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Supplementary Materials

3-(2,2,2-trifluoroethoxy)propionitrile-based electrolytes for high energy density lithium metal batteries

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Computational analysis

Two model systems were considered for molecular dynamic (MD) simulation and density functional theory (DFT) analyses: one system with 1:1 volume fraction of FEC and FEON solvents (1:1) and one system with 1:3 volume fraction of FEC and FEON solvents (1:3). Both systems employed the same concentration of salts: LiODFB (0.29 M) and LiTFSI (0.88 M). Table S1 lists the number of entities present in each system. The PACKMOL package [S1] was used to construct the initial configurations by random distribution of molecules in cubic boxes with initial side length 18.0 Å .

Table S1. Number of each specie present in the systems FEC:FEON 1:1 and 1:3.

Compound	1:1	1:3
FEC	19	10
FEON	11	17
LiODFB	1	1
LiTFSI	3	3

Next, classical MD simulations with periodic boundary conditions were performed using the GROMACS package [S2]: first a 5 ns NVT (modified V-rescale thermostat[S3]), then a 5 ns NPT (modified V-rescale thermostat and Berendsen barostat [S4]), and then a production run of 150 ns NPT (modified V-rescale thermostat and Parrinello-Rahman pressure coupling [S5]). All simulations were carried out at 300 K with a time step of 1 fs using particle mesh Ewald summation for long-range electrostatic interactions. The van der Waals and electrostatic cutoff was 8 Å. A MKTOP script [S6] was used to construct the molecular topologies using the OPLS-AA force field as implemented in GROMACS to describe the bonded and non-bonded interactions of FEON and FEC molecules. Partial charges for the FEC molecule were determined at B3LYP STO-3G level of theory using the PolyParGen platform[S7]. Restrained Electrostatic Potential (RESP) charges were used to obtain charges for the FEON molecule with the same set-up as described below in the single point ab initio calculations. Force field parameters for the ODFB ion were originally developed by Han and Borodin[S8] while the parameters for the TFSI ions were taken from Padua and Lopes[S9].

After equilibration by classical MD, the systems were further refined through ab initio molecular dynamics (AIMD). Due to the high computational cost of AIMD, radial distribution functions (RDFs) were obtained for both 1:1 and 1:3 systems from classical MD trajectories in periods of 14 ns in order to extract 6 (3 per system) distinctive starting configurations and use these as starting points for the AIMD simulations. Due to that the initial snapshots were extracted from NPT simulations, each simulation cell varied between 17.51 and 17.97˚A. Next, 2.5 ps of equilibration was followed by 40 ps of production run for each starting configuration in the NVT ensemble with a time step of 0.5 fs. The temperature was kept constant at 320 K by means of a Nose-Hoover thermostat with a time constant of 20 fs and a chain length of three. Density functional theory (DFT) calculations employing a Becke-Lee-Yang-Parr (BLYP) functional[S10], [S11] and Grimmes D3 dispersion correction [S12] was used for every ab initio calculation. Godecker-Tetter-Hutter [S13] norm-conserving pseudo potentials were used to account for the nuclear cores. The Kohn-Sham orbitals were expanded with double-ζ valence polarized functions. Moreover, a cutoff of 400 Ry was used to truncate the auxiliary plane wave basis set.

In order to study the coordination environment of each Li^+, the coordination numbers (CNs) were calculated for every individual lithium ion present in the 1:1 and 1:3 systems. The 6 AIMD trajectories allowed us to calculate the RDF using a self-implemented python script. Next, we obtained the CNs by integrating each RDF function up to the first minimum located at the distance equal 2.75 Å. Moreover, the analysis and manipulation of trajectories was facilitated by MDAnalysis python package [S14], [S15].

In addition, single point calculations were performed to determine the HOMO and LUMO orbitals in several clusters and isolated molecules; i.e. the lithium ion and its first solvation shell. This was done by extracting relevant snapshots from the AIMD simulations and isolating the ion with its first solvation shell. The setup was kept as in the AIMD calculations, but with each cluster being centered in a non-periodic cubic box with side length equal to 25 Å. The charge in the calculation was varying between -2 to 0 depending on the number of anions present in the cluster. Both AIMD simulation as well as single point calculations for determination of the HOMO and LUMO levels were performed with the CP2K package [S16].

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