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# **Transport Phenomena in Low Temperature Lithium-Ion Battery Electrolytes**

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Lithium-ion batteries face low temperature performance issues, limiting the adoption of technologies ranging from electric vehicles to stationary grid storage. This problem is thought to be exacerbated by slow transport within the electrolyte, which in turn may be influenced by ion association, solvent viscosity, and cation transference number. How these factors collectively impact low temperature transport phenomena, however, remains poorly understood. Here we show using all-atom classical molecular dynamics (MD) simulations that the dominant factor influencing low temperature transport in LP57 (1 M LiPF<sub>6</sub> in 3:7 ethylene carbonate (EC)/ethyl methyl carbonate (EMC)) is solvent viscosity, rather than ion aggregation or cation transference number. We find that ion association decreases with decreasing temperature, while the cation transference number is positive and roughly independent of temperature. In an effort to improve low temperature performance, we introduce  $\gamma$ -butyrolactone (GBL) as a low viscosity co-solvent to explore two alternative formulations: 1 M LiPF<sub>6</sub> in 15:15:70 EC/GBL/EMC and 3:7 GBL/EMC. While GBL reduces solution viscosity, its low dielectric constant results in increased ion pairing, yielding neither improved bulk ionic conductivity nor appreciably altered ion transport mechanisms. We expect that these results will enhance understanding of low temperature transport and inform the development of superior electrolytes.

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Energy, power, and cycling capabilities of lithium-ion batteries (LIBs) are substantially diminished at low temperature, <sup>1–4</sup> presenting a significant technical barrier to LIB integration in electric vehicles, stationary grid storage, defense operations, space exploration, and more. Several factors may limit low temperature performance, including slow solid-state Li diffusion,<sup>2</sup> phase separation,<sup>5</sup> high resistance of the solid-electrolyte interphase (SEI),<sup>6</sup> slow bulk transport within the electrolyte,<sup>7</sup> and/or slow charge transfer kinetics.<sup>8</sup> Of these potential factors, resistance to bulk transport within the liquid electrolyte has been identified as a key performance determinant with potential for improvement.<sup>9,10</sup>

Despite the importance of slow low temperature electrolyte transport,  $^{4,11-13}$  fundamental understanding of the behavior is limited. Previous studies of ion transport as a function of temperature have primarily relied upon experimental characterizations of ionic conductivity and electrochemical performance, 3,11,14-17 and less commonly, cation transference number<sup>12</sup> and ion association.<sup>18,19</sup> Previous experimental work provides a useful framework for understanding the issue, but in general sheds little light on the molecular origins of low temperature transport behavior. Moreover, direct measurements of the latter two properties are difficult to obtain experimentally and are often necessarily reliant upon assumed and idealized conditions.<sup>20,21</sup> Computer simulation methods such as molecular dynamics (MD), however, are wellsuited to address these challenges, as they are compatible with the time and length scales associated with ion transport. MD has been successfully used to characterize ion transport in various electrolyte systems, including binary salt systems of LiPF<sub>6</sub> and LiTFSI,<sup>22</sup>, solid polymers,<sup>24–26</sup> aqueous polyelectrolytes, <sup>27–29</sup> and biological electrolyte systems.<sup>29</sup> Herein, we use all-atom classical MD

simulations to characterize bulk transport phenomena within the standard commercial LP57 electrolyte blend (1 M LiPF<sub>6</sub> in 3:7 ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (wt/wt)) at atomic-scale resolution. To our knowledge, MD study of low temperature transport in the given system has not been attempted previously. MD simulations of low temperature ionic conductivity are first validated by comparison to experimental measurements. We then analyze ion speciation, solvent self-diffusion coefficients, and the cation transference number to decouple the factors impacting low temperature transport. We find that solvent viscosity exerts a stronger influence on low temperature transport phenomena than ion association or cation transference number. Further, adding evidence to the ongoing debate in the literature,<sup>30–34</sup> we unequivocally observe mixed EC/EMC solvation of  $Li^+$  in the baseline electrolyte. Next, we explore the implications and viability of using  $\gamma$ -butyrolactone (GBL) as a co-solvent to create novel, EC-lean electrolytes. Via computation of static and dynamic transport properties, we find that GBL does not improve ionic conductivity, nor does it shift Li ion transport mechanisms toward faster diffusion modes. We expect that the molecular underpinnings of low temperature transport phenomena clarified in the present work will inform the development of superior low temperature electrolytes.

### Methods

All-atom classical MD simulations were performed using the LAMMPS MD simulation package and OPLS force field parameters.<sup>35</sup> The OPLS force field has been previously shown to produce accurate results in similar electrolyte systems.<sup>36–38</sup> Partial charges and atom types were assigned using values from MacroModel and the Maestro graphical interface (Schrödinger).<sup>39</sup> To account for electronic polarization neglected in the non-polarizable force field used in this study, ionic charges were scaled to a value of 0.8.<sup>40–43</sup>

Each system involved a cubic simulation box filled with 500 solvent molecules (EC, EMC, and/or GBL in varying weight

fractions) and enough LiPF<sub>6</sub> salt to produce an overall salt concentration of 1 M. A system size of 500 molecules was identified as suitably large after finding consistent results with larger box sizes, indicating that results were not likely influenced by finite-size effects. The exact numbers of salt and solvent molecules used in each simulation are listed in Table S1 in the Supporting Information (SI) available at stacks.iop.org/JES/168/080501/mmedia. The initial configuration of molecules in the box was randomly generated using the PACKMOL package.<sup>44</sup>

All systems were first equilibrated for 3 ns in the isothermalisobaric (NPT) ensemble at a temperature of 25 °C and pressure of 1 atm. Simulations with a desired final temperature less than 25 °C were cooled to the target temperature over 3 ns in the NPT ensemble. This cooling rate was deemed sufficiently slow by verifying that cooling at a slower rate (over a 10 ns period) did not affect the final potential energy for the lowest temperature investigated (see Fig. S1). Cooled systems were then simulated in the NPT ensemble for an additional 3 ns at a pressure of 1 atm to permit equilibration at the temperature of interest. Production runs were subsequently performed in the canonical ensemble (NVT) for a duration of at least 50 ns. Temperature and pressure were controlled using a Nosé-Hoover thermostat  $^{45-47}$  and barostat  $^{48}$  with temperature and pressure damping parameters of 0.1 ps and 1.0 ps respectively. The equations of motion were numerically integrated using the velocity-Verlet algorithm and a simulation timestep of 2 fs. System boundaries were periodic in the x, y, and z directions. Electrostatic calculations relied on the PPPM method with an accuracy of  $1.0 \times 10^{-5}$  to compute long-range Coulombic interactions.<sup>4</sup> Short-range potentials were computed using a distance cutoff of 15 Å.

The first 10 ns of the production run were omitted from subsequent data analysis, which relied on the MDAnalysis Python module in conjuction with an in-house code.<sup>50,51</sup> The Visual Molecular Dynamics (VMD) computer program was also used to visualize simulation trajectories and render schematics of molecular species.<sup>52</sup> All error bars for reported data are given by the standard deviation of three simulation replicates.

Successful modeling of transport in the 3:7 EC/EMC electrolyte first involved validation of the chosen MD force field parameters by benchmarking simulation data with experimental results. Accordingly, we consider simulated ionic conductivity results in comparison with experimental values in Fig. 1. Simulated ionic conductivity was computed using a Green-Kubo relation (Eq. S3) listed in the SI. Methods for experimental conductivity measurements are also detailed in the SI. We find that simulated values of ionic conductivity show strong reproduction of the experimental trends and quantitative accuracy within acceptable margins. Deviation between experimental and simulated ionic conductivity is likely attributable to overestimation of the partial charges of ionic species, which increases the computed strength of Coulombic interactions and leads to overestimated ion association and diminished ionic conductivity. We also note that the deviation between experimental and simulated ionic conductivity appears to increase at larger temperatures. Though a detailed understanding of this phenomenon would warrant further study, it may in part be attributable to limitations of the OPLS force field-the accuracy of which has been previously shown to exhibit slight temperature dependence in certain organic solvents.<sup>53</sup> Generally speaking, MD simulations using non-polarizable force fields (as in this study) have been observed to underestimate the speed of bulk transport in models using unscaled partial charges (i.e., wherein the net charges of monovalent ionic species are  $\pm 1.0$ ). <sup>54</sup> The accuracy of these models, however, can be dramatically improved by reducing partial charges by a scaling factor between 0.7 and  $0.8^{41,55}$  As previously mentioned, we scale the partial charges of  $Li^+$  and  $PF_6^-$  by a factor of 0.8. While this scaling value was found to give better agreement with experimental conductivity than a value of 0.7 (Fig. S2), further



**Figure 1.** Comparison of simulated ionic conductivity in 1 M LiPF<sub>6</sub> in 3:7 EC/EMC (wt/wt) with experimental data.

refinement of the charge scaling value could yield more accurate results.

#### **Results and Discussion**

1 M LiPF<sub>6</sub> in 3:7 EC/EMC (LP57) electrolyte characterization.—The apparent decline in ionic conductivity of the 3:7 EC/ EMC electrolyte and its subsequent effect on the viability of Li-ion battery technologies provides strong motivation for atomistic investigation of low temperature electrolyte properties. Broadly speaking, ionic conductivity is influenced by two factors: the concentration of free charge carriers and the speed at which free charge carriers migrate in solution. These factors are in turn influenced by the extent of ion association, the solvent dielectric constant, the size and shape of the charge-carrying species, and the solvent viscosity, some of which may be dependent on temperature.<sup>10,11,56</sup> Herein, we seek to identify the molecular processes influencing low temperature ionic conductivity and evaluate existing hypotheses in the literature.

We first consider the temperature-dependent role of ion association in determining the number of free charge carriers in solution. Intuitively, as ion aggregates form, fewer Li ions are able to freely respond to the electric field, leading to decreased conductivity.<sup>10,20,56,57</sup> An intuitive concept of how ion pairing behavior changes as a function of temperature, however, is not immediately obvious. In the context of Bjerrum's treatment of ion pairing,<sup>58</sup> it would be reasonable to expect increased ion aggregation at low temperature. The Bjerrum length ( $\lambda_B$ ) describes the separation distance at which the electrostatic interaction between two charges is equal to the thermal energy.  $\lambda_B$  is equivalent to twice the maximum distance at which ion pair formation is expected and is given by the following equation:<sup>10,20,59,60</sup>

$$\lambda_{\rm B} = \frac{|z_i z_j| e^2}{4\pi\epsilon_0 c k_{\rm B} T}$$
[1]

where  $z_i$  is the charge of ion *i*, *e* is the elementary charge,  $e_0$  is the permittivity of a vacuum, e is the solvent dielectric constant (which is assumed to be a constant),  $k_B$  is Boltzmann's constant, and *T* is the temperature. Per Eq. 1, increases in temperature are roughly expected to reduce the Bjerrum length, thereby decreasing the

likelihood of ion pair formation. Indeed, previous investigators have suggested that ion aggregation may increase at low temperature due to the reduction of thermal energy.<sup>11,61</sup> However, it seems that a complete picture is significantly more nuanced. Ding et al. hypothesize that at low temperature, the extent of ion aggregation is under the influence of competing effects.<sup>11</sup> On one hand, per the Bjerrum concept of ion pairing, reduced thermal motion at low temperature is likely to encourage ion association. On the other hand, ion pairing may decrease in response to changes in the solvent dielectric constant, which is expected to increase at low temperature due to reduced thermal disruption of solvent dipole alignment.<sup>11,62,63</sup> High permittivity solvents help attenuate coulombic attractions between ions, leading to reduced ion aggregation.<sup>11</sup> Consistent with the latter hypothesis, Krachkovskiy and coworkers used PFG-NMR to show that ion pairing decreases in 1:1 ethylene carbonate/dimethyl carbonate (DMC) at low temperatures.<sup>18</sup> While these hypotheses and a small number of experimental studies exist,<sup>11,18</sup> the question of low temperature ion association behavior has yet to be addressed directly for this system.

To investigate ion pairing directly with MD simulations, we compute the fraction of free charge carriers in solution based on the radius of the primary Li ion solvation shell. The radius (5.2 Å at all temperatures studied), obtained from inspection of the first minimum of the Li-P radial distribution function (RDF) plotted in the SI (Fig. S3), permits classification of Li ions as free, in contact ion pairs (CIP), and in clusters including positive triple ions (PTI), negative triple ions (NTI), and larger aggregates (AGG) (see the SI for detailed methodology). Figure 2 shows trends in ion speciation as a function of temperature, where we observe that the fraction of free ions increases monotonically with decreasing temperature. This result is consistent with increased mixed solvent dielectric constant at low temperatures, which leads to increased attenuation of ionic attractions and reduced ion pairing. Indeed, experimental static permittivity measurements made by Hall et al. showed that the dielectric constant of 3:7 EC/EMC increases from roughly 16 at 70 ° C to approximately 18.5 at 25 °C.<sup>62</sup> We further consider another possible influence: the entropy of ion pairing. We might intuitively expect ion pairing to be entropically unfavorable due to the loss of translational degrees of freedom of the ions. However, previous studies suggest that ion pairing for certain systems is actually entropically favorable ( $\Delta S_{ip}^{o} > 0$ ), wherein entropic gains are attributed to the release of electrostricted solvent molecules from the ions'

solvation shells into the bulk solvent.<sup>20</sup> The trend in ion pairing for the baseline electrolyte studied herein is consistent with a positive change in entropy upon ion pairing: at low temperature, entropic gains to the free energy of ion pairing are weaker, leading to reduced ion pairing. Such a reduction in ion pairing implies an increase in the number of free Li ion charge carriers at low temperature, which does not explain the observed decrease in ionic conductivity. This inconsistency suggests that the number of free charge carriers may not be the dominant factor inhibiting ionic transport at low temperature.

The trends in ion speciation as a function of temperature (Fig. 2) reveal that cation-anion correlations from ion pairing are not a limiting factor for low temperature conductivity. The ionicity (*I*), also known as the inverse Haven ratio,  $^{64,65}$  is a closely related property which captures ion pairing effects as well as other long-range and like-ion correlations.  $^{66-69}$  *I* is given by the following equation,  $^{69}$ 

$$I = \frac{\sigma}{\sigma_{NE}}$$
[2]

where  $\sigma$  is the actual conductivity computed by Eq. S3 and  $\sigma_{NE}$  is the ideal Nernst-Einstein conductivity,<sup>70</sup> which assumes no correlation between species and is computed by Eq. S4. We observe no significant temperature dependence of the ionicity (Fig. S4, S5), implying that the extent of ion correlations is not a key property governing the decrease in conductivity at low temperature.

The next major factor influencing ionic conductivity is solvent viscosity.<sup>15,71,72</sup> It is well-known that liquid viscosity increases at low temperature,<sup>73</sup> an effect that is expected to reduce charge carrier mobility. To decouple the effects of solvent viscosity and ion association at low temperature, we computed the self-diffusion coefficient of solvent species in solution. Solvent self-diffusion coefficients were computed as a proxy for solvent viscosity due to the substantial inaccuracies associated with computing viscosity from MD <sup>74</sup> and the utility of solvent self-diffusion coefficients for prediction of additional solution properties such as the diffusion length (see below). Self-diffusivity is approximately related to viscosity via the Stokes-Einstein equation,<sup>75</sup>



**Figure 2.** Ion speciation trends in 1 M LiPF<sub>6</sub> in 3:7 EC/EMC computed from MD data. (a) The fraction of Li ions in each ion speciation state as a function of temperature. (b) Schematics representing the ion speciation states depicted in (a): free ions, contact ion pairs (CIP), positive triple ions (PTI), negative triple ions (NTI), and larger aggregates (AGG). Pink spheres represent Li ions, gray clusters represent  $PF_6^-$  anions, and purple molecules represent solvent species.



Figure 3. Self-diffusion coefficients of EC, EMC,  $PF_6^-$  and  $Li^+$  in 1 M  $LiPF_6$  in 3:7 EC/EMC computed by MD as a function of temperature.



**Figure 4.** The cation transference number computed by MD as a function of temperature compared to results predicted by the current interrupt method. Both data sets are taken with reference to the solvent velocity (see SI for methods, Fig. S23) and fully account for solution non-idealities. Data points and error bars for experimental data were digitized from Landesfeind and Gasteiger.<sup>12</sup>

$$D = \frac{k_{\rm B}T}{6\pi\eta r}$$
[3]

where *D* is the self-diffusion coefficient,  $\eta$  is the solvent viscosity, and *r* is the particle radius. To evaluate the validity of the Stokes-Einstein relationship for viscosity prediction in LiPF<sub>6</sub> electrolytes, we compare simulated self-diffusion coefficients and experimental viscosity data in Figs. S6, S7, and S8. We find that self-diffusivity and inverse viscosity give comparable trends with temperature, suggesting that solvent self-diffusion is a reasonable proxy for solvent viscosity. In line with these results, the approximate validity of Eq. 3 in neat carbonate solvents has been shown by Hayamizu et al.,  $^{76}$  and for carbonate-based electrolytes using experimental data from Kondo et al.  $^{77}$ 

In Fig. 3, we plot the self-diffusion coefficients of species in the baseline electrolyte for temperatures ranging from -20 to 25 °C. As temperature decreases, the self-diffusion coefficient of all species declines significantly. Notably, EMC exhibits the fastest selfdiffusion, followed by the second solvent component, EC. This may be a consequence of the lower viscosity of neat EMC compared to EC<sup>14</sup> and the relatively larger fraction of EMC that exists within the bulk solvent. Because EMC is in much larger abundance than EC, a greater proportion of EMC molecules are not involved in Li ion solvation, which is expected to increase the average self-diffusivity of EMC.<sup>32,78</sup> Slow solvent diffusion at low temperatures has important effects on ionic conductivity: decreased self-diffusion coefficients (or increased solvent viscosity by Eq. 3) translate to slow mobility of charge carriers. Indeed, direct computation of the electrophoretic mobility confirms this result; cation and anion mobility is plotted as a function of temperature in Fig. S9. The observed behavior of solvent self-diffusion, in conjunction with our ion speciation data, vields our first important conclusion regarding the baseline electrolyte: while ion pairing does not increase at low temperature, solvent-self diffusion slows substantially. By the Stokes-Einstein equation (Eq. 3), slow solvent self-diffusion translates to increased solvent viscosity, a result which is confirmed experimentally for temperatures ranging from 30 °C down to 0 °C in Fig. S10. Accordingly, we conclude that that the most important factor limiting low temperature bulk transport in 3:7 EC/EMC is the viscosity of the solvent rather than increased ion aggregation. In addition to solvent self-diffusion, we plot ion self-diffusion as a function of temperature in Fig. 3. Consistent with results from previous studies,<sup>79</sup> anion transport in solution is faster than that of the cation, likely due to the bulkiness of the Li<sup>+</sup> solvation shell and lack of anion/solvent association.8

Additionally relevant to low temperature transport-related electrolyte performance is the cation transference number  $(t_+)$ , defined as the fraction of ionic conductivity carried by the Li ion.<sup>7</sup> <sup>0,81</sup> Most conventional electrolytes exhibit  $t_+$  less than 0.5, indicating that more than half of the ionic conductivity is due to anionic motion.<sup>2</sup> Migration of the anion, which occurs in the direction opposite to migration of the cation, can cause the development of large concentration overpotentials, limit the operating voltage of Li-ion cells, induce Li plating, and diminish cell lifetime.<sup>82</sup> Recent data produced by Landesfeind and Gasteiger using the current interrupt method suggest that  $t_{+}$  decreases and even becomes negative in the 3:7 EC/EMC electrolyte with decreasing temperature, indicating that  $t_{+}$  may have a substantial effect on low temperature cell performance. The authors rationalize this behavior by theorizing that an increasing fraction of NTI species may be present at low temperature; cations in negatively charged aggregates migrate in the opposite direction of free cations (toward more positive potential) and thus could be responsible for negative transference.<sup>12</sup> Work by other authors, however, contradicts these results. Gering and Duong, using the Advanced Electrolyte Model, predict a change of less than 5% in  $t_+$  measured at 60 °C vs -30 °C in the baseline electrolyte.<sup>83</sup> Krachkovskiy et al. estimated  $t_{+}$  in similar electrolytes using pulsedfield gradient nuclear magnetic resonance (PFG-NMR) data and also found weak temperature dependence over a smaller temperature range (5 °C-35 °C).<sup>18</sup> The disparity between authors reporting negative versus positive cation transference numbers at low temperature likely arises because  $t_{+}$  is notoriously difficult to measure.<sup>2</sup> The current interrupt method, as used by Landesfeind and Gasteiger in the aforementioned study,<sup>12</sup> faces signal to noise ratio challenges associated with deconvolution of the various resistances measured by polarization experiments. More specifically, large and unstable resistances from the lithium metal SEI may obfuscate smaller transport-related contributions from Ohmic and concentration



**Figure 5.**  $Li^+$  coordination by EC, EMC, and the PF<sub>6</sub><sup>-</sup> anion in 3:7 EC/EMC computed from MD data as a function of temperature.

potential drops.<sup>84</sup> Other common methods of  $t_{+}$  measurement, such as the Bruce and Vincent method and PFG-NMR estimation, assume ideal, infinitely dilute solutions of non-interacting ions, fundamentally limiting their accuracy.  $^{\rm 82,85}$  In contrast, MD circumvents these issues and presents an alternative method for rigorous measurement of  $t_{+}$ .<sup>81</sup> In Fig. 4, we plot  $t_{+}$  values obtained from Green-Kubo relations for the electrophoretic mobility with measurements made by Landesfeind and Gasteiger using the current interrupt method<sup>86,87</sup> for comparison. Interestingly, the present work finds no indication of negative  $t_{+}$ , values, nor evidence that NTI clusters might increase in prevalence at low temperature (Fig. 2). This suggests that changes in ion speciation and coordination with temperature may not be significant enough to influence  $t_+$ . Thus, we find that while  $t_+$  is undoubtedly a parameter of interest, the apparent temperature independence implies that that  $t_{+}$  is not a limiting factor in low temperature applications. This reaffirms our previous conclusion that solvent viscosity, rather than other factors, is the predominant limitation for low temperature electrolyte transport.

Though solvation structure is an important feature of the electrolyte, the exact composition of the primary Li ion shell in carbonate electrolyte blends remains controversial. While most authors agree that Li ion total coordination numbers are generally between four and six, <sup>32,78,88,89</sup> less consensus exists as to how different solvent species participate. Previous authors have indicated that Li ions will exhibit strong preference for coordination by EC in EC/EMC based LiPF<sub>6</sub> electrolytes.<sup>30,31</sup> Xu and coworkers, for example, used electrochemical impedance spectroscopy and NMR to argue that Li ions will be solvated exclusively by EC in solvent blends exceeding 30 percent EC content.<sup>90</sup> Indeed, EC solvation is expected to be enthalpically preferable to EMC coordination on account of its greater polarity and electron pair donicity.<sup>78,91</sup> Others still argue otherwise.<sup>32–34</sup> Ong et al. used MD to show that Li<sup>+</sup>

solvation sheaths in 3:7 EC/EMC often contain both two EC and two EMC molecules.<sup>32</sup> In line with authors reporting mixed EC/EMC solvation, our findings in Fig. 5 show that Li ions are roughly equally coordinated by EC and EMC. Despite presumed enthalpic preference for EC coordination,<sup>78</sup> we propose that EMC is capable of competitive solvation in part due to entropic favorability on account of its greater abundance in solution. In order to better understand entropic preferences for EMC coordination in EMC-rich solvents, we performed an additional simulation of 1 M LiPF<sub>6</sub> in a 1:1 EC/EMC number ratio at room temperature. Interestingly, we found that while EMC remains a prominent component of the Li<sup>+</sup> solvation shell, the average number of participating EMC molecules decreases from roughly 2 in the baseline electrolyte to 1.6 in the 1:1 electrolyte. In contrast, the average number of EC molecules in the primary shell increases from roughly 2 to 2.8. This EC/EMC ratio is consistent with results produced by 1:1 simulations of EC/DMC by Borodin et al.<sup>33</sup> The RDF and coordination number analysis associated with the 1:1 EC/EMC number ratio simulation is plotted in Fig. S11. As expected for the baseline electrolyte, we observe a total Li<sup>+</sup> coordination number of approximately five, including an average of roughly four solvent molecules and a single coordinated anion. Notably, we observe that the coordination number of  $PF_6^$ decreases slightly at low temperatures, consistent with our previous findings showing decreased low temperature ion association. We also note that EMC coordination appears to increase slightly above EC at -20 °C. Because we expect higher solvent permittivity at lower temperatures, this result is consistent with findings from Borodin et. al, which suggest greater DMC contributions to the Li<sup>+</sup> solvation shell in mixed EC/DMC electrolytes with higher solvent dielectric constants.<sup>33</sup> We do not observe any change in the radius of the solvation shell as shown by the Li<sup>+</sup>/solvent RDFs (see Figs. S12, S13, S14).

Engineering novel low temperature electrolytes.—Our characterization of the baseline electrolyte shows that the factor most strongly limiting low temperature transport is reduced solvent viscosity—not increased ion association or low  $t_{\perp}$ . Accordingly, we designed two alternative electrolytes with an additional cosolvent,  $\gamma$ -butyrolactone (GBL), to produce less viscous solutions and probe the interplay between solvent viscosity and permittivity: 1 M LiPF<sub>6</sub> in 15:15:70 EC/GBL/EMC (wt/wt/wt) and 3:7 GBL/EMC (wt/wt). Previous authors have attempted to produce superior low temperature electrolytes, primarily by introducing low viscosity glymes, lactones, and esters.<sup>14,15,17,92–96</sup> Unfavorable reactivity of many of these co-solvents, especially in low molecular weight candidates, led to little success in engineering stable electrolytes with desirable electrode passivation properties.<sup>16,95</sup> Other efforts have been made to improve the low temperature viability of electrolytes by creating EC-lean ternary and quaternary blends of more conventional carbonate solvents such EC, EMC, DMC, propylene carbonate, and diethyl carbonate.<sup>4,16</sup> Despite some success in producing solvents with greater ionic conductivity, it may be possible to further tune or optimize electrolyte conductivity via cosolvent selection. GBL has been previously studied for use in Li-ion batteries<sup>97–99</sup> and may be a promising candidate thanks to its various favorable properties, including reduced viscosity compared to EC, low melting point, and high permittivity.<sup>10,100,101</sup> We expect that GBL may also be a judicious choice on account of its boiling point and flash point, which closely resemble those of EC. Similar flash and boiling points are expected to permit the development of EC-

Table A1. Selected properties of EC, GBL, a	and EMC.
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Solvent	Viscosity	Dielectric constant	Boiling point	Melting point	Flash point	Ref
EC	1.85 cP	89.6	243 ℃	38 °C	160 °C	13,16
GBL	1.7 cP	39	204 ℃	−43.53 °C	95.5 °C	100,103
EMC	0.65 cP	2.96	107.5 ℃	−14 °C	23.5 °C	16,103



**Figure 6.** Simulated ionic conductivity of 1 M LiPF<sub>6</sub> in 3:7 EC/EMC compared to the simulated conductivity of 1 M LiPF<sub>6</sub> in 3:7 GBL/EMC and 1 M LiPF<sub>6</sub> in 15:15:70 EC/GBL/EMC as a function of temperature.

lean solvents without dramatically increasing flammability.<sup>102</sup> Solvent properties of EC, GBL, and EMC are compared in Table A1.

Consistent with the primary conclusion surrounding the 3:7 EC/ EMC electrolyte, reduced viscosity solvents incorporating GBL were expected to exhibit greater low temperature ionic conductivity. However, Fig. 6 suggests that the alternative solvent formulations confer little to no benefit in ionic conductivity over the 3:7 EC/EMC baseline electrolyte. We believe that despite the large importance of solvent viscosity relative to ion aggregation in the baseline electrolyte, competition between these two effects may limit conductivity gains in the alternative solvents. Though the addition of a lower viscosity co-solvent was expected to facilitate faster bulk transport, EC replacement by GBL is also expected to reduce the bulk solvent permittivity, which may lead to increased ion pairing.<sup>104</sup> Simulated trends in ionic conductivity of 3:7 GBL/EMC and 15:15:70 EC/ GBL/EMC are consistent with experimental data, shown in Figs. S15 and S16.

We again rely on ion speciation fractions and solvent selfdiffusivity as a proxy for solvent viscosity to decouple the solvent properties influencing low temperature ionic conductivity. In Fig. 7, the fraction of free ions, contact ion pairs (CIP), and larger aggregates (AGG) are plotted to compare the effect of EC content on ion speciation. We find that the fraction of free Li ions is strongly influenced by EC content; as expected, the fraction of free ions at all temperatures studied is largest in the 3:7 EC/EMC electrolyte. Interestingly, while free and AGG speciation fractions exhibit a clear trend with temperature across solvent formulations, we observe that CIP speciation fractions appear to remain approximately constant across the temperature range. We propose that the formation of AGG species, here defined as any cluster with greater than two ions, may exhibit stronger apparent temperature dependence due to a potentially larger entropic free energy contribution, as large aggregate formation may release a larger number of solvent molecules into the bulk than CIP formation. We also note that this trend is likely influenced by complex equilibria which exist between different ion speciation states. Increased fractions of CIP and AGG speciation states and fewer free ions in the alternative electrolytes are expected to reduce the ionic conductivity of the EC-lean electrolytes; thus, lower permittivity of the alternative electrolytes may indeed be limiting gains in ionic conductivity. Detailed resolution of ion speciation in the alternative electrolytes (including NTI and PTI states) is shown in Figs. S17 and S18.

We also reconsider the other ionic conductivity factor of interest: solvent viscosity. As in the case of the baseline electrolyte, we again rely on solvent self-diffusion coefficients to describe changes in solvent viscosity. As expected, we observe faster solvent self-diffusion in the EC-lean electrolytes. Of the alternative solvents, the 3:7 GBL/EMC blend achieves the greatest increase in self-diffusivity, though the change is not dramatic. The viscosity of GBL, while lower than that of EC, is still fairly high (1.7 cP at 25 °C) relative to that of EMC (0.65 cP at 25 °C). Though the differences in solvent self-diffusion coefficients in Fig. 8 are fairly small across solvent types, we believe these results suggest that increased ion pairing in the alternative solvents may be balanced by faster diffusion to yield the observed composition-independent conductivities.

In addition to transport properties, we are also interested in the mechanism for Li ion diffusion, which can be assessed by further study of the dynamic Li ion solvation shell environment. We first consider the solvent residence time  $(\tau_j)$ , defined as the average duration a species *j* spends in the solvation shell of a Li ion prior to exchange with another ion or solvent molecule.  $\tau_i$  values for various solvent components provide a more detailed picture of the evolution of solvation structures and are of critical importance to transport phenomena.<sup>82,105</sup>  $\tau_j$  is influenced by two primary factors: solution viscosity and Li ion diffusion mechanism, wherein decreased viscosity and structural-type diffusion motifs are consistent with shorter  $\tau_i$ . In contrast to vehicular type diffusion, in which Li ions diffuse through the electrolyte with their solvation shells intact, structural diffusion is marked by ion hopping and rapid solvation shell exchange.<sup>82,106</sup> In Fig. 9, we first observe that in general,  $\tau_i$ increases at low temperature. We also find that the low temperature residence times of EC, EMC, and GBL decrease in the EC-lean solvents compared to the baseline electrolyte, as expected due to reduced viscosity of the EC-lean formulations. Procedures used to compute  $\tau_i$  are included in the SI.

It is unclear whether trends in  $\tau_j$  across temperature and solvent formulation are the result of changes in solution viscosity or shifts in diffusion mechanism. To decouple these factors, we compute the diffusion length ( $L_j$ ), defined as the average distance that a species *j* diffuses with a Li ion before separating.  $L_j$  allows us to directly compare solvent diffusion mechanisms by normalizing for solvent viscosity changes via the following equation,<sup>22,82,107</sup>

$$L_j = \sqrt{6D\tau_j} \tag{4}$$

where D is the composition weighted average of the solvent selfdiffusion coefficients. In Fig. 10 we plot  $L_j$  as a function of temperature in the three solvents. Solvent self-diffusion coefficients in the alternative electrolytes are included in Figs. S19 and S20. Large values of  $L_i$  are consistent with vehicular type diffusion, while smaller values indicate structural diffusion associated with faster bulk transport.<sup>60,107,108</sup> Accordingly, it is desirable to introduce a cosolvent that decreases  $L_j$ , shifting the Li<sup>+</sup> diffusion mechanism toward more structural diffusion. Figure 10 shows that  $L_i$  is largely unchanged for each of the solvent molecules in the alternative electrolytes. This implies that changes in  $\tau_i$  displayed in Fig. 9 are not due to changes in the diffusion mechanism (i.e., shifts from vehicular to structural type diffusion), but rather are consistent with reduction of the electrolyte viscosity. Within the same electrolyte, we note that  $L_j$  does appear to vary with temperature. Figure 10 shows that EC, EMC, and GBL diffusion lengths increase at low temperatures, though the change is fairly small. This change in  $L_i$  is consistent with shifts toward more vehicular type diffusion involving concerted motion of the Li ion and the constituents of its primary solvation shell. Of the solvents, EMC exhibits the shortest diffusion lengths and overall appears the least temperature sensitive. This may be attributable to weaker Li<sup>+</sup>/EMC association due to EMC's



Figure 7. Ion speciation states computed from MD data, including (a) free ions, (b) contact-ion pairs (CIP), and (c) larger aggregates (AGG) compared for each solvent formulation. Here, the AGG state includes contributions from triple ions as well as larger ion clusters.



Figure 8. Self-diffusion coefficients of (a) EC, (b) EMC, and (c) GBL computed by MD as a function of temperature for each solvent formulation.



Figure 9. Residence times ( $\tau_j$ ) of (a) EC, (b) EMC, and (c) GBL in the primary Li<sup>+</sup> solvation shell computed by MD as a function of temperature for each solvent formulation.

weaker dipole moment and lower donor number compared to EC and GBL.<sup>91,109</sup> EC and GBL appear to exhibit very similar values of  $L_j$  across solvent types and temperatures. Hahn et al. argued that the local structure of a coordinating solvent exerts a stronger effect on ion coordination than bulk dielectric constant.<sup>110</sup> Accordingly, similarity in EC/GBL diffusion lengths may be attributable to the likeness of their donor numbers and short-range solvent-ion

interactions. Given the association between diffusion mechanism and the speed of transport, the similarity in EC and GBL diffusion lengths is also consistent with the observed lack of improvement in ionic conductivity of the EC-lean electrolytes. Our results suggest that future co-solvent candidates should not simply be lower in viscosity—it may be advantageous to alter the diffusion mechanism as well, perhaps via a chemically dissimilar co-solvent. As



Figure 10. Diffusion lengths  $(L_i)$  of (a) EC, (b) EMC, and (c) GBL computed from MD data as a function of temperature for each solvent formulation.

mentioned previously, it has been suggested that structural diffusion may be associated with faster transport.

#### Conclusions

All-atom classical MD simulations were used to decouple the factors influencing low temperature ionic conductivity and probe the interplay between solvent viscosity and dielectric constant in EClean electrolyte formulations. Our investigation of the state-of-theart 3:7 EC/EMC electrolyte sheds new light on the low temperature effects of ion association, solvent viscosity, and cation transference number. We conclude that despite contradictory evidence presented in the literature, solvent viscosity, or by proxy solvent selfdiffusivity, exerts a stronger effect on low temperature ionic conductivity than ion association. We also found that the cation transference number, in contrast to the negative transference numbers previously reported for the given system, remains positive and roughly constant from -20 °C to 25 °C. Likewise in contrast to some previous results, we found that Li<sup>+</sup> solvation in the baseline electrolyte is competitive and involves both EC and EMC. Elucidating the origin of low temperature transport limitations of the baseline electrolyte motivated new formulations in the direction of low-viscosity co-solvents. As such, GBL was selected as a promising candidate based on its relatively high dielectric constant, low melting point, and lower viscosity compared to EC. However, we found that the inclusion of GBL to form two alternative electrolytes of 15:15:70 EC/GBL/EMC and 3:7 GBL/EMC conferred little benefit in ionic conductivity. We ascribe this result to competition between ion aggregation and solvent self-diffusivity at low temperature. Comparison of the residence times and diffusion lengths among the three solvents indicated that EC-lean solvents were less viscous (consistent with shorter residence times), but generally exhibited similar  $L_i$  values across solvent types, indicating no change in the diffusion mechanism. Similarity in EC/GBL diffusion lengths in particular suggests that while replacement of EC by GBL may reduce solvent viscosity, it does not induce shifts toward structural diffusion modes potentially consistent with faster transport. Ultimately, future efforts should focus on identifying cosolvent candidates and electrolyte blends which adequately curtail ion aggregation while simultaneously facilitating rapid Li ion migration. A judicious choice might involve a co-solvent with dissimilar chemistry rather than reduced viscosity alone to enable a shift from vehicular to structural diffusion types. We expect that these results will enhance understanding of carbonate solvent systems and inform future work to develop low temperature electrolytes.

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