

# Mechanistic understanding of the correlation between structure and dynamics of liquid carbonate electrolytes: Impact of polarization

Moumita Maiti,<sup>†</sup> Anand Narayanan Krishnamoorthy,<sup>‡</sup> Youssef Mabrouk,<sup>‡</sup>  
Nataliia Mozhzhukhina,<sup>¶</sup> Aleksandar Matic,<sup>¶</sup> Diddo Diddens,<sup>‡</sup> and Andreas  
Heuer<sup>\*,†</sup>

<sup>†</sup>*Institute of Physical Chemistry, University of Münster, Corrensstrasse 28/30, 48149  
Münster, Germany*

<sup>‡</sup>*Forschungszentrum Jülich GmbH, Helmholtz-Institute Münster (IEK-12), Corrensstraße  
46, 48149 Münster, Germany*

<sup>¶</sup>*Department of Physics, Chalmers University of Technology, 41296 Göteborg, Sweden*

E-mail: andheuer@wwu.de

## Supplementary Information

### Equilibration

Starting configurations are randomly generated using PACKMOL for all studied compositions, and trajectories are considered for analysis after equilibration. Structural quantity like radial distribution function(rdf) is calculated for different time windows starting from zero time, and rdf saturates after equilibration. This criteria is implemented for three force field models and from Fig. S1 we conclude the electrolyte solutions reach to equilibrium above

4 ns, and both variants of non-polarizable force field model saturate above 20 ns. Fig. S1 shows data for 0.95 M which is valid even for other compositions.

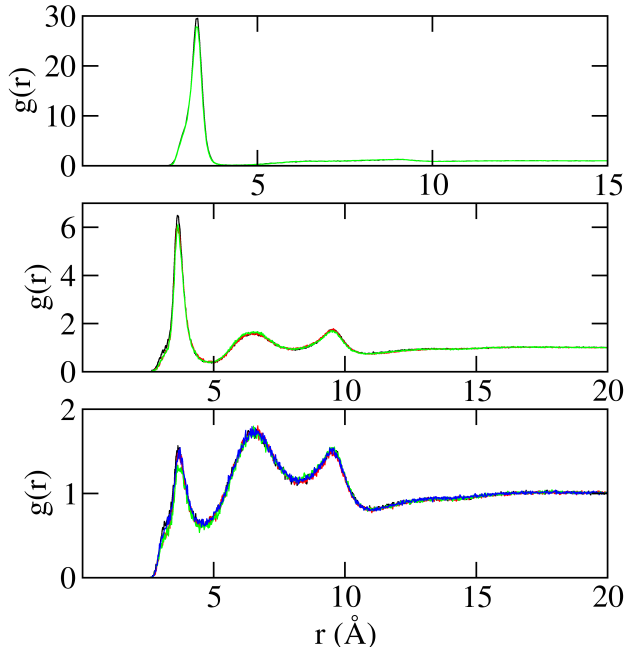


Figure S1: Upper panel: Radial distribution function of P of  $\text{PF}_6^-$  anions around Li ion for 0.95 M salt concentration from polarizable force field model. Coloring is done on time windows 0 – 2ns(black), 2 – 4 ns(red), 4 – 6 ns(green). Red and green lines overlap on each other. Middle panel: Radial distribution function of centre of mass of  $\text{PF}_6^-$  ions around Li ion from OPLS force field. Coloring is done on time windows 0 – 10 ns(black), 10 – 20 ns(red), and 20 – 30 ns(green). Last two lines are same. Lower panel: Same data as middle panel from OPLS force field model with charge rescaling. An extra time window of 30 – 40 ns (blue) is added to it. Here as well last two lines overlap.

## Density

Density of a composition is calculated by using the following formula  $\frac{M}{V}$ , where  $M$  is total molar mass of the composition *i.e.* sum of molar masses of  $\text{LiPF}_6$ , EC, and EMC and  $V$  is the box volume. We observe in Fig. S2(a,b) density increases with increasing EC:EMC ratio and salt concentration. In Fig. S2(a) the experimental value is shown to compare with MD data, and the polarizable force field model gives a decent agreement with experiment.

In Fig. S2(b) different force field data are shown, and charge rescaling reduces the density, which explains faster dynamics due to charge rescaling.

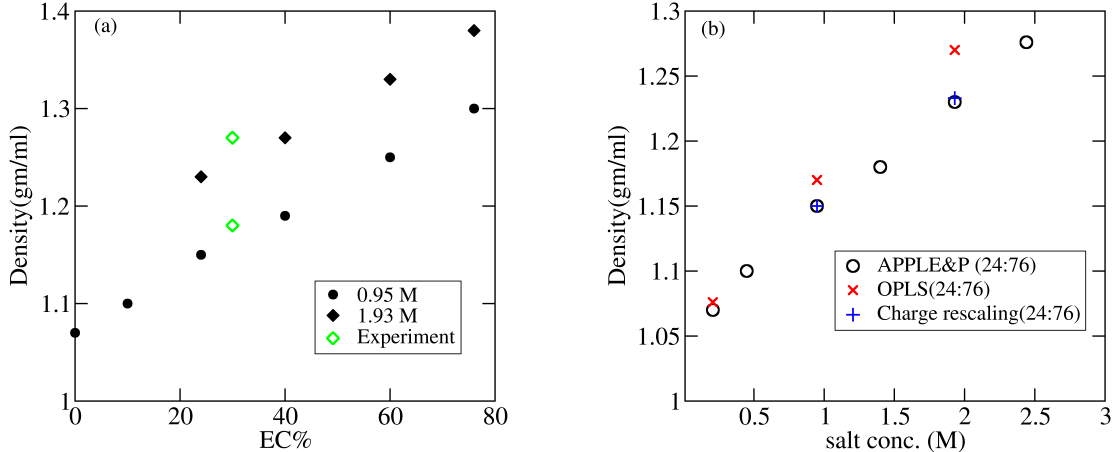


Figure S2: (a) Density vs EC% obtained from polarizable force field model for 0.95 M and 1.93 M compositions. Experimental data are shown for two compositions and EC% = 30. (b) Densities vs salt concentrations obtained using different force field models are compared.

## Diffusion constant

The mean square displacement (MSD),  $\langle \Delta r_i^2(t - t_0) \rangle = \langle (\vec{r}_i(t) - \vec{r}_i(t_0))^2 \rangle$ , is calculated as a function of time  $t$  for both ions separately, where  $t_0$  is a reference time. At late time MSD is linear, hence  $D = \langle \Delta r_i^2(t - t_0) \rangle / (6t)$  is flat as a function of time. Fig. S3 shows  $D$  vs  $t$  for all studied salt concentrations, which becomes flat at late time. The flat regime is fit with a constant which is nothing but the self diffusion coefficient Eq.(2),  $D_+$  for  $\text{Li}^+$  ion and  $D_-$  for  $\text{PF}_6^-$  ion.

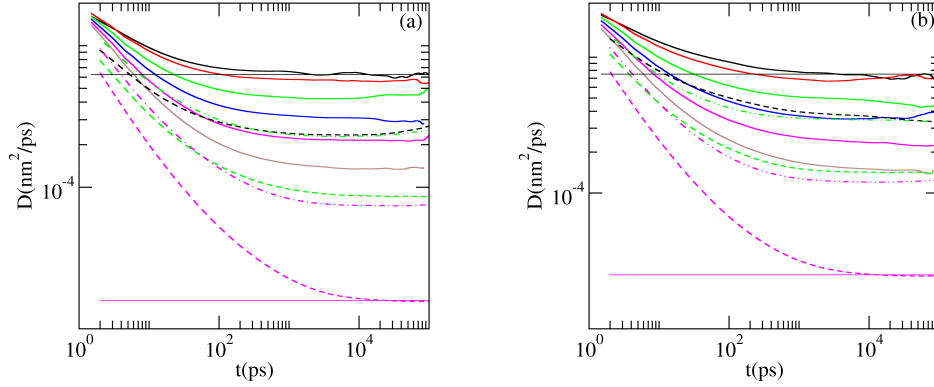


Figure S3: (a)  $D$  (look for definition in the text) vs  $t$  for Li<sup>+</sup> ion. (b)  $D$  vs  $t$  for PF<sub>6</sub><sup>-</sup> ion. All salt concentrations 0.208 M (black), 0.45 M (red), 0.95 M (green), 1.4 M (blue), 1.93 M (magenta), and 2.44 M (brown) are shown. Also different force field data, polarizable force field (solid line), standard OPLS (dashed line), and charge rescaling (dot-dashed line) are shown. For two data sets the fitting curves are shown.

## Ionic conductivity

Ionic conductivity  $\sigma$  is extracted from late time behaviour of Fig. S4(a) by fitting the flat regime to a constant. Fig. S4(a) shows also  $\sigma_+$  which is used to calculate the transference number  $t^+$ . Individual distinct correlation components  $\sigma_{++}^d$ ,  $\sigma_{--}^d$ , and  $\sigma_{+-}^d$  are plotted in Fig. S4(b,c,d).  $\sigma_{++}^d$  and  $\sigma_{--}^d$  are almost zero at lower salt concentrations, and decreases by increasing concentrations, but interestingly saturates at higher concentrations. The negative value is expected as same charges repel. With same analogy  $\sigma_{+-}^d$  is positive, at early time the dependence on salt concentrations is monotonic but surprisingly it changes to non-monotonic nature at late time. The total contribution from distinct correlations is negative, hence G-K conductivity is smaller than N-E conductivity.

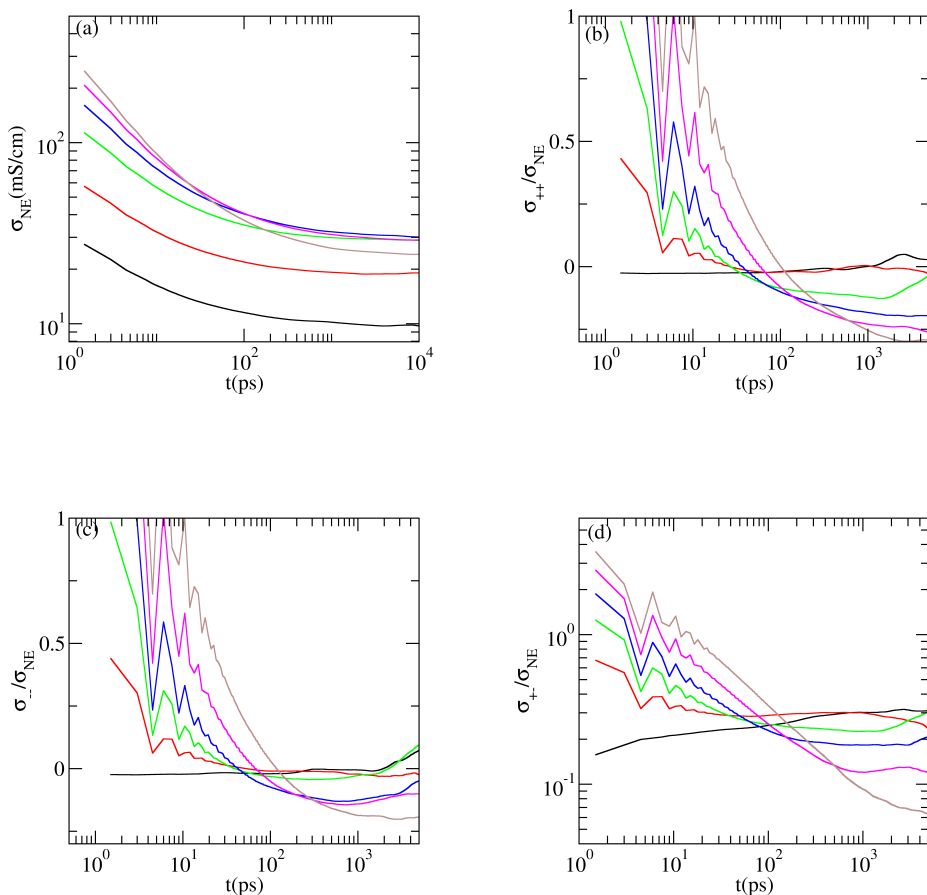


Figure S4: (a) Self correlation  $\sigma_{NE}$  for different salt concentrations. Coloring is done on salt concentrations 0.208 M (black), 0.45 M (red), 0.95 M (green), 1.4 M (blue), 1.93 M (magenta), and 2.44 M (brown). (b)  $\sigma_{++}/\sigma_{NE}$  for same set of salt concentrations as (a). (c)  $\sigma_{--}/\sigma_{NE}$  for salt concentrations same as (a). (d)  $\sigma_{+-}/\sigma_{NE}$  for same set of salt concentrations as (a).

## Infrared spectroscopy data

### Radial distribution function

Fig. S6(a,b) show radial distribution functions of Li around double bonded Oxygen of EC/EMC molecules for 0.95 m composition. The peak position is at smaller interatomic distance for polarizable force field (1.95 Å) than non-polarizable force field (2.05 Å) for both molecules. Radial distribution function of Li ions around Fluorine is shown in Fig. S6(c).

Table 1: Band assignments and peak fitting results for 1M LiPF<sub>6</sub> in EC:EMC 3:7 wt% (LP57) and 2M LiPF<sub>6</sub> in EC:EMC 3:7 wt% infrared spectra.

Electrolyte	Peak assignment	Position, cm <sup>-1</sup>	Height	Area
1 M	EC C=O	1806	0.25	15.5
1 M	EC C=O + Li+	1772	0.31	17.3
1 M	EMC C=O	1744	0.35	26.2
1 M	EMC C=O + Li+	1716	0.28	18.1
1 M	PF <sub>6</sub> <sup>-</sup>	838	0.81	43.1
1 M	Ion pairs	822	0.13	5.8
1 M	Ion pairs	861	0.08	6.4
2 M	EC C=O	1809	0.13	6.8
2 M	EC C=O + Li+	1776	0.20	13.8
2 M	EMC C=O	1741	0.25	21.2
2 M	EMC C=O + Li+	1713	0.40	25.0
2 M	PF <sub>6</sub> <sup>-</sup>	838	0.78	45.4
2 M	Ion pairs	821	0.29	13.9
2 M	Ion pairs	861	0.14	6.1

There are two peaks for polarizable and OPLS force fields, and by charge rescaling the first peak diminishes and the second peak disappears. The first peak position from polarizable force field model is smaller (1.8 Å) than the peak position of EC/EMC, and ion-pairs are in contacts with Li ions are observed, whereas for non-polarizable force field the first peak position shifts to higher value (2.15 Å), so anions are sitting at marginal positions compared with EC/EMC. Also the height of first peak is smaller, hence more contacts form in polarizable force field than both variants of non-polarizable force field.

Fig. S6(d) shows radial distribution function of pairs Li-PF<sub>6</sub> where centre of mass of PF<sub>6</sub> is considered for different salt concentrations. The first peak height decreases with increasing salt concentration unlike the reported data<sup>1</sup> produced using the GAFF model. In the main text it is shown that the coordination number increases with increasing salt concentration unlike the first peak in radial distribution function. Our findings indicate the number of ion-pairs does not increase in proportion with increase in the number density.

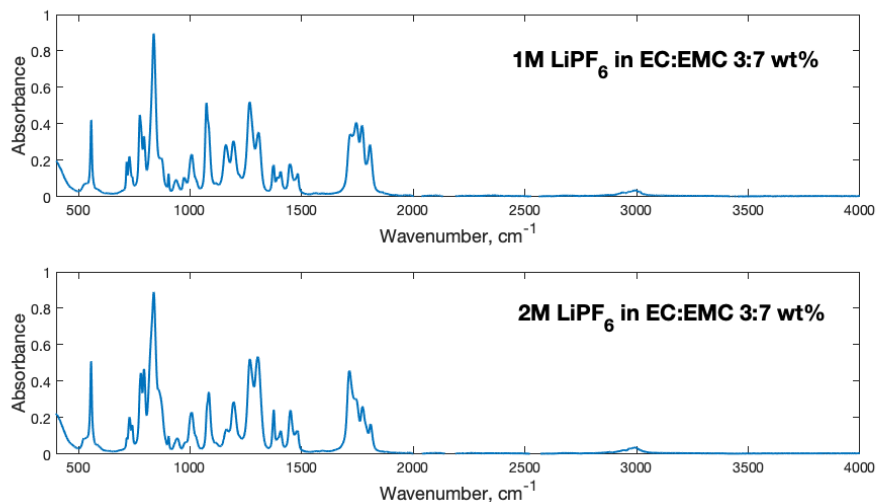


Figure S5: FTIR spectra of 1M LiPF<sub>6</sub> in EC:EMC 3:7 wt% (LP57) and 2M LiPF<sub>6</sub> in EC:EMC 3:7 wt% electrolytes.

## Viscosity calculation

The value of viscosity depends on the frequencies of saving trajectories. Fig. S8 shows autocorrelation of pressure tensor averaged for six components  $P_{xy}$ ,  $P_{xz}$ ,  $P_{yz}$ ,  $\frac{1}{2}(P_{xx} - P_{yy})$ ,  $\frac{1}{2}(P_{xx} - P_{zz})$ , and  $\frac{1}{2}(P_{yy} - P_{zz})$  and  $\eta$  using Einstein's relation for different frequencies. Auto correlation becomes insensitive to the output frequency below 12 fs. Now, Green-Kubo formula for viscosity calculation is proportional to this auto correlation function which is reformulated to Einstein's relation. Hence viscosity should have same dependence on the output frequency as the auto correlation and it does not depend on the output frequency as well below 12 fs. Viscosity data for different compositions are tabulated in Table 4.

Table 2: Viscosity for different compositions at several temperatures.

T (° C)	EC:EMC weight ratio	LiPF <sub>6</sub> concentration	Viscosity(cP)
50	24:76	0.45 M (0.44 m)	1.04
60	24:76	0.45 M (0.44 m)	0.81
70	24:76	0.45 M (0.44 m)	0.72
80	24:76	0.45 M (0.44 m)	0.63
50	24:76	1.93 M (2.1 m)	3.64
60	24:76	1.93 M (2.1 m)	2.62
70	24:76	1.93 M (2.1 m)	2.25
80	24:76	1.93 M (2.1 m)	2.05
60	24:76	0.208 M	0.71
60	24:76	0.95 M	1.22
60	24:76	1.4 M	2.15
60	24:76	2.44 M	3.97
60	0:100	0.95 M	0.825
60	10:90	0.95 M	1.0
60	40:60	0.95 M	1.63
60	60:40	0.95 M	2.0
60	76:24	0.95 M	2.7



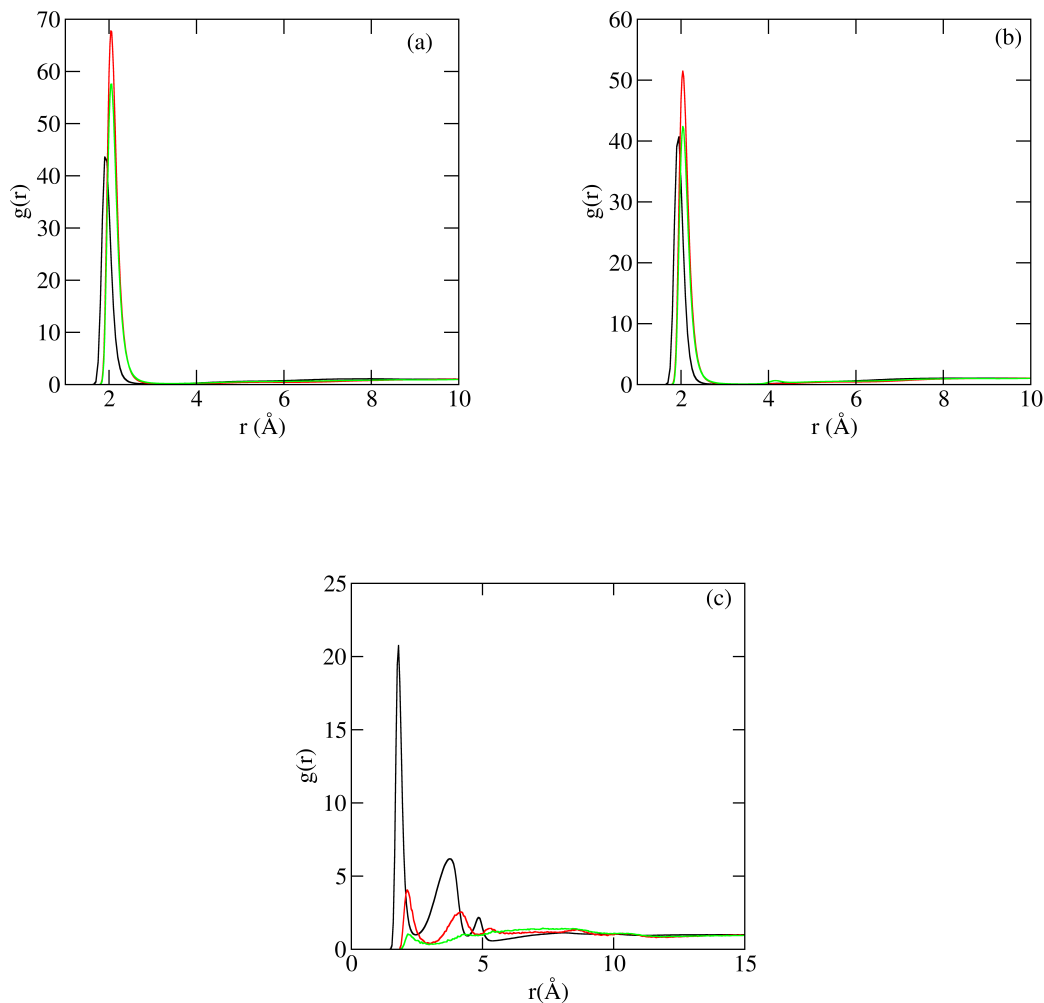


Figure S6: (a) Radial distribution function of Li ions around double bonded Oxygen of EC molecules from three force field models, polarizable(black), OPLS without charge rescaling(red), and OPLS with charge rescaling(green) for 0.95 M composition. (b) Radial distribution function of Li ions around double bonded Oxygen of EMC molecules and coloring is done on different force fields same as (a). (c) Radial distribution function of Li ions around Fluorine atom of  $\text{PF}_6^-$  anion from three force field models, and coloring is done same as (a).

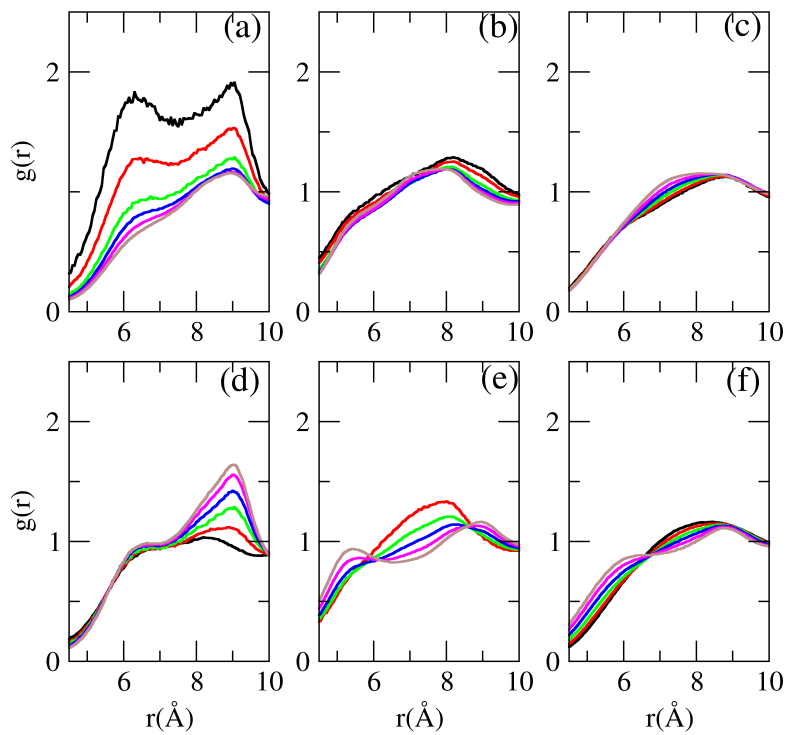


Figure S7: The second solvation shell in  $g(r)$  is shown for same data set as Fig. ??.

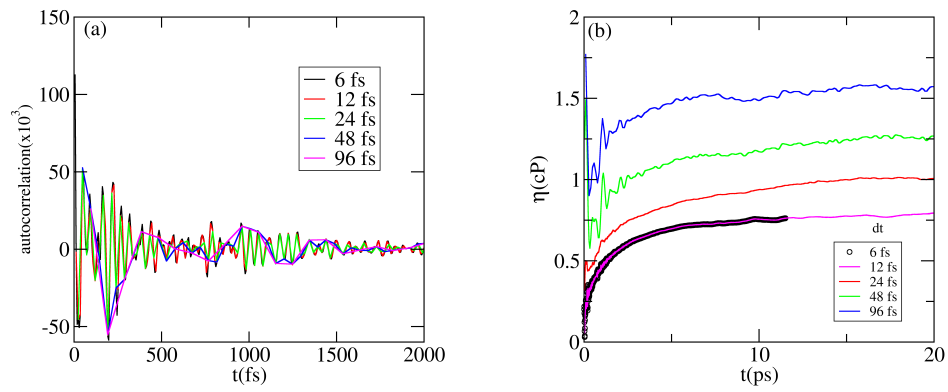


Figure S8: (a) Auto correlation of six components of pressure tensor(see main text) are calculated then taken an average which is plotted against time for different trajectory saving frequencies  $dt$ . (b) $\eta$  using Einstein's relation is plotted against  $t$  for same sets of  $dt$  as left panel.

## References

- (1) Mallarapu, A.; Bharadwaj, V. S.; Santhanagopalan, S. Understanding extreme fast charge limitations in carbonate mixtures. *J. Mater. Chem. A* **2021**, *9*, 4858–4869.
- (2) Logan, E. R.; Tonita, E. M.; Gering, K. L.; Ma, L.; Bauer, M. K. G.; Li, J.; Beaulieu, L. Y.; Dahn, J. R. A Study of the Transport Properties of Ethylene Carbonate-Free Li Electrolytes. *Journal of The Electrochemical Society* **2018**, *165*, A705–A716.