Electronic Supplementary Information
Impact of Li, Na and Zn metal cation concentration in EMIM-TFSI ionic liquids on ion clustering, structure and dynamics

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1 Box size of all the systems

Table 1 Box sizes of metal cation-IL systems in Å

System	Li	Na	Zn
0.04	51.155	51.186	51.504
0.12	50.504	50.468	51.582
0.24	49.492	49.612	51.757

2 Duration of the production simulations of all the systems

Table 2 Production run duration in ns of all the systems. To ensure uniform and faster dynamics analysis, 393 K was chosen for our studies. The ion-pair lifetimes for the Zn system ran for 180 ns, due to the long stability lifetimes of Zn-TFSI pairs.

Temperature (K)		313	333	353	373	393
System	Concentration	Duration (ns)				
Li	0.04	40	50	50	50	50
	0.12	40	40	40	40	50
	0.24	50	50	50	50	50
Na	0.04	60	60	40	50	50
	0.12	50	40	40	40	50
	0.24	60	60	50	40	50
Zn	0.04	70	70	50	50	50
	0.12	70	70	50	50	50
	0.24	70	70	50	50	50

3 Density Study of all the systems

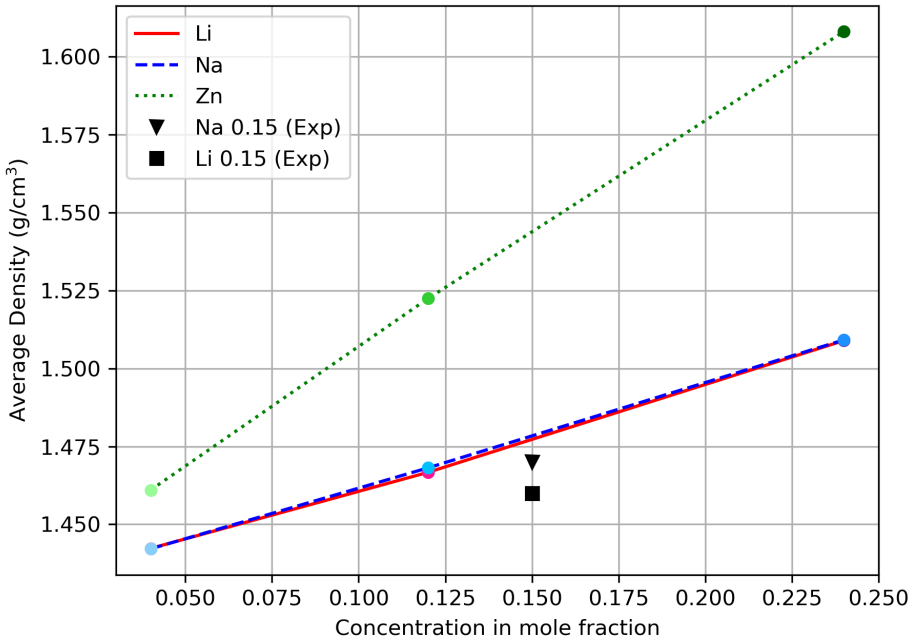


Figure 1 Density of all the systems studied as a function of concentration. For the Li and Na systems, the values at 0.15 mole fraction of the salt were taken by extrapolating the density values from previous experimental work.[1] There is a less than 2% deviation observed between the values obtained in our simulation studies and the experimental work. For Zn systems, there is a lack of density studies in the literature, and the closest one that was relevant for our study has reported the density of 0.5 mole fraction (1:1 ratio EMIM TFSI and $Zn(TFSI)_2$) at 343K to be 1.76 g/cm^3.[2] On consideration of temperature and concentration, our values are expected to be within the acceptable deviation range. Hence, we can say that the density values are in good agreement.

4 NVT vs NVE ensemble

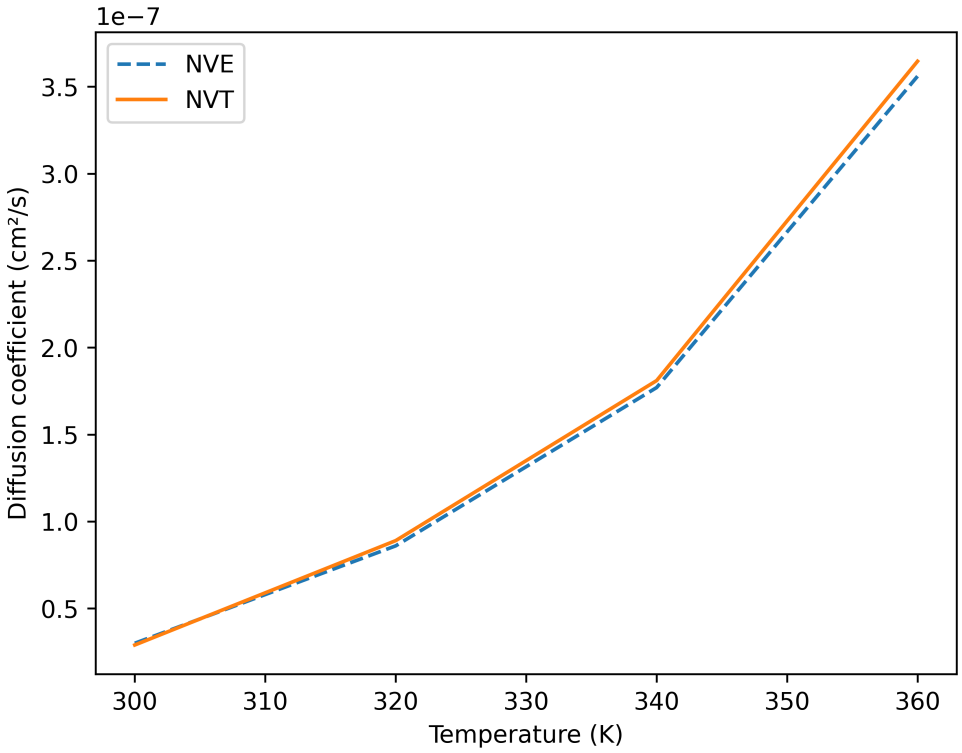


Figure 2 Comparison of NVT and NVE ensemble effects on the diffusion of TFSI anion in neat EMIM-TFSI with respect of the temperature. The Nose-Hover thermostat implemented in LAMMPS does not affect the dynamics significantly and then is a good approximation that can be used instead of NVE ensemble (faster and more stable).

5 Diffusion Coefficients of Na system as a function of temperature

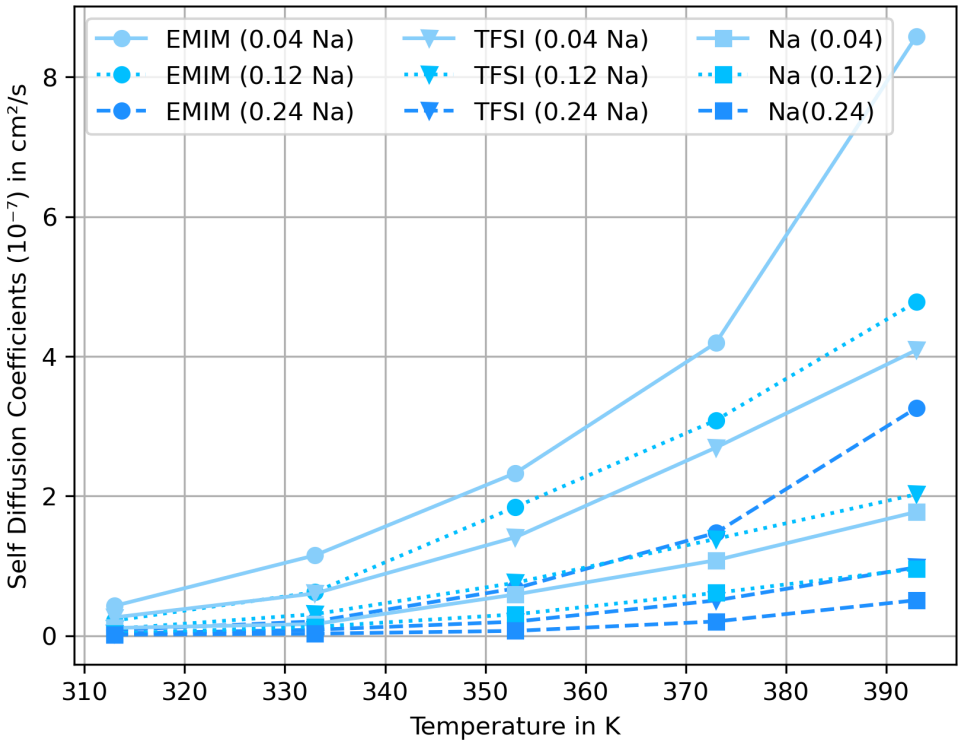


Figure 3 Diffusion Coefficients of Na system as a function of temperature.

6 Diffusion Coefficients of Zn system as a function of temperature

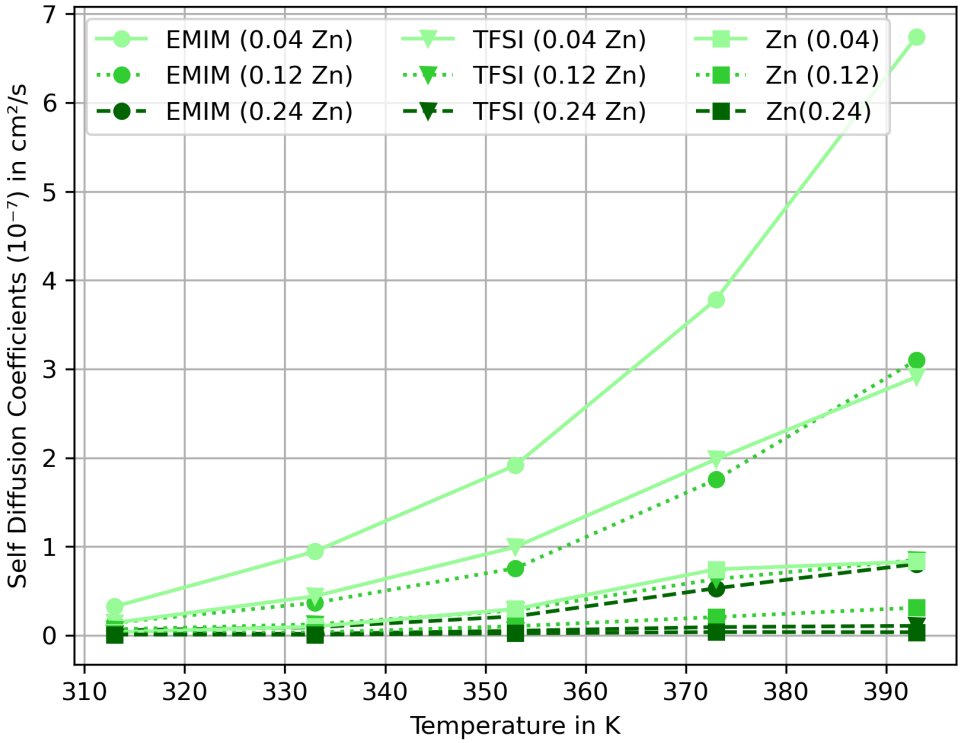
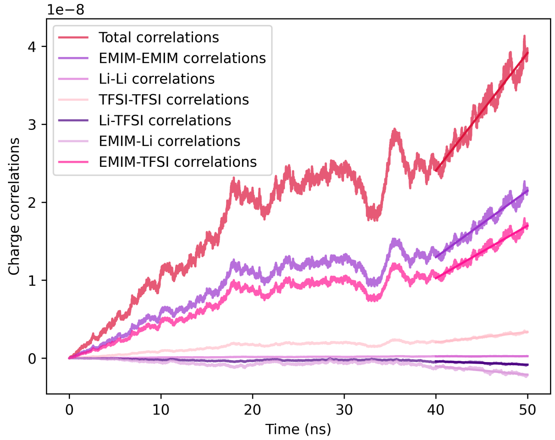


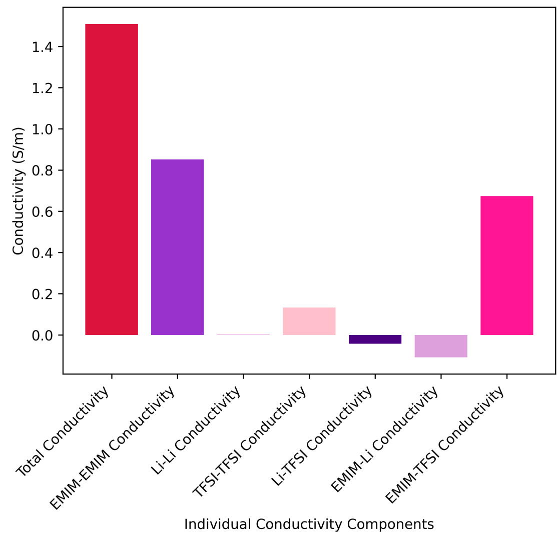
Figure 4 Diffusion Coefficients of Zn system as a function of temperature.

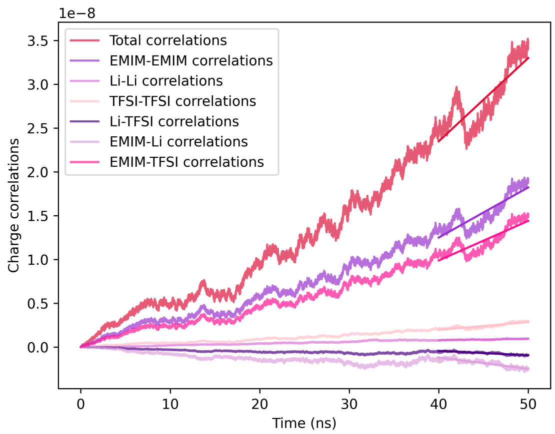
7 Conductivity

The following figures represent the charge correlations (on the left hand side) and the conductivity (on the right hand side). For each system, the contribution of each ion pair type is represented. Red-like, blue-like and green-like curves are respectively Li, Na and Zn systems.

All conductivities decrease with metal concentration. The statistics is not good enough to analyse precisely the trend of each component.


1e−8
Total correlations
EMIM-EMIM correlations
Li-Li correlations
TFSI-TFSI correlations
Li-TFSI correlations
EMIM-Li correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)


Conductivity (S/m)
Total Conductivity
EMIM-EMIM Conductivity
Li-Li Conductivity
TFSI-TFSI Conductivity
Li-TFSI Conductivity
EMIM-Li Conductivity
EMIM-TFSI Conductivity
Individual Conductivity Components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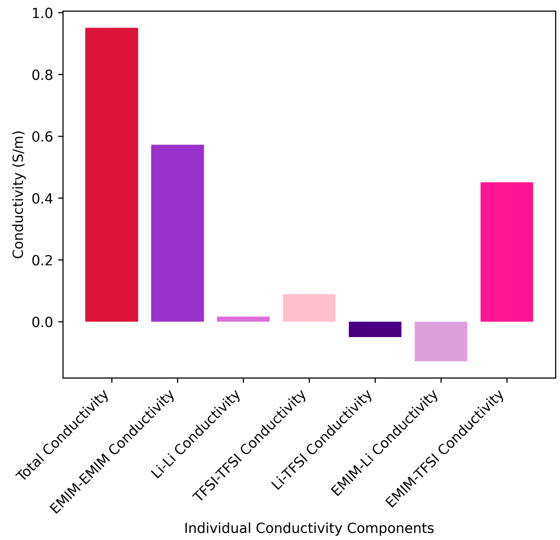
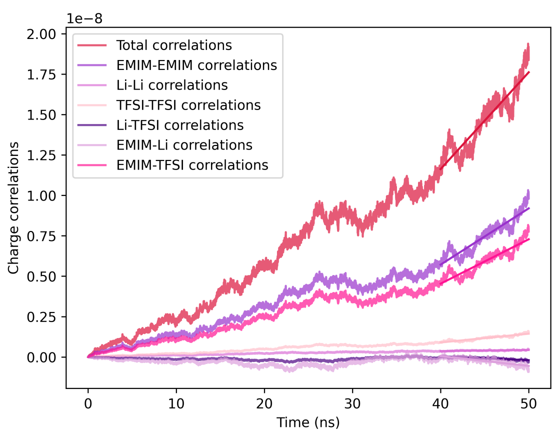
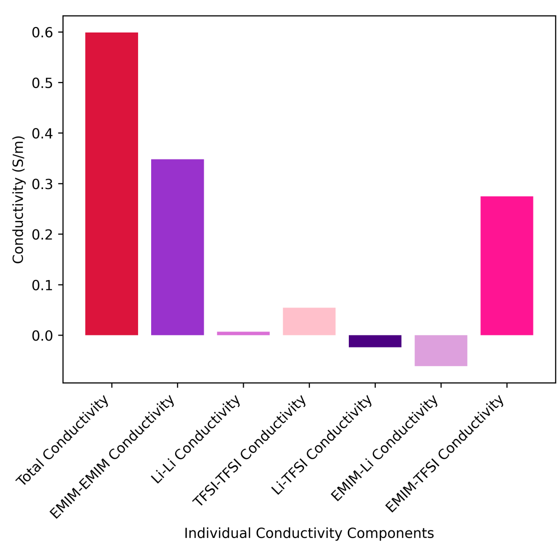
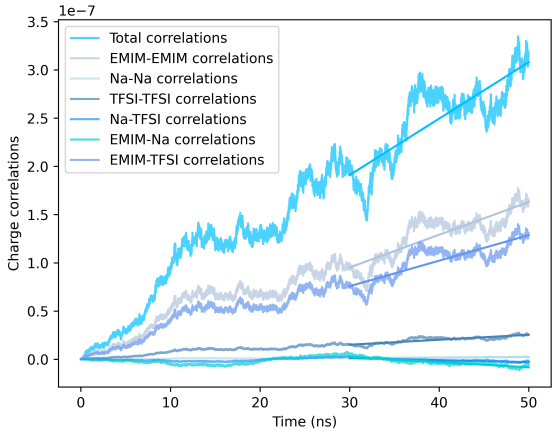
Total correlations
EMIM-EMIM correlations
Li-Li correlations
TFSI-TFSI correlations
Li-TFSI correlations
EMIM-Li correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)


Conductivity (S/m)
Total Conductivity
EMIM-EMIM Conductivity
Li-Li Conductivity
TFSI-TFSI Conductivity
Li-TFSI Conductivity
EMIM-Li Conductivity
EMIM-TFSI Conductivity
Individual Conductivity Components


1e−8
Total correlations
EMIM-EMIM correlations
Li-Li correlations
TFSI-TFSI correlations
Li-TFSI correlations
EMIM-Li correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)


Conductivity (S/m)
Total Conductivity
EMIM-EMIM Conductivity
Li-Li Conductivity
TFSI-TFSI Conductivity
Li-TFSI Conductivity
EMIM-Li Conductivity
EMIM-TFSI Conductivity
Individual Conductivity Components


1e−7
Total correlations
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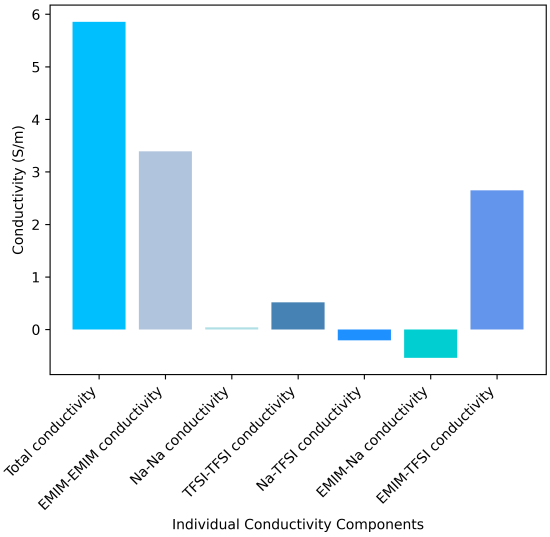
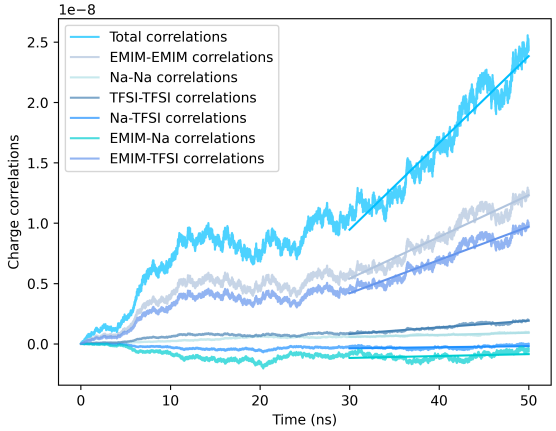
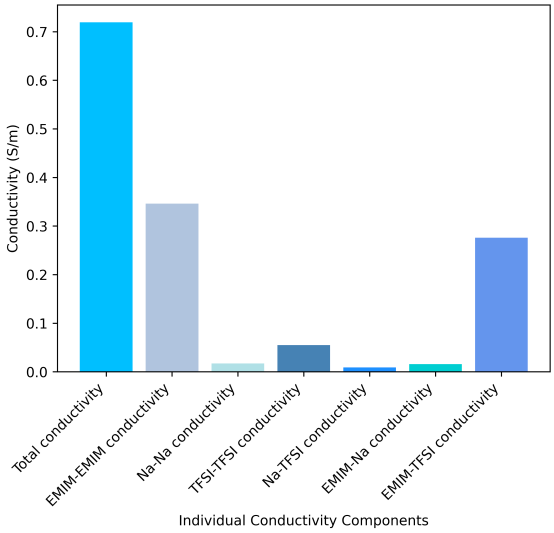
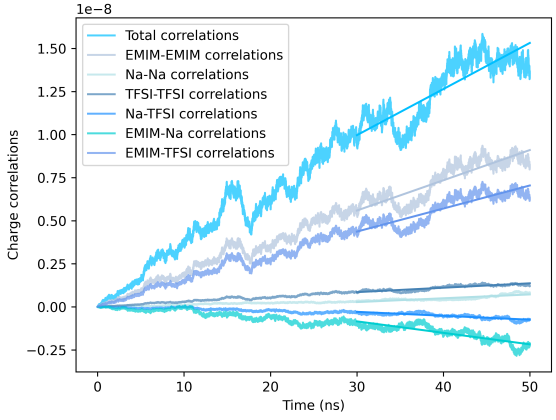
Na-Na correlations
TFSI-TFSI correlations
Na-TFSI correlations
EMIM-Na correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)


Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Na-Na conductivity
TFSI-TFSI conductivity
Na-TFSI conductivity
EMIM-Na conductivity
EMIM-TFSI conductivity
Individual Conductivity Components


1e−8
Total correlations
EMIM-EMIM correlations
Na-Na correlations
TFSI-TFSI correlations
Na-TFSI correlations
EMIM-Na correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)


Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Na-Na conductivity
TFSI-TFSI conductivity
Na-TFSI conductivity
EMIM-Na conductivity
EMIM-TFSI conductivity
Individual Conductivity Components


1e−8
Total correlations
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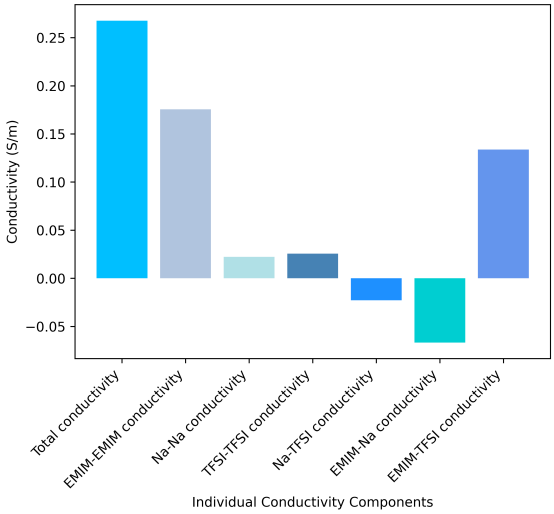
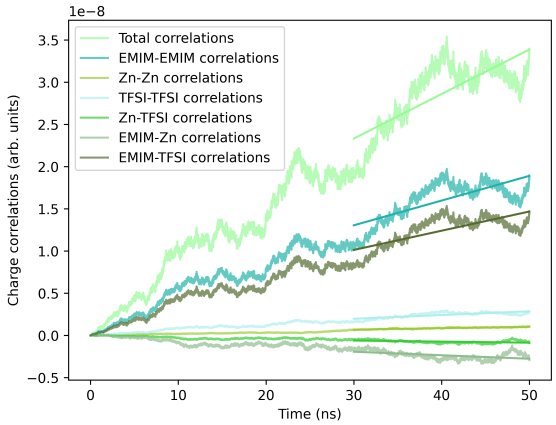
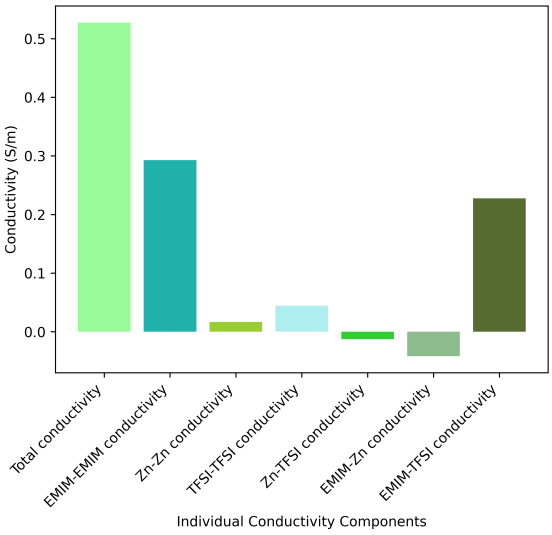
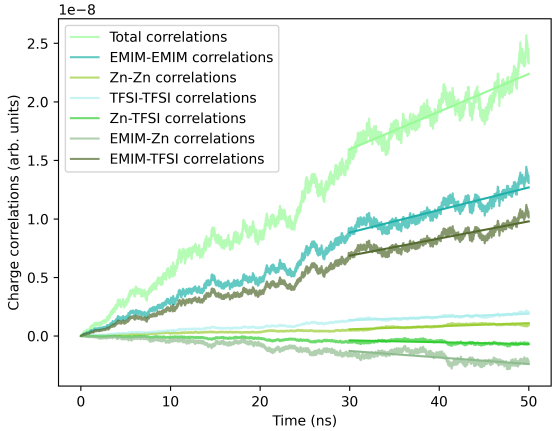
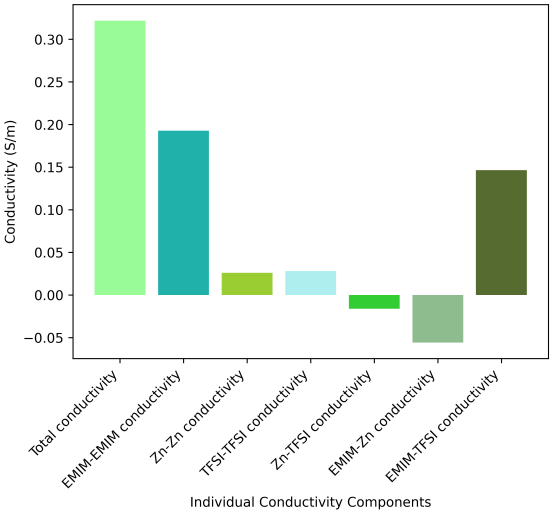
Na-Na correlations
TFSI-TFSI correlations
Na-TFSI correlations
EMIM-Na correlations
EMIM-TFSI correlations
Charge correlations
Time (ns)

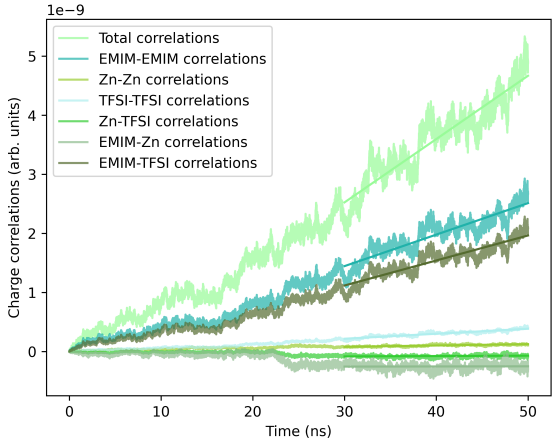

Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Na-Na conductivity
TFSI-TFSI conductivity
Na-TFSI conductivity
EMIM-Na conductivity
EMIM-TFSI conductivity
Individual Conductivity Components


1e−8
Total correlations
EMIM-EMIM correlations
Zn-Zn correlations
TFSI-TFSI correlations
Zn-TFSI correlations
EMIM-Zn correlations
EMIM-TFSI correlations
Charge correlations (arb. units)
Time (ns)


Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Zn-Zn conductivity
TFSI-TFSI conductivity
Zn-TFSI conductivity
EMIM-Zn conductivity
EMIM-TFSI conductivity
Individual Conductivity Components


1e−8
Total correlations
EMIM-EMIM correlations
Zn-Zn correlations
TFSI-TFSI correlations
Zn-TFSI correlations
EMIM-Zn correlations
EMIM-TFSI correlations
Charge correlations (arb. units)
Time (ns)


Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Zn-Zn conductivity
TFSI-TFSI conductivity
Zn-TFSI conductivity
EMIM-Zn conductivity
EMIM-TFSI conductivity
Individual Conductivity Components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Total correlations
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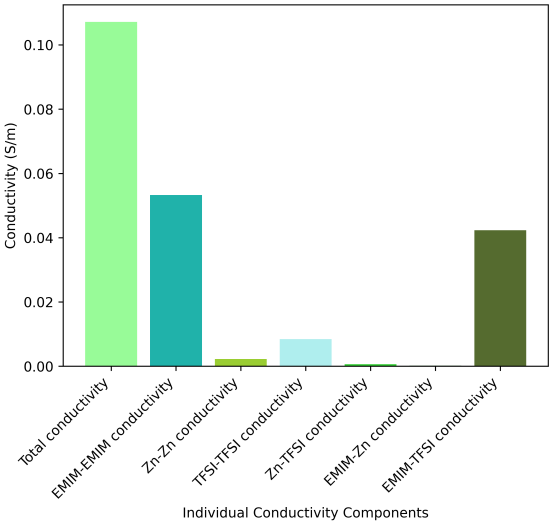
Zn-Zn correlations
TFSI-TFSI correlations
Zn-TFSI correlations
EMIM-Zn correlations
EMIM-TFSI correlations
Charge correlations (arb. units)
Time (ns)


Conductivity (S/m)
Total conductivity
EMIM-EMIM conductivity
Zn-Zn conductivity
TFSI-TFSI conductivity
Zn-TFSI conductivity
EMIM-Zn conductivity
EMIM-TFSI conductivity
Individual Conductivity Components

Notes and references

[1] D. Monti, E. Jónsson, M. R. Palacín and P. Johansson, *Journal of Power Sources*, 2014, **245**, 630–636.
[2] T. Liu, R. Vilar, S. Eugénio, J. Grondin and Y. Danten, *Journal of Applied Electrochemistry*, 2015, **45**, 87–93.