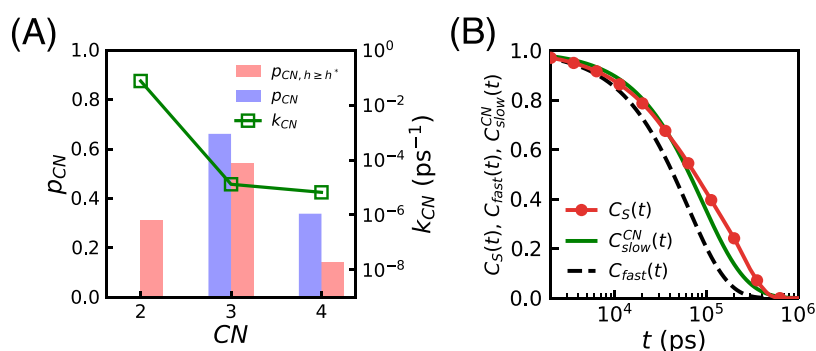


Figure 3. (A) Fractions (p_{CN} and $p_{\text{CN}, h \geq h^*}$) of Li^+ ions that are coordinated by CN PF_6^- anions. Note that p_{CN} (blue) is averaged over all Li^+ ions, while $p_{\text{CN}, h \geq h^*}$ (red) is averaged over Li^+ ions that hops with $h_i(t) \geq h^*$. The green line corresponds to the hopping rate constant (k_{CN}) of Li^+ ion in the substate of CN . (B) Survival probabilities obtained from simulations and hop function analysis ($C_S(t)$), the fast-fluctuation limit ($C_{\text{fast}}^{\text{CN}}(t)$), and the slow fluctuation limit ($C_{\text{slow}}^{\text{CN}}(t)$) with the coordination number (CN) as a slow variable.

Collective Anion Rearrangement Mechanism for Li^+ Ion Transport

The lack of correlation between Li^+ hopping and the rotation of neighbor matrix ions indicates that the conventional paddle-wheel picture does not fully account for Li^+ transport. We therefore analyze the event-resolved structural evolution surrounding Li^+ ions during individual hopping events and search for the slow variables that govern the non-Poisson hopping statistics and kinetics. The hop function analysis reveals that Li^+ hopping is governed by a cooperative rearrangement of surrounding PF_6^- anions, which collectively defines the transition-state configuration for hopping. These findings point to a transport mechanism in which Li^+ hopping is controlled by cage reorganization rather than by rotational activation of neighboring matrix ions.

Li^+ ions are surrounded mostly by PF_6^- anions. As shown in the radial distribution functions ($g_{A,B}(r)$'s in Figure 1B and Supporting Information), the first shell of neighboring PF_6^- anions around Li^+ is formed at a distance of less than 5 Å, while the first shell of neighboring $[\text{MMIM}]^+$ cations is located more than 5 Å away. We find from $g_{\text{Li}^+, \text{PF}_6^-}(r)$ that the average coordination number of Li^+ is about 3.4. This indicates that the cage, which confines Li^+ before hopping occurs, usually consists of either 3 or 4 PF_6^- anions. In addition, the structure of the cage (or the local environment of Li^+) is heterogeneous due to the rotational disorder of PF_6^- anions, and its structural relaxation is slow because $[\text{MMIM}][\text{PF}_6]$ OIPC is in the crystalline solid state. Then, the kinetics of Li^+ hopping out of the cage depends on how quickly the local environment of the Li^+ fluctuates.

In a fast fluctuating limit where the structure of the cage fluctuates very quickly, the hopping kinetics is influenced only by the average cage structure and is determined by a single rate constant (k_{fast}). Then, the survival probability $C_S(t)$, the fraction of Li^+ ions remaining in the cage state during time t before hopping, exhibits an exponential decay, i.e., $C_S(t) \approx C_{\text{fast}}(t) = \exp(-k_{\text{fast}}t)$. Its randomness parameter R is also 1, indicating that the hopping event statistics would follow the Poisson process in this limit. As discussed in the Methods section, when assuming the fast fluctuating limit, k_{fast} can be obtained by counting the total number of hopping events during simulations.

In a slow fluctuation limit, the local environment fluctuates so slowly that the cage structure does not change much during a Li^+ hopping event. The cage structure may be characterized

by structural descriptors, referred to as slow variables. Because the slow variable does not change during the event in this limit, the Li^+ ion can be considered as residing in a particular quasi-static substate characterized by the slow variable. Then, the survival probability $C_S(t)$ can be approximated as $C_S(t) \approx C_{\text{slow}}(t) = \sum_{i=1}^{N_s} p_i \exp(-k_i t)$. Here, i is the index of the substate and N_s denotes the total number of substates considered. k_i is the rate constant of Li^+ hopping in the i th substate, and p_i corresponds to the fraction of Li^+ ions in the i th substate (see the Methods section for details).

We find from our simulation results and hop function analysis that the randomness parameter R is about 3 for Li^+ hopping statistics. This implies that the Li^+ hopping should follow the non-Poisson process, and there would be slow variables that govern and describe the hopping kinetics properly. Since the cage consists mostly of PF_6^- anions, we consider two types of structural descriptors as slow variables: (1) the transient coordination number (CN) of PF_6^- anions around Li^+ and (2) the distance (d_n) between Li^+ and its n th nearest PF_6^- anion.

The Transient Coordination Number (CN) as a Slow Variable. Li^+ is usually caged by either three or four PF_6^- anions at a given moment, such that the average coordination number of Li^+ ions is about 3.4. As shown in Figure 3, the fraction (p_{CN}) of Li^+ with the transient coordination number CN is about 0.66 and 0.34 for $\text{CN} = 3$ and 4, respectively (blue bars). On the other hand, $p_{\text{CN}} = 6.6 \times 10^{-5}$ for $\text{CN} = 2$, indicating that Li^+ ion is hardly coordinated by two PF_6^- anions and the free energy of $\text{CN} = 2$ is the highest among the three coordination states. Note that p_{CN} is averaged over all Li^+ ions in our simulations. We also investigate the coordinating environment of Li^+ when the Li^+ hops by calculating the fraction ($p_{\text{CN}, h \geq h^*}$) of Li^+ with the transient coordination number CN and $h_i(t) \geq h^*$ (red bars). A substantial fraction of Li^+ ions successfully hops when they are coordinated with only two PF_6^- anions. More interestingly, the Li^+ hopping rate becomes much faster when $\text{CN} = 2$. We calculate the hopping rate constant (k_{CN}) when Li^+ resides in the substate CN (the green line in Figure 3A). When $\text{CN} = 2$, k_{CN} is faster by 4 orders of magnitude than $\text{CN} = 3$ and 4. The product ($\nu_{\text{CN}} \equiv p_{\text{CN}} k_{\text{CN}}$) of p_{CN} and k_{CN} indicates the contribution of Li^+ configuration of CN to the hopping kinetics. $\nu_{\text{CN}} \approx 5.0 \times 10^{-6}$, 8.7×10^{-6} , and $2.3 \times 10^{-6} \text{ ps}^{-1}$ for $\text{CN} = 2, 3$, and 4, respectively. This suggests that the configuration of Li^+ with $\text{CN} = 2$ also contributes significantly to the hopping kinetics

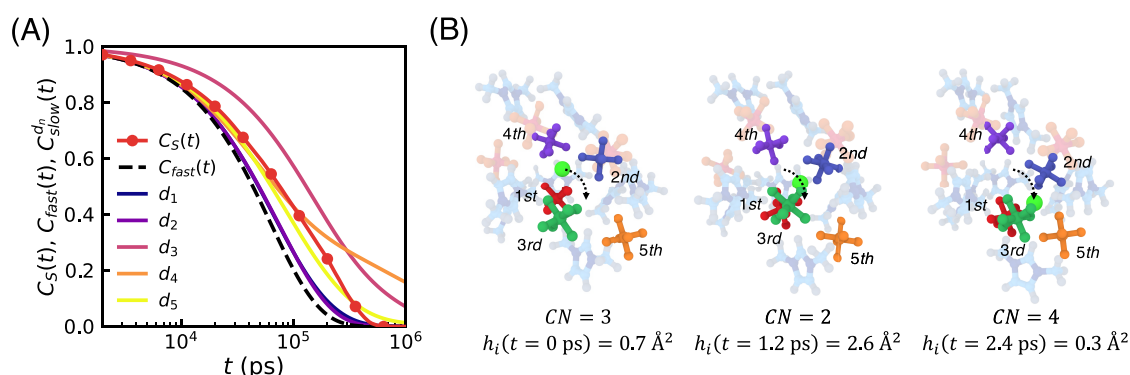


Figure 4. (A) Survival probabilities obtained from simulations and hop function analysis ($C_S(t)$), the fast-fluctuation limit ($C_{fast}(t)$), and the slow fluctuation limit ($C_{slow}^{CN}(t)$) with the distance (d_n) between Li^+ and the n th nearest PF_6^- anion as a slow variable. (B) Representative simulation trajectory snapshots illustrating the Li^+ transport mechanism. Initially at $t = 0$, the transient coordination number (CN) of Li^+ is 3 and $h_i(t = 0) = 0.7 \text{ \AA}^2$, thus Li^+ rattling within a cage. At $t = 1.2$ ps, the fourth nearest PF_6^- anion moves away from Li^+ opening the old cage and the fifth PF_6^- anion moves close to Li^+ forming a new cage. At this moment, CN of Li^+ becomes 2 and Li^+ hopping event occurs with $h_i(t = 1.2 \text{ ps}) = 2.6 \text{ \AA}^2 \geq h^*$. At $t = 2.4$, the new cage confines Li^+ well, thus CN becoming 4 and Li^+ rattling within the new cage with $h_i(t = 2.4 \text{ ps}) = 0.3 \text{ \AA}^2$. Notably, each label refers to the n th nearest anion at $t = 1.2$ ps.

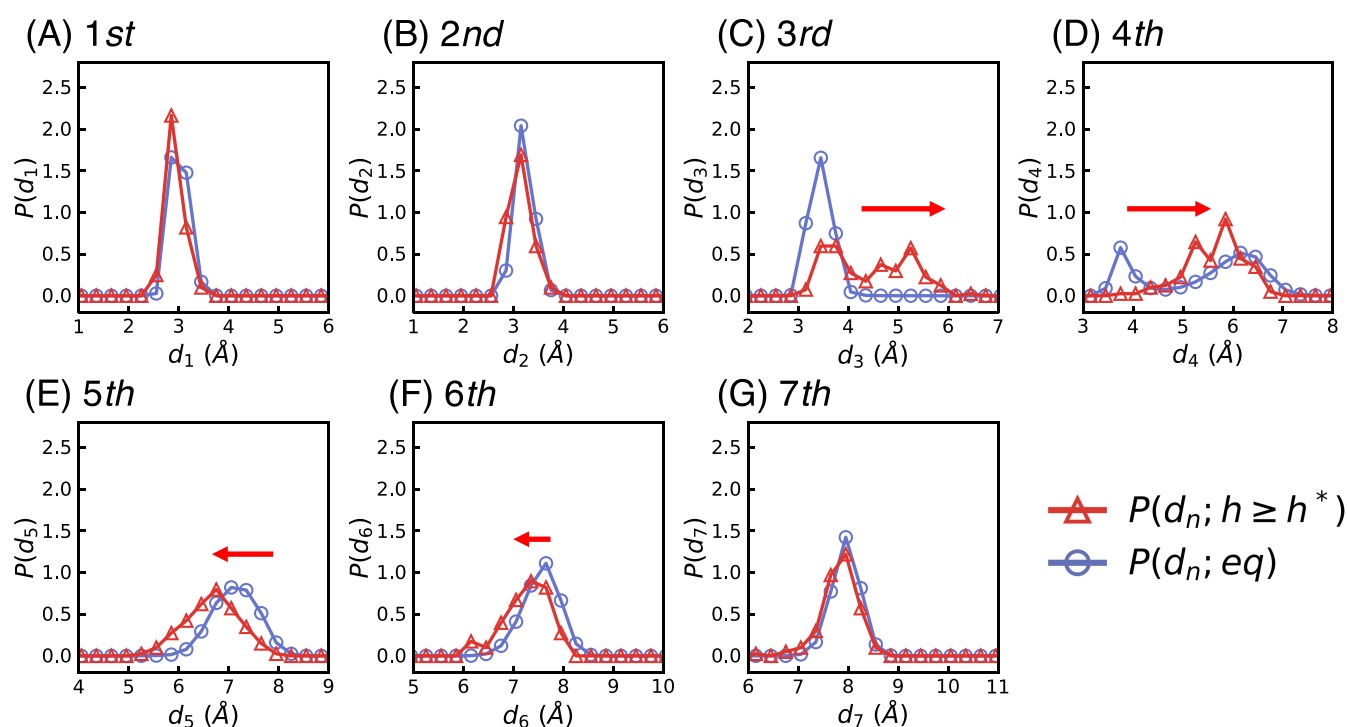


Figure 5. (A–G) Probability distribution functions ($P(d_n; eq)$ and $P(d_n; h \geq h^*)$) of distances (d_n) between Li^+ and its n th nearest PF_6^- anions. $P(d_n; eq)$ (blue) corresponds to the distribution functions averaged over all Li^+ ions, while $P(d_n; h \geq h^*)$ (red) corresponds to the distribution functions averaged over Li^+ ions that undergo hopping motions with $h_i(t) \geq h^*$.

and distortion of the typical three- or four-anion cage is often required for Li^+ hopping.

The coordination number, CN, is a good slow variable that describes the survival probability $C_S(t)$ successfully. Figure 3B depicts the survival probabilities $C_S(t)$, $C_{fast}(t)$, and $C_{slow}^{CN}(t)$. While $C_S(t)$ is obtained exactly from simulations, $C_{slow}^{CN}(t)$ is the survival probability estimated under the slow fluctuating limit with the slow variable of CN. $C_{fast}(t)$ is the survival probability estimated under the assumption of the fast-fluctuation limit. As shown in Figure 3B, $C_{fast}(t)$ decays too fast compared to $C_S(t)$. It is not surprising that Li^+ hopping statistics deviates from Poisson statistics with $R \approx 3$. On the other hand, $C_{slow}^{CN}(t)$ is in good agreement with $C_S(t)$, thus suggesting that the transient

coordination number (CN) should be a good slow variable to track the Li^+ transport mechanism. Considering that Li^+ ions with CN = 2 are very rare with a high free energy but contribute significantly to the hopping kinetics, the cage structure of the CN = 2 closely relates to the transition-state configuration for Li^+ ion transport, which shall be discussed more in the following subsection.

The Distance (d_n) between Li^+ and Its n th Nearest PF_6^- as a Slow Variable. In this subsection, we investigate how individual PF_6^- anions in a cage around Li^+ affect the hopping kinetics beyond the coordination number (CN). We consider the distance (d_n) between Li^+ and its n th nearest PF_6^- anion as a slow variable. In order to monitor the cage

reorganization before and after a hopping event, we examine up to the seventh nearest PF_6^- anions. Because the average coordination number is about 3.4, those seven nearest PF_6^- anions belong to either the old cage before Li^+ hopping or the new cage formed after the hopping event. We find that the first and the second nearest PF_6^- anions are often shared by old and new cages.

We calculate the survival probability $C_{\text{slow}}^{d_n}(t)$ under the assumption of the slow fluctuation limit with the slow variable d_n ($n = 1-7$). Comparing $C_S(t)$ with $C_{\text{slow}}^{d_n}(t)$ (Figure 4A), we find that $C_S(t) \approx C_{\text{slow}}^{d_4 d_5}(t)$, which indicates that d_4 and d_5 should be good slow variables that describe the non-Poisson Li^+ hopping kinetics properly. On the other hand, the variables of d_1 and d_2 do not capture the non-Poisson statistics of Li^+ hopping events properly because $C_{\text{slow}}^{d_1}(t)$ and $C_{\text{slow}}^{d_2}(t)$ decay too quickly compared to $C_S(t)$. In case of d_3 , $C_{\text{slow}}^{d_3}(t)$ decays more slowly than $C_S(t)$, indicating that d_3 is the most critical slow variable among d_n 's during the Li^+ hopping process.⁵⁸ Taken together, these findings suggest that the third, fourth, and fifth nearest PF_6^- anions around Li^+ should play critical roles in Li^+ hopping.

The probability distribution function ($P(d_n)$) of the distance (d_n) between Li^+ and its n th nearest PF_6^- anions provides insight into how the cage structure changes during the hopping event. We estimate $P(d_n)$ in two different ways: $P(d_n; eq)$ corresponds to the probability distribution function of d_n averaged over all possible configurations, while $P(d_n; h \geq h^*)$ corresponds to the distribution when Li^+ hops with $h_i(t) \geq h^*$. Therefore, $P(d_n; h \geq h^*)$ represents the structure of the cage when Li^+ undergoes hopping motions. The difference between $P(d_n; eq)$ and $P(d_n; h \geq h^*)$ reveals the critical structural change related to the hopping event.

Figure 5 depicts both $P(d_n; eq)$ and $P(d_n; h \geq h^*)$ for all seven nearest PF_6^- anions. In case of the first, second, and seventh nearest PF_6^- anions, there is little difference between $P(d_n; eq)$ and $P(d_n; h \geq h^*)$. In case of the third and fourth nearest anions (which belong to the old cage), the peaks in $P(d_n; eq)$ shift to the larger distance in $P(d_n; h \geq h^*)$. This indicates that the third and fourth nearest PF_6^- anions move away from Li^+ during the hopping event, thus opening the old cage and providing space for the Li^+ to hop. The formation of the critical configuration with $\text{CN} = 2$ occurs with the rearrangement of the third nearest anion. On the other hand, in the case of the fifth and sixth nearest anions (which belong to the new cage), the peaks in $P(d_n; eq)$ shift to the smaller distance in $P(d_n; h \geq h^*)$. This indicates that the fifth and sixth nearest PF_6^- anions move close to Li^+ , thus forming the new cage and confining Li^+ .

Figure 4B shows a representative simulation trajectory of a Li^+ hopping event and neighbor PF_6^- anions. The hop function $h_i(t)$ of this particular Li^+ changes from 0.7 to 2.6 to 0.3 Å² during this trajectory. Before and after the hopping event, its coordination numbers (CN) are 3 and 4, respectively. But when the hopping event occurs with $h_i(t = 1.2 \text{ ps}) = 2.6$ Å², the third and fourth nearest PF_6^- anions move away from Li^+ such that CN decreases down to 2, opening the old cage. This is consistent with our observation in the previous subsection that when $\text{CN} = 2$, the hopping rate constant k_{CN} is faster by 4 orders of magnitude than $\text{CN} = 3$ and 4. The cooperative motion of neighbor anions constructs the critical configuration (with $\text{CN} = 2$) of both old and new cages, which defines the key transition-state configuration governing Li^+ ion transport mechanism.

Taken together, these results establish a clear mechanistic distinction between matrix ion transport and Li^+ transport in Li-doped [MMIM][PF_6] OIPC. While matrix ion dynamics remain consistent with the paddle-wheel picture, Li^+ hopping is governed by cooperative rearrangements of surrounding PF_6^- anions that define the critical configurations for the Li^+ ion transport. This ion-specific mechanism highlights the importance of slow structural variables associated with coordination cage reorganization, providing a microscopic framework that goes beyond conventional rotation-assisted transport models.

CONCLUSIONS

In this work, we reassess the widely invoked paddle-wheel mechanism for ion transport in organic ionic plastic crystals using atomistic MD simulations combined with hop function analysis. We find that while translational hopping of matrix ions is strongly coupled to rotational motions of neighboring ions, consistent with the paddle-wheel picture, Li^+ hopping is largely decoupled from the rotational dynamics of its surrounding matrix ions. Instead, the hop function analysis reveals that Li^+ transport is governed by cooperative rearrangements of surrounding PF_6^- anions that reorganize the cage around the Li^+ . In particular, collective motions of the third, fourth, and fifth nearest PF_6^- anions define the transition-state configuration associated with a transient coordination number of two, enabling Li^+ to escape its original cage and enter a newly formed cage. When the transient coordination number is 2, the hopping rate increases by 4 orders of magnitude compared to other coordination states, enabling Li^+ to escape the cage effectively. These findings reveal that Li^+ transport in this system is controlled by slow structural variables related to cage reorganization rather than by rotation-assisted hopping. This work demonstrates that hop function analysis provides a powerful event-resolved framework for identifying microscopic transport mechanisms in heterogeneous solid electrolytes. We believe that the framework can be applicable to a wide range of plastic crystalline and complex ionic materials.

METHODS

Model and Molecular Dynamics Simulations

We perform atomistic molecular dynamics simulations for Li-doped [MMIM][PF_6] OIPCs. We take advantage of the unit cell structure from X-ray crystallography⁷⁸ and construct 40 independent initial configurations of $4 \times 4 \times 2$ supercells with 256 pairs of molecular ions. We introduce Schottky-type vacancies by randomly choosing and removing pairs of [MMIM]⁺ and PF_6^- ions from the supercell. This does not violate the charge neutrality condition, which is essential to the convergence of the calculation of long-range Coulomb interactions. The concentration (c_s) of Schottky vacancies is $c_s = 0.78$ mol % in this study. Four Li^+ ions are, then, doped by replacing four [MMIM]⁺ cations.

We employ the CL&P force field developed based on the OPLS-AA force fields and optimized for ionic liquids.^{79,80} A recent simulation study on [MMIM][PF_6] without Li^+ showed that polarizability does not significantly affect the crystal structure and rotational dynamics of matrix ions at $T = 300 \text{ K}$.⁸¹ Furthermore, as many-body polarizable force fields are computationally demanding, the nonpolarizable CL&P force field is used in this study. The CL&P force field has been reported to successfully describe the crystalline structure and diffusion of molecular ions compared to experiments.^{79,80,82-84} For example, simulation results for the diffusion coefficients of molecular ions in methyl-ethylimidazolium dicyana-

vide at 303 K were consistent with experimental values.⁸⁵ Its functional form is as follows

$$V_{\text{tot}} = \sum_{\text{bonds}} k_b(r - r_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} \sum_{m=1}^n \frac{k_\chi}{2} [1 + (-1)^{m+1} \cos(m\chi)] + \sum_{\text{impropers}} \sum_{m=1}^n \frac{k_\psi}{2} [1 + (-1)^{m+1} \cos(m\psi)] + \sum_{i=1}^{N-1} \sum_{i < j}^N \left[4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right] \quad (1)$$

Here, r , θ , χ , and ψ denote the bond distance, bond angle, dihedral angle, and improper angle, respectively. The nonbonding interactions (Lennard-Jones and Coulomb potentials) are truncated and shifted at the cutoff distance of 12 Å. The long-range Coulomb interaction beyond the cutoff distances is calculated by using the particle-mesh Ewald (PME) algorithm. Force field parameters are obtained from the ffitool package made by the Pádua group.^{86,87} We propagate the OIPC systems by using OpenMM package.⁸⁸

We equilibrate OIPC systems by conducting isobaric–isothermal (NPT) ensemble simulations at 1 atm and 300 K. We employ the Langevin thermostat with a friction coefficient of 1 ps^{−1} and the anisotropic Monte Carlo barostat, attempting a volume change every 25 fs. We equilibrate systems during 100 ns and check that the total energies and densities converge to equilibrium values. After equilibration, canonical (NVT) ensemble simulations are conducted with the Nose-Hoover thermostat to obtain structural and dynamic properties. The integration time step for all processes is fixed to 1 fs. For the estimation of equilibrium properties, we obtain 40 independent 60 ns long trajectories. All the error bars in the figures represent a standard error over 40 ensembles. Additionally, we obtain a single 2 μs long trajectory to calculate the survival probability ($C_s(t)$) as shall be discussed below. The trajectory data are recorded at every 200 fs to monitor the transient hopping event.

To investigate the structure of ions in Li-doped [MMIM][PF₆], we calculate pair correlation functions of ions as follows

$$g_{A,B}(r) = \frac{V}{4\pi r^2 N_A N_B} \sum_{i \neq j} \langle \delta(r - |\vec{r}_i - \vec{r}_j|) \rangle \quad (2)$$

where V , N_A , and N_B are the volume and the numbers of A and B ions, respectively. Here, $\vec{r}_i$ denotes the position vector of the center of mass of the i th A ion. $\langle \dots \rangle$ represents ensemble averaging. To monitor the mobilities of Li⁺, [MMIM]⁺, and PF₆[−] in [MMIM][PF₆], we calculate the mean squared displacements ($\langle \Delta \vec{r}(t)^2 \rangle$) of the centers of mass of ions, i.e., $\langle \Delta \vec{r}(t)^2 \rangle \equiv \langle (\vec{r}(t) - \vec{r}(0))^2 \rangle$, where $\vec{r}(t)$ is the position vector of the center of mass of an ion at time t .

We investigate the rotational motions by calculating the angular displacement, $\theta_i = \arccos(\vec{v}_i(t + \Delta t/2) \cdot \vec{v}_i(t - \Delta t/2))$. Here, $\vec{v}_i(t)$ is the characteristic unit vector that represents the rotational motion of the i th ion. In this study, we consider two types of rotational modes (Figure 1A). In case of [MMIM]⁺ cations, $\vec{v}_{[\text{MMIM}]^+}(t)$ is the unit vector normal to a imidazolium ring at time t and captures the flip-flop rotation of [MMIM]⁺. In case of PF₆[−] anions, $\vec{v}_{\text{PF}_6^-}(t)$ corresponds to the unit vector pointing from the P atom to the F atom at time t . $\vec{v}_{[\text{MMIM}]^+}(t)$ and $\vec{v}_{\text{PF}_6^-}(t)$ are used to calculate the angular displacement distribution functions $P(\theta, \Delta t)$ of θ , i.e., how much the ion rotates during Δt .

Hop Function Analysis for the Microscopic Transport Mechanism

In order to identify individual hopping events of ions, we define the hop function $h_i(t)$ as follows

$$h_i(t) = \sqrt{\langle (\vec{r}_i(t) - \langle \vec{r}_i(t) \rangle_B)^2 \rangle_A \langle (\vec{r}_i(t) - \langle \vec{r}_i(t) \rangle_A)^2 \rangle_B} \quad (3)$$

Here, $\vec{r}_i(t)$ is the position vector of the center of mass of the i th ion at time t . $\langle X \rangle_A$ and $\langle X \rangle_B$ are the backward and forward time averages of X in two different time windows A and B, respectively, i.e., $\langle X \rangle_A = \frac{1}{\Delta t/2} \int_{t-\Delta t/2}^t X(\tau) d\tau$ and $\langle X \rangle_B = \frac{1}{\Delta t/2} \int_t^{t+\Delta t/2} X(\tau) d\tau$. $\langle (\vec{r}_i(t) - \langle \vec{r}_i(t) \rangle_B)^2 \rangle_A$ in the above equation quantifies the variance of the ion displacement from its forward time average calculated in the backward time window of $(t - \Delta t/2, t)$. Similarly, $\langle (\vec{r}_i(t) - \langle \vec{r}_i(t) \rangle_A)^2 \rangle_B$ is the variance from the backward-time displacement average calculated in the forward time window of $(t, t + \Delta t/2)$. Coupling two terms symmetrically makes the hop function $h_i(t)$ respond sensitively when the i th ion undergoes a hopping motion. $h_i(t)$ was, therefore, employed successfully to elucidate the transport mechanism of various heterogeneous systems, including supercooled water and dense granular media.^{58,60–63} Because the identification of individual hopping motions of particles is important, there have been variants of $h_i(t)$. For example, Wu et al. employed an accumulation hop function to identify the proton hopping event successfully.⁸⁹ In order to determine Δt and time windows in the eq 3, we calculate the mean squared displacements ($\langle \Delta \vec{r}(t)^2 \rangle$) of the centers of mass of ions.

Δt is determined as the time of minimum diffusivity where $\frac{d \log \langle \Delta \vec{r}(t)^2 \rangle}{d \log t}$

is the smallest. In this study, $\frac{d \log \langle \Delta \vec{r}(t)^2 \rangle}{d \log t}$ reaches its minimum at $t = 2.4$ ps for all ionic species such that $\Delta t = 2.4$ ps (Supporting Information).

To distinguish the local rattling motion (a cage state) and the hopping motion (a hop state) of ions, we calculate the probability distribution function $P(h) \left(\equiv \frac{1}{N_{\text{tot}}} \sum_i^{N_{\text{tot}}} \delta(h - h_i(t)) \right)$ of $h_i(t)$ and its cumulative distribution $R(h) \equiv \int_h^\infty P(h') dh'$ (Supporting Information). Here, N_{tot} is the total number of events used for the estimation of $h_i(t)$. $R(h)$ decreases rapidly up to $h = h^*$ and shows an exponential decay for $h \geq h^*$ with less frequent but large hopping motions. Small rattling motions with $h < h^*$ are correlated with each other, while large hopping motions with $h \geq h^*$ are independent events such that $R(h)$ decays exponentially at $h \geq h^*$. h^* is, therefore, a criterion between hop and cage states such that a Li⁺ ion can be assigned at time t to either a cage state with $h_i(t) < h^*$ or a hop state with $h_i(t) \geq h^*$. We determine the value of h^* by using the equation $\frac{d \ln R(h)}{dh} \Big|_{h=h^*} = 0$ and find that $h^* = 2.3$ Å² for all ion species (Supporting Information).

Once the individual hopping events are identified and cage (or hop) states are assigned based on $h_i(t)$ and h^* , we estimate how long ions stay confined within cages before making hopping motions by calculating the residence time distribution, $\psi(t)$. This corresponds to the probability distribution function that an ion remains in the cage state with $h_i(t) < h^*$ for a duration t before hopping. In case the ion hopping events follow Poisson statistics, $\psi(t) = k \exp(-kt)$ and the randomness parameter R becomes 1. R is defined as follows^{58,90}

$$R = \frac{\langle t^2 \rangle - \langle t \rangle^2}{\langle t \rangle^2} \quad (4)$$

where $\langle t^n \rangle = \int t^n \psi(t) dt$. Deviation of R from 1 indicates that the hopping event statistics becomes non-Poisson, thus serving as a sensitive metric for cooperative and disordered hopping processes.

We define the residence probability $C_R(t)$, the probability that an ion remains trapped in a cage state during at least time t as follows

$$C_R(t) = \int_t^\infty \psi(\tau) d\tau \quad (5)$$

$C_R(t)$, then, allows us to estimate the survival probability $C_s(t)$ that quantifies the fraction of ions remaining in the cage beyond time t , i.e.

$$C_s(t) = \frac{1}{\langle t \rangle} \int_t^\infty C_R(\tau) d\tau \quad (6)$$

If the hopping event were to follow Poisson statistics with $\psi(t) = k \exp(-kt)$, both residence and survival probabilities become

exponential, i.e., $C_R(t) = C_S(t) = \exp(-kt)$. Note that because we obtain $\psi(t)$ from hop functions $h_i(t)$, $C_S(t)$ can be obtained directly from a 2 μ s long trajectory.

The microscopic ion transport mechanism can be revealed by investigating the decay of the survival probability $C_S(t)$, which follows a first-order differential equation as follows

$$\frac{dC_S(t)}{dt} = -k(t)C_S(t) \quad (7)$$

where $k(t)$ is a time-dependent hopping rate constant. $k(t)$ may fluctuate due to the change in the local environment around an ion. The formal solution to this differential equation is $C_S(t) = \langle \exp(-\int_0^t k(\tau)d\tau) \rangle$.⁵⁷ There are two limiting cases to this formal solution: (1) fast-fluctuation limit, where the local environment fluctuates at much shorter time scales than the average cage residence time ($\langle t \rangle$), and (2) slow fluctuation limit, where the fluctuations of local environment, which modulate the hopping motions, occur on time scales much longer than $\langle t \rangle$.

In the fast-fluctuation limit where local environments fluctuate so quickly, $k(t)$ is already averaged over local environment fluctuations during a hopping event such that $C_S(t)$ reduces to an exponential decay with an average rate constant of k_{fast} , i.e., $C_S(t) \approx C_{\text{fast}}(t) = \exp(-k_{\text{fast}}t)$. When assuming this fast fluctuating limit, k_{fast} can be obtained from simulation results by using $k_{\text{fast}} = N_{\text{hop}}/T_{\text{tot}}$ where N_{hop} is the total number of individual hopping events with $h_i(t) \geq h^*$ during a trajectory and T_{tot} is the total duration of the trajectory.

In the second limit of slow fluctuation, the local environment does not change much during a hopping event and individual ions experience different heterogeneous local environments during their hopping events such that $C_S(t)$ is given by the linear combination ($C_{\text{slow}}(t)$) of multiple exponential functions weighted by the distribution of k , i.e.

$$C_{\text{slow}} = \langle \exp(-kt) \rangle_k \quad (8)$$

The slow fluctuation and the distribution of k relate closely to the slow variables of local environments that critically determine the local hopping kinetics. Therefore, the ion can be considered as residing in quasi-static substates of slow variables.

In order to explore various potential slow variables that critically influence the decay of the survival probability $C_S(t)$ of Li^+ ions, we consider two different types of structural descriptors: (i) the transient coordination number (CN) of PF_6^- ions around Li^+ ions and (ii) the distance (d_n) between a particular Li^+ and its n th nearest neighboring PF_6^- anion. Then, $C_{\text{slow}}(t)$ can be estimated as follows

$$C_{\text{slow}}(t) = \sum_{i=1}^{N_s} p_i \exp(-k_i t) \quad (9)$$

$$= \sum_{i=1}^{N_s} \frac{N_{\text{hop},i}}{N_T} \exp\left(-\frac{N_{\text{hop},i}}{N_{T,i}} \Delta T\right) \quad (10)$$

Here, i and N_s denote the index of a substate and the total number of substates considered in this study, respectively. For example, when we consider the transient coordination number (CN) as the structural descriptor, $i = 3$ corresponds to the substate where the Li^+ ion is coordinated by three PF_6^- anions with $\text{CN} = 3$. When the distance d_n is employed, we discretize the distance d_n into multiple substates with a bin width of $\Delta r = 0.3 \text{ \AA}$. $i = 7$ corresponds to a substate of the Li^+ ion with the distance from the n th nearest PF_6^- anion between $6\Delta r$ and $7\Delta r$. $N_{\text{hop},i}$ is the number of hopping events that occur while the Li^+ ion is in the i th substate. $N_{T,i}$ is the total number of the simulation configurations with Li^+ ion in the i th substate and $N_T = \sum_i N_{T,i}$. ΔT is the time interval between simulation configurations obtained such that the rate constant k_i of the substate i is $k_i = \frac{N_{\text{hop},i}}{N_{T,i} \Delta T}$. Identifying a slow variable that yields $C_{\text{slow}}(t)$ that accurately reproduces $C_S(t)$ provides insight into the ion transport mechanism at a molecular level.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c04713>.

Simulation results for the radial distribution functions ($g_{A,B}(r)$), time-dependent exponents of mean squared displacements ($\langle \Delta \vec{r}(t)^2 \rangle$), cumulative probability distributions $R(h)$ of hop function values, representative time traces of hop functions ($h_i(t)$), probability distribution functions ($P(\theta, \Delta t)$) of the angular displacement (θ) of neighbor ions for translation-rotation couplings at different time scales of $\Delta t = 10$ and 100 ps, and quaternion-based rotational analysis (PDF)

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Notes

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