

Quantifying the Partitioning of Vehicular and Structural Lithium Transport in Binary Carbonate Electrolytes

Aaron P. Charnay,[#] Benjamin P. Charnay,[#] Junkun Pan, Yan Zhang, Matthew W. Kanan, Weizhong Zheng,^{*} and Michael D. Fayer^{*}



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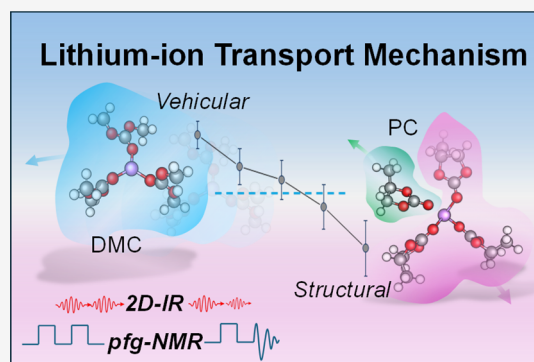


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Supporting Information

ABSTRACT: Lithium-ion batteries use mixed-solvent electrolytes, but the effect of solvent composition on the mechanism of lithium-ion transport is not well understood. Here, we quantify the partitioning between vehicular and structural Li^+ transport mechanisms for binary mixtures of dimethyl carbonate (DMC) and propylene carbonate (PC) using a combination of 2D infrared spectroscopy and pulsed-field gradient NMR. The primary transport mechanism varies monotonically, with 65% vehicular transport in pure DMC and only 35% vehicular transport in pure PC. Li^+ structural step lengths of 1.2–1.5 Å were determined from the experimental data. The outcomes of this study are compared to previously described molecular dynamics simulations. The results presented here indicate that typical carbonate electrolytes cannot tailor structural transport and that new solvent chemistries may be required to enhance this diffusion pathway.



An open question in LIB electrolytes is the mechanism of Li^+ transport, which is commonly separated into two categories: vehicular transport, where Li^+ diffuses with an intact solvent shell, and structural transport, in which the diffusion is induced by Li^+ dissociation from the solvating species.^{1,2} It is accepted that both mechanisms occur in pure battery electrolytes^{3,4} though quantitative measurements of transport mechanism partitioning are lacking. To date, the best attempts at understanding the Li^+ transport mechanism involve the use of pulsed field gradient nuclear magnetic resonance (pfg-NMR) spectroscopy to extract diffusion coefficients,^{5,6} MD simulations to estimate solvent dissociation times,^{7–9} and quasi-inelastic neutron scattering to measure solvent–ion interaction lifetimes.^{10,11} Here, we present the results of an approach that combines direct measurements of Li^+ –solvent dissociation times, solvent structure, and diffusion to determine the percentages of transport by vehicular and structural diffusion in binary solvent electrolytes (dimethyl carbonate (DMC) and propylene carbonate (PC)) over the full range of composition. This approach is compared with a previously reported method for ascertaining the transport mechanism using molecular dynamics simulations. We also determine the average translation distance of Li^+ that gives rise to the structural diffusion random walk.

Mixtures of solvents are often used as battery electrolytes because carbonates with lower viscosity can facilitate higher conductivity but generally have lower dielectric constants, e.g., dimethyl carbonate (DMC) $\epsilon = 3.11$,¹² vs higher viscosity propylene carbonate (PC) $\epsilon = 64.9$.¹² Here, we select a representative binary system of DMC and PC. The liquid state of PC gives access to the entire range of compositions. A salt-to-solvent molar ratio of 1:7 was used for all solvent compositions, where the ratio is given as 1 LiTFSI: $n\text{PC} + m\text{DMC}$, where $n + m = 7$. The molarity with this ratio is ~ 1.3 M, slightly higher than previously studied lithium salt/electrolyte systems¹³ and thereby improving spectral resolution.

The long-lived vibrational probe phenyl selenocyanate (PSC) was used at a low concentration (250 mM) to eliminate changes in solution properties and prevent vibrational excitation transfer.^{14,15} It has previously been shown that

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PSC and PC have almost identical Li^+ binding energies.¹⁶ We have performed DFT calculations on a representative DMC- Li^+ structures to confirm that its Li^+ binding strength is also similar to that of PSC (see Supporting Information (SI), S1). PSC exhibits two CN stretching peaks in its FT-IR spectrum (Figure 1A). The peak at 2155 cm^{-1} arises from PSC that is

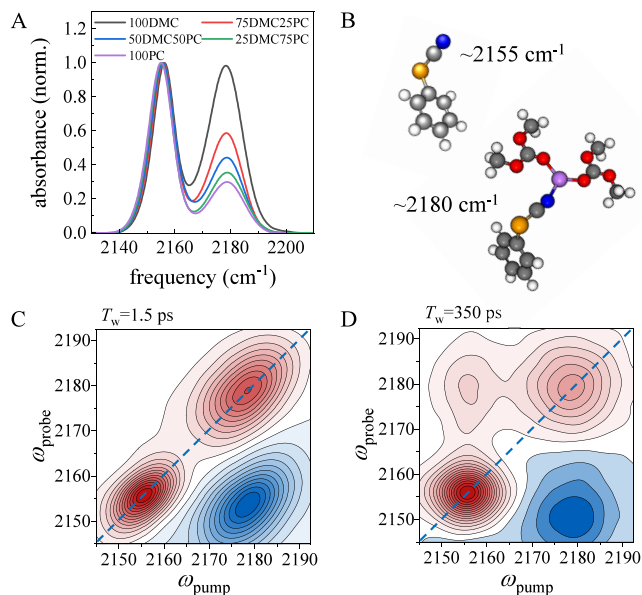


Figure 1. (A) FT-IR spectra of CN stretch of PSC in 1:7 LiTFSI: solvent systems ranging from pure dimethyl carbonate to pure propylene carbonate. (B) Scheme depicting the origin of the two peaks in the FTIR spectrum, where the PSC CN coordinated to a Li^+ is shifted from 2155 cm^{-1} to $\sim 2180\text{ cm}^{-1}$. (C) 2D-IR spectrum of 25DMC75PC at a waiting time of 1.5 ps. Two on-diagonal peaks (red) are clearly visible with one off-diagonal 1–2 peak (blue). (D) 2D-IR spectrum of 25DMC75PC at a waiting time of 350 ps. An off-diagonal exchange peak corresponding to PSCs originally free in solution, which have become bound to lithium, is now clearly visible above the diagonal (dashed blue line), and the on-diagonal peaks themselves are less elongated along the diagonal, indicating spectral diffusion.

not bound to Li^+ , while the peak at 2180 cm^{-1} arises from PSC bound to Li^+ (Figure 1B). These two populations are in equilibrium and exchange by association with and dissociation from Li^+ . The exchange can be measured quantitatively using ultrafast two-dimensional Infrared spectroscopy (2D-IR).¹⁷ Recent MD studies show conflicting results for the solvation shell dissociation times for different electrolytes and the partitioning between different transport mechanisms. Andersson et al. found dissociation times of 246 and 327 ps for EC and DMC, respectively, in a 1:1 mixture of EC: DMC with 1 M LiPF_6 .¹⁸ These values are relatively close to the range of values measured by 2D-IR for the dissociation of PSC and PC with various LiTFSI concentrations (400–1000 ps).¹⁶ However, Self et al. reported dissociation times of several nanoseconds,⁴ significantly exceeding experimentally observed values.¹⁶ Han et al. reported dissociation times of $\sim 30\text{ ps}$ for both EC and DMC with 1 M LiPF_6 ,¹⁹ an order of magnitude faster than those observed experimentally with 2D-IR techniques.¹⁶

2D-IR is uniquely suited to measure Li^+ dissociation times over a broad range of time scales, as it can observe the exchange between molecules that are unbound and bound to

Li^+ . In the 2D-IR spectrum for an electrolyte with 25% DMC and 75% PC (25DMC75PC), three peaks are observed at short time, ($T_w = 1.5\text{ ps}$) (Figure 1C). The two red peaks on the diagonal (dashed line) correspond to the two peaks in the FT-IR spectrum. The higher frequency peak is from the bound probe, and the lower frequency peak is from PSC free in solution. They are both from the vibrational 0–1 transitions. The blue peak below the diagonal arises from the 1–2 transition of the bound probe and is shifted to lower frequency by the vibrational anharmonicity.²⁰ It is only necessary to analyze the red 0–1 peaks to obtain all the dynamical information.

There are four pulses in a 2D-IR experiment. The first two pulses, separated by time τ , label the probe molecules' initial frequencies (ω_{pump} , horizontal axis). The third pulse arrives after a waiting time, T_w , and stimulates the emission of a fourth pulse: the vibrational echo, which is the signal. The vibrational echo carries the final frequencies after the system has evolved for time T_w (ω_{probe} , vertical axis). At a later time, $T_w = 350\text{ ps}$ (Figure 1D), a peak is observed above the diagonal. This exchange peak is from the population of PSC that becomes bound at later T_w . It was free when initially excited by the pump (horizontal axis frequency), but subsequently becomes complexed to Li^+ with the bound frequency (vertical axis frequency). Another exchange peak also occurs when the initially bound population becomes unbound, but it is obscured by the 1–2 transition blue peak. Because the system is in equilibrium, the rate of free-to-bound equals the rate of bound-to-free; the increase in the two off-diagonal exchange peak volumes with increasing T_w is identical. Therefore, only one exchange peak volume is necessary to obtain the exchange dynamics (see SI, note S2.1).

From the T_w dependence of the volumes of the two on-diagonal peaks and the exchange peak above the diagonal (Figure 1D), exchange times can be extracted by fitting to a set of kinetic equations for two species.¹⁷ The diagonal peaks decay with the vibrational probe lifetime and exchange time, and the off-diagonal peak initially grows with exchange time and eventually decays with the probe lifetime. To fit the volumes to the kinetic model, the transition dipole ratio between the bound and free peaks was measured. Details for measuring the transition dipole ratio are given in SI, note S2.2.

Figure 2A shows the data (symbols) for the two diagonal peaks and the exchange peak for the DMC25%PC75% solution. One set of parameters must fit the three time-dependent curves. As is apparent from Figure 2A, the fits (solid curves) using the kinetic model are excellent. This same analysis was performed on the mixtures of DMC and PC, ranging from pure PC to pure DMC. The association time of the probe with a Li^+ solvation cluster (red points, Figure 2B) increases monotonically with increasing PC. This trend is attributed to the increase in concentration of free probe relative to bound probe, as evident in the FT-IR spectrum in Figure 1A. The slight difference in the binding energy of DMC and PC to Li^+ leads to differences in the equilibrium concentrations of bound and free PSC and, consequently, in the association time.²¹ By contrast, the more important dissociation time exhibits nonmonotonic behavior with a minimum at 25% DMC and 75% PC, $\sim 15\%$ below the maximum, which is well outside the error bars (inset Figure 2B). Nonmonotonic behavior in the dissociation times has been observed in MD simulations of mixed carbonate electrolytes.^{19,22}

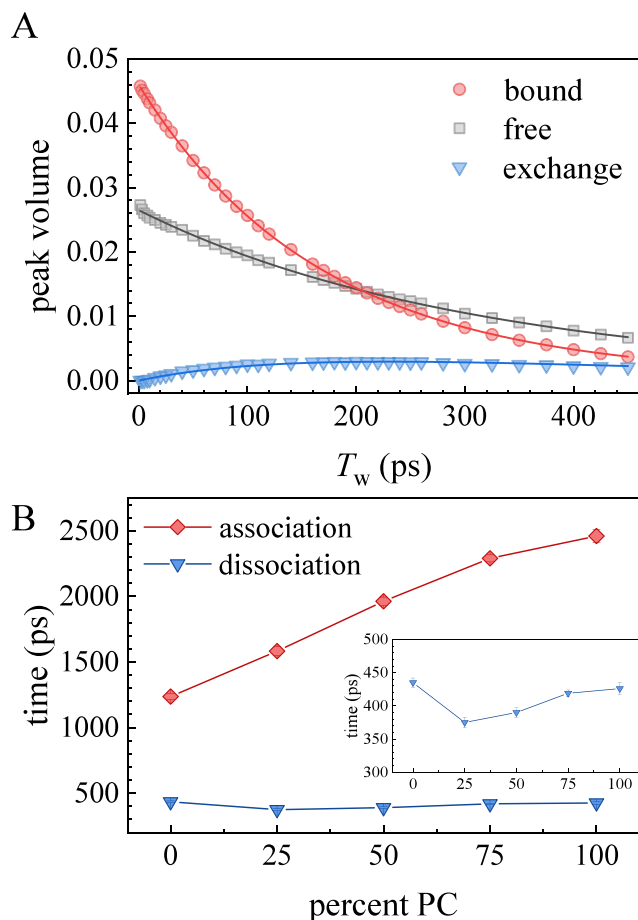


Figure 2. (A) Peak volumes data (symbols) for the 25DMC75PC system as a function of waiting time with fits (solid lines) to the two-species kinetic model. (B) Association (red diamonds) and dissociation (blue triangles) times for all solvent compositions considered. The inset shows the dissociation times with an enlarged y-axis to emphasize the nonmonotonic behavior with a minimum at 75DMC25PC.

Previous spectral diffusion measurements, which also measure dissociation times, have shown that the dissociation times of PSC and PC are nearly identical.¹⁶ The same analysis was applied to DMC and likewise confirms very similar dissociation times for PSC, DMC, and PC (see SI, note S2.3 and Figure S4B). The similarity of the dissociation times for PSC and DMC is further supported by the near-identical binding energy of PSC-Li⁺ and DMC-Li⁺ in representative clusters calculated using DFT (see SI, note S1.4, Figure S1).

Polarization selective pump probe (PSPP) spectroscopy was applied to the CN stretch of the PSC in the DMC/PC/LiTFSI system to elucidate the structures of the solvation sheaths. The pump pulse prepares an anisotropic orientational distribution of vibrationally excited CNs, and the probe pulse measures the decay of the anisotropy to a random orientation with increasing time. PSPP measures orientational relaxation of free PSC and of the entire Li⁺ solvation cluster when PSC is bound. Reorientation times are described by the Stokes–Einstein–Debye (SED) relation,²³ which is linear in the volume of the reorientating species, the viscosity, and the inverse of the temperature. Because it has a smaller volume, the reorientation time of free PSC will be faster than that of the solvation cluster.

Figure 3A shows the orientation decay time constants, τ_m , for the free and bound species (Figure S7 for anisotropy

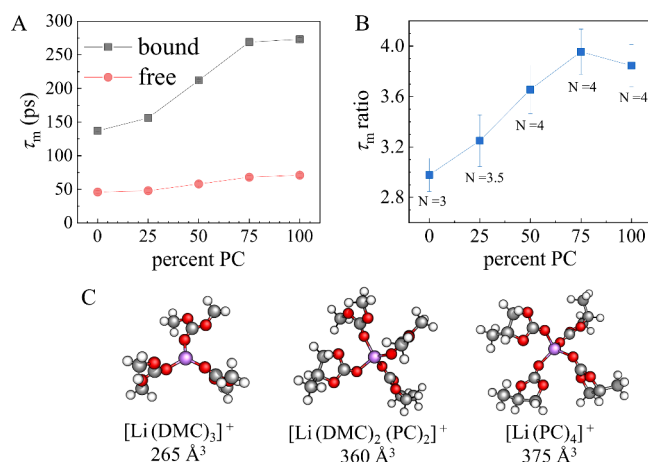


Figure 3. (A) Full reorientation time, τ_m , for the bound and free PSC from biexponential wobbling-in-a-cone fits of the PSPP data for each solvent composition. (B) Ratios of the full reorientation times for each solvent composition. Coordination numbers for each solvent composition are given below each point as calculated in SI, section S2.4. (C) Representative geometry-optimized structures for possible cluster compositions are shown with their respective volumes.

curves). The free reorientation time varies with the concentration of DMC and PC due to viscosity changes. The bound reorientation time changes both because the solvation shell structure and viscosity change with concentration. The ratios of the bound to free reorientation times are given in Figure 3B. The ratio of the times is equal to the ratio of the bound and free species volumes (see Supporting Information, S2.4). The volume of the free PSC (see structure in Figure 1B) was obtained from high level DFT calculations,²⁴ and is 109 Å³. The volumes of the bound species vary nearly monotonically from 327 Å³ to 414 Å³ as the solvent composition is varied. The differences in the bound volumes are attributed to two effects. The major effect is the reported lower average solvation number of DMC compared to those of PC.^{21,25,26} DMC has a coordination number of 3–4 per Li⁺ compared to ~4 for PC. More minor, DMC is smaller than PC (72 Å³ compared to 81 Å³). DFT calculations were used to determine the structures and volumes of various possible solvation shell compositions. Examples of structures consistent with the measured volumes are shown in Figure 3C. We devised a quantitative approach that determines the fraction of vehicular and structural transport (see Figure 4A) that combine to give the measured diffusion constant. Figure 4B shows a plot of the concentration-dependent diffusion coefficients of Li⁺ measured by pfg-NMR versus 1/viscosity (black points). The points fall on a line, consistent with the slope from the Stokes–Einstein (SE) equation. However, there is a constant positive offset for each point, a distinct deviation from the SE prediction. Plotting the SE predicted vehicular diffusion coefficients (red points) from the radii for the solvated Li⁺ obtained from a combination of ultrafast anisotropy and DFT calculations (see SI, note S1.2 for complete discussion) shows a line parallel to the experimentally observed diffusion constants with an intercept of zero. The parallel lines indicate that the measured diffusion

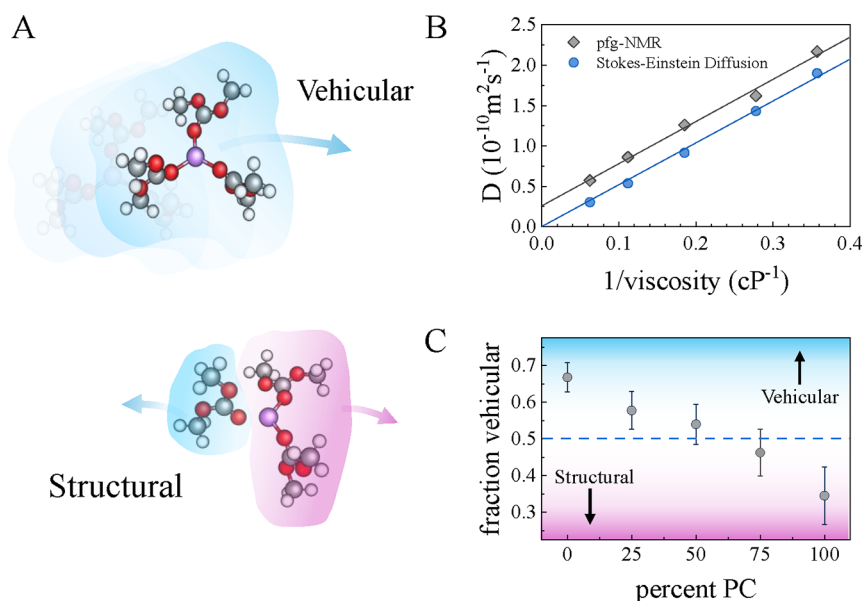


Figure 4. (A) Scheme depicting vehicular (top) and structural (bottom) diffusion for a representative DMC-Li cluster. For the vehicular case, the lithium ion and its solvent sheath travel together, as indicated by the blue arrow. In the structural case, a dissociation event drives a single solvent molecule (blue) in a unique direction from the lithium ion and its remaining solvent sheath (purple). (B) Plot of diffusion coefficient vs $1/\text{viscosity}$ for all solvent compositions (black points) with a linear fit (solid black curve) showing a clear positive offset. Stokes–Einstein diffusion coefficients, calculated using the radii from SI, section S2.5 (red points), also fit a line (solid red curve), indicating a parallel but offset relationship to the experimental diffusion coefficients, likely due to structural diffusion. Using the offset as the structural diffusion coefficient yields Structural Step Lengths from pure DMC to pure PC of 1.49 ± 0.05 Å, 1.28 ± 0.05 Å, 1.22 ± 0.06 Å, 1.27 ± 0.06 Å, and 1.28 ± 0.06 Å. (C) The fraction of vehicular transport for each solvent composition decreases monotonically with increasing PC concentration.

constants exhibit SE behavior, plus an additional diffusive contribution that is constant for all PC concentrations and independent of viscosity. We attribute this offset to structural diffusion.

This constant structural diffusion contribution to the total diffusion for all mixture concentrations will occur if the solvation shell dissociation times are nearly the same when the correct time measure is used. As shown in Figure 3B, the coordination number, N , of Li^+ increases from 3 to 4 with increasing PC concentration. The 2D-IR measured time for the PSC probe to dissociate is nearly the same as that of a solvent molecule dissociation for PC and DMC. However, structural diffusion is caused by the translation of Li^+ by the dissociation of any of the N solvation shell members.²⁷ Therefore, the appropriate time associated with structural diffusion is $\tau_s = \tau_d/N$. N for each solvent composition is determined by the results of the PSPP experiments and DFT calculation (see SI, note S1.4). By using $\tau_{ss} = \tau_d/N$ and the structural diffusion constant found by fitting the experimental diffusion constants as a function of $1/\text{viscosity}$ to a line with constant offset, we can determine the average Structural Step Length (SSL). The SSL is the step size in the random walk that results in the structural diffusion constant, D_s .

$$\text{SSL} = \sqrt{6D_s\tau_{ss}} \quad (1)$$

The right-hand side of eq 1 is the structural root-mean-squared displacement in time τ_{ss} . The SSLs range from 1.2 to 1.5 Å (Figure S10).

The fraction of the total vehicular Li^+ diffusion measured by pfg-NMR is given by

$$f_v = \frac{\sqrt{6D_{\text{NMR}}\tau_{ss}} - \text{SSL}}{\sqrt{6D_{\text{NMR}}\tau_{ss}}} \quad (2)$$

In this analysis, a value >0.5 is predominantly vehicular and a value <0.5 is predominantly structural. The fractions of vehicular transport vary from $\sim 65\%$ for pure DMC to $\sim 35\%$ for pure PC. This conclusion of predominantly structural transport in the pure PC system agrees with the work of Borodin et al. for the related EC/ LiPF_6 system² and prior experiments on LiTFSI/PC .¹⁶

Given that the structural diffusion remains essentially unchanged as the relative concentrations of PC and DMC are varied, but the extent of vehicular diffusion increases with the inverse of viscosity, in agreement with the SE equation, one might expect the total conductivity to also increase with decreasing viscosity (i.e., increasing DMC concentration). However, this is not typically the case with mixed solvent electrolytes. DMC should have significantly higher cation–anion correlated motion compared to PC because of its much lower dielectric constant.^{28,29} To confirm this, conductivity measurements were performed on all DMC/PC mixtures studied here, as well as additional pfg-NMR on the ^{19}F nuclei of TFSI[−] to extract its diffusion constants. By using the experimentally observed diffusion constants of Li^+ and TFSI[−] and their concentrations in the Nernst–Einstein equation, the expected conductivities were calculated. The ratio of experimentally observed EIS conductivity to the Nernst–Einstein-predicted conductivity is a measure of ionicity and an indicator of the extent of correlated ion motion (see Figure S12). It was found that ionicity increases from 30% in pure DMC to 45% in the 50/50 mixture, then approximately plateaus. The Onsager conductivity coefficients were also

calculated (see SI, note S3.6 for the discussion of ion–ion and ion–solvent correlations).

MD simulations have attempted to determine the dominant mechanism of Li^+ transport in carbonate electrolytes by first finding the distance, L^c , that Li^+ travels in the time, τ_{res} , for a solvation molecule to dissociate from the solvation shell. The 2D-IR observable τ_d is identical to τ_{res} .

$$L^c = \sqrt{6D_{\text{NMR}}\tau_{\text{res}}} \quad (3)$$

Here, D_{NMR} is the Li^+ diffusion coefficient determined via pulsed-field-gradient NMR (pfg-NMR), and $\sqrt{6D_{\text{NMR}}\tau_{\text{res}}}$ is the root-mean-squared displacement in time, τ_{res} . L^c is compared to L^s , which was defined as the approximate maximum structural step length lithium takes in the dissociation time.⁴ We have calculated the L^s values for solvent mixtures studied here via all-atom MD simulations. In this qualitative approach, if

$$L^c/L^s > 1 \quad (4)$$

the transport mechanism is predominantly vehicular and vice versa. This qualitative approach was implemented for the mixtures studied here using MD simulations and is presented in the SI, section S3.3.

In summary, a new method is described that combines 2D-IR and pfg-NMR to quantitatively determine the primary transport mechanism in various binary electrolytes ranging from pure DMC to pure PC. It was found that the contribution from structural transport remains essentially unchanged over the concentration range due to the near-identical structural times for PC and DMC. However, the contribution of vehicular transport varies with viscosity. Furthermore, the Structural Step Length for each concentration was obtained (1.2–1.5 Å). The results presented here provide a framework for experimental and theoretical studies to quantify Li^+ transport mechanisms in various solvent environments, and they suggest the need to move away from carbonate mixtures to maximize structural transport.

■ ASSOCIATED CONTENT

Data Availability Statement

Requests for materials regarding experiments and MD simulations should be sent to the corresponding authors.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.5c03096>.

Additional experimental details, materials, and methods, including sample preparation, laser system details, pfg-NMR experimental method and fitting, molecular dynamics simulations details, density functional theory details, conductivity experimental methods and results. Additional figures are presented, including 2D-IR residuals, 2D-IR kinetic fits, polarization selective pump probe results, MD diffusion and radius probability distributions, and a plot of structural step lengths (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Michael D. Fayer – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-0021-1815; Phone: 650 723-4446; Email: fayer@stanford.edu

Weizhong Zheng – State Key Laboratory of Chemical Engineering and Low-carbon Technology, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China; orcid.org/0000-0002-3866-4932; Email: wzzheng@ecust.edu.cn

Authors

Aaron P. Charnay – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-1797-9465

Benjamin P. Charnay – Department of Chemistry, Stanford University, Stanford, California 94305, United States

Junkun Pan – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0001-6128-1844

Yan Zhang – State Key Laboratory of Chemical Engineering and Low-carbon Technology, School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Matthew W. Kanan – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-5932-6289

Complete contact information is available at:

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Author Contributions

*These authors contributed equally to this work (A.P.C. and B.P.C.).

Notes

The authors declare no competing financial interest.

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