

# Supplementary Information

## Cluster Analysis as a Tool for Quantifying Structure-Transport Properties in Simulations of Superconcentrated Electrolyte

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### Graph-theory-based Cluster Analysis

From the point of view of graph theory, the simulation system can be viewed as a graph made up vertices (also called nodes) which are connected by edges. In our particular cases, the  $\text{Li}^+$  and  $\text{TFSI}^-$  ions can be treated as nodes. For each node, it forms an edge with the nearest counter-ion node, provided meeting the following criterion: the distance between Li and the either O atom in  $\text{TFSI}^-$  is less than 3.00 Å or the distance between Li and the N atom in  $\text{TFSI}^-$  is less than 5.26 Å. This criterion was set based on the radial distribution functions between  $\text{Li}^+$  and two possible bonding sites in  $\text{TFSI}^-$  (as shown in Figure S1). Once the nodes and the edges of the graph are set up, one can differentiate all ionic species

by finding out all all connected components in the graph (as illustrated in Figure S2). It is important to note that in our method, the edge can only be formed between a node and its nearest neighbor, despite some other nodes may also meet the distance criterion (see Figure S3 for rationale).

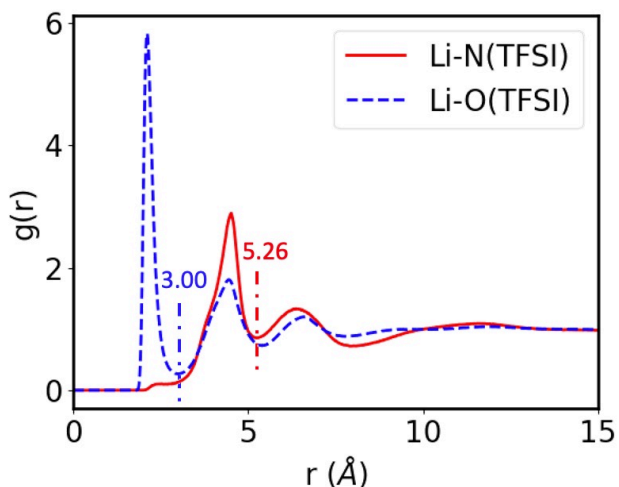


Figure S1: Radial distribution functions of  $\text{Li}^+\text{-N}(\text{TFSI}^-)$  and  $\text{Li}^+\text{-O}(\text{TFSI}^-)$ . The distance criteria are set up based on the minima following the first peaks in the RDFs.

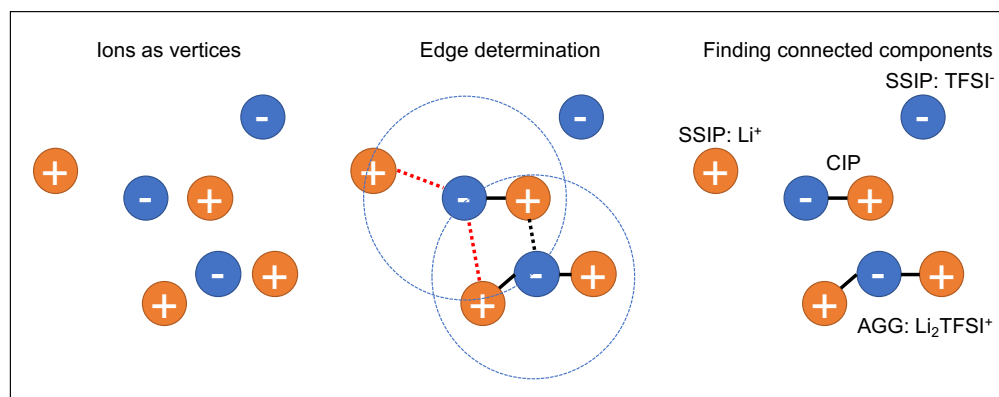


Figure S2: Schematics of the developed graph-theory-based cluster analysis developed for differentiating different cluster species. Note that in the Edge determination step, only the black solid lines are considered as edges. The red dashed lines indicate non-compliance with the distance criterion detailed in Figure S1, while the black dashed lines signify that, although the distance criterion was met, the node is not the nearest counter-ion.

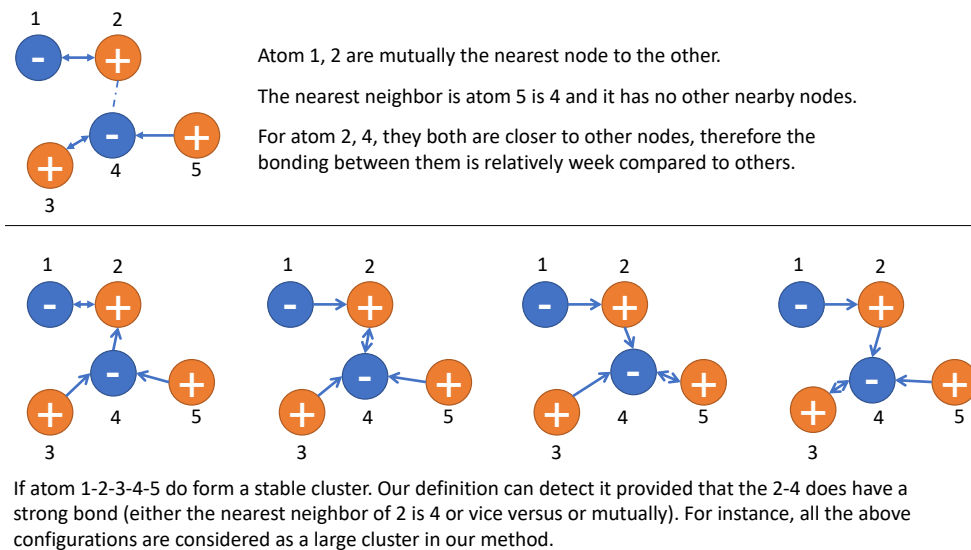


Figure S3: Rationale of the edge determination step.

## Supplementary Figures

Table S1: Simulation Cell Parameters

Molality (mol kg <sup>-1</sup> )	N (Li-TFSI)	N(H <sub>2</sub> O)
1	18	1000
4	72	1000
7	126	1000
10	180	1000
15	270	1000
21	378	1000

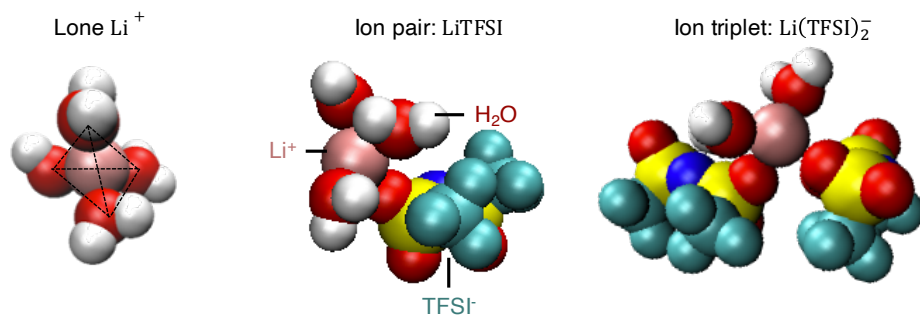


Figure S4: Snapshots of different solvation structures.

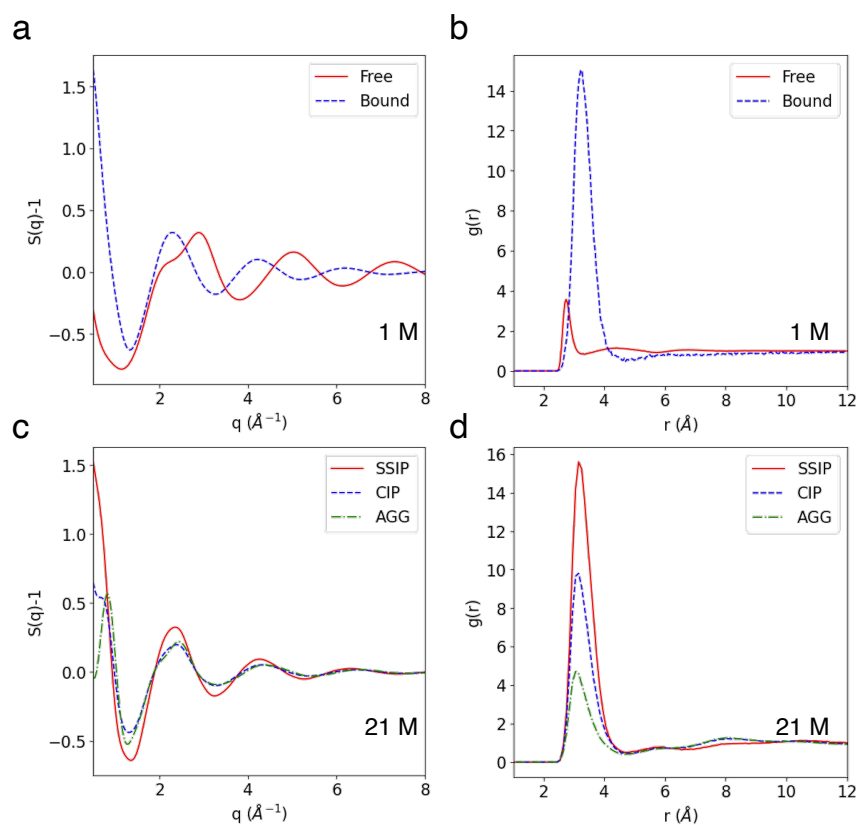


Figure S5: (a, b) Partial structure factors (a) and radial distribution functions (b) for O(water)-O(water) in the free and bound water in a 1 m dilute electrolyte. (c, d) For the 21 m WiSE electrolyte, partial structure factors (c) and radial distribution functions (d) of O(water)-O(water) for bound water in various ionic species.

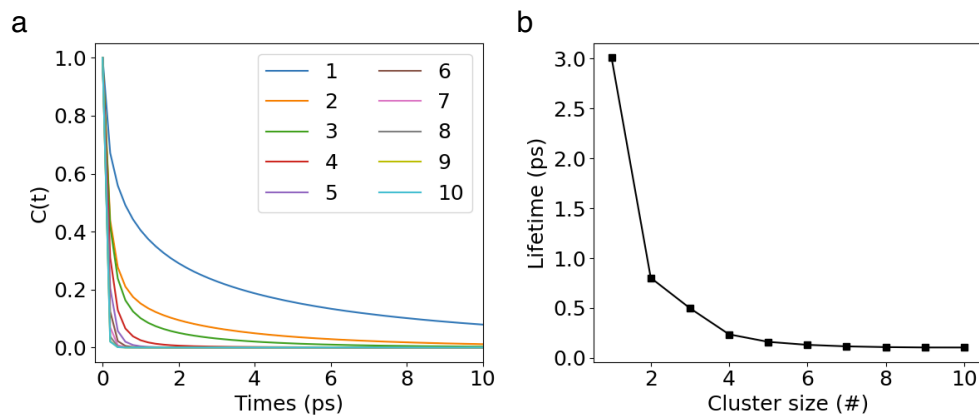


Figure S6: (a) The survival probability functions of cations and anions in different ionic clusters. The legend number indicates the total ions in an ionic cluster. (b) Mean residue time for clusters with different sizes.

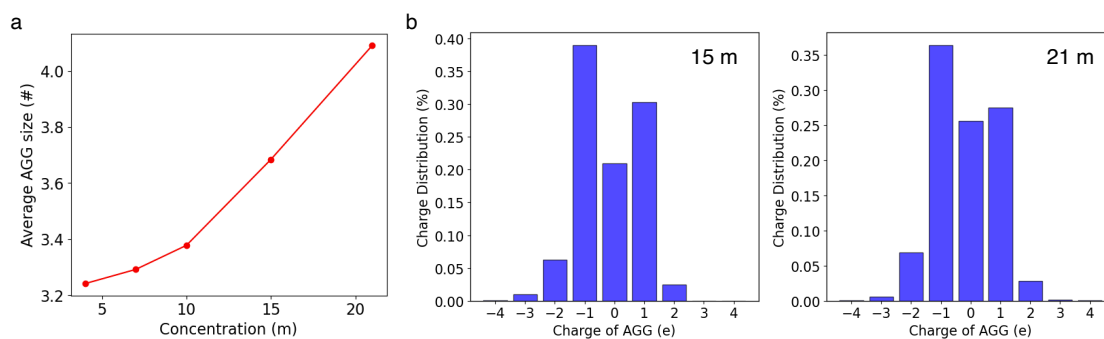


Figure S7: (a) The average number of ions in AGGs in the LiTFSI electrolyte at various concentrations. (b) The distribution of the charges of AGGs in the 15 m and 21 m WiSE electrolytes

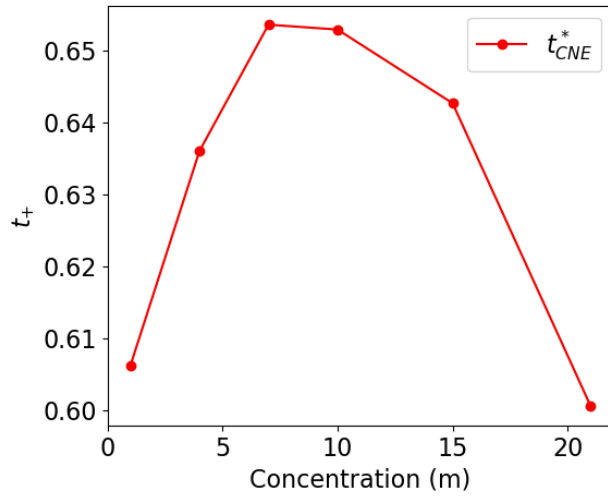


Figure S8: The  $\text{Li}^+$  transference number of LiTFSI electrolytes computed by  $t_+^{CNE*} = \frac{D_+^{SSIP}}{D_+^{SSIP} + D_-^{SSIP}}$ .