



Molecular simulations of electrolyte structure and dynamics in lithium–sulfur battery solvents



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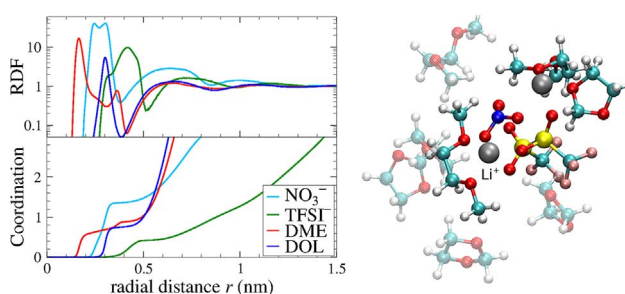
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HIGHLIGHTS

- Molecular simulation force-field for Li/S battery electrolytes developed.
- Strong temperature-dependence for Li⁺ diffusion predicted.
- Conductivity and related ion pairing effects unveiled.
- Molecular insights on detailed solvation structure around Li⁺ reported.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of modern lithium-sulfur (Li/S) battery systems critically depends on the electrolyte and solvent compositions. For fundamental molecular insights and rational guidance of experimental developments, efficient and sufficiently accurate molecular simulations are thus in urgent need. Here, we construct a molecular dynamics (MD) computer simulation model of representative state-of-the-art electrolyte–solvent systems for Li/S batteries constituted by lithium-bis(trifluoromethane)sulfonimide (LiTFSI) and LiNO₃ electrolytes in mixtures of the organic solvents 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). We benchmark and verify our simulations by comparing structural and dynamic features with various available experimental reference systems and demonstrate their applicability for a wide range of electrolyte–solvent compositions. For the state-of-the-art battery solvent, we finally calculate and discuss the detailed composition of the first lithium solvation shell, the temperature dependence of lithium diffusion, as well as the electrolyte conductivities and lithium transference numbers. Our model will serve as a basis for efficient future predictions of electrolyte structure and transport in complex electrode confinements for the optimization of modern Li/S batteries (and related devices).

1. Introduction

Lithium–sulfur (Li/S) batteries are discussed as a cost efficient key technology for future applications in portable electronic devices, electromobility, and as a backup storage system for the reliable use of

renewable energies [1–10]. Because of their high theoretical electrochemical capacity of 1675 mAhg⁻¹, Li/S batteries represent in principle an efficient energy storage system. Moreover, the abundance and low-cost of their raw materials are important advantages of this battery concept.

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The actual performance delivered by Li/S batteries is proving to be severely limited in many cases, which is directly related to the role of the electrolyte [6–8,10–14]. Ultimately, the successful development of the Li/S battery requires careful coordination of the choice of electrolyte with the specific nature of the cathode material. In particular, the optimal electrolyte has to fulfill several boundary conditions, as such to maximize charge carrier conductivity and high ionic dissociation but also to guarantee Li^+ dissolution and stabilization of the lithium anode [15]. For the latter, the most prominent example is lithium nitrate (LiNO_3), which has been introduced to stabilize the anode by a protective layer formed on the electrode surface [16,17]. Recent developments have empirically demonstrated that lithium TFSI (bis(trifluoromethane)sulfonimide) salts (at about 1 M concentration) in 1:1 mixtures of the organic solvents 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) are found to be a suitable electrolyte solution for Li/S batteries, satisfying many of the requirements [7,18]. More generally, these and similar electrolyte/solvent compositions are also relevant for the development of lithium–oxygen and lithium–air batteries [12,14,19,20] as well as for Na/S batteries [21].

For fundamental structural insights on a molecular level and rational guidance of experimental developments, efficient and accurate molecular simulations are of significant importance. For this, classical polarizable or non-polarizable all-atom force field simulations promise the best compromise between accuracy and efficiency [22–35]. For example, they can demonstrate how the details of local solvation structures or ion pairing affinities can be linked to transport properties, such as diffusion and conductivity, i.e., they establish *structure-property relationships*. In particular, they elucidate the effects of organic solvents on the lithium ion solvation and transport in ionic liquid electrolytes [29], i.e., the solvate structures of LiTFSI electrolytes [31,32] as well as the influence of cations on lithium ion coordination and transport [30]. However, despite their importance for modern Li/S battery development, the simulation studies of the structural properties of the lithium salts in mixtures of DME/DOL solvents are scant [76]. Of particular interest is, for instance, an accurate structural characterization of the local lithium solvation structure, which is decisive for ion permeation and capacitance build-up within the commonly used porous organic electrode materials. Once a good basic electrolyte model is available, further extensions can successively be built up on this (e.g., by including the sulfur component, electrode materials, etc.) and combinatorial solvent/electrolyte optimization and the establishment of quantitative structure-property-function relationships of Li/S battery systems come into closer reach.

Here, we construct a molecular dynamics (MD) computer simulation model of representative state-of-the-art electrolyte–solvent systems [7,18] for Li/S batteries constituted by LiTFSI and LiNO_3 electrolytes in mixtures of DME and DOL. We focus on a force field without explicit many-body polarizability as often used before [33] in order to enhance computing speed and invoke less parameters, aiming at comparable accuracy of structural and dynamic properties. We benchmark and verify our simulations by comparing those calculated structural and dynamic features with various available reference systems, i.e., structure, density, dielectric constant, and viscosity of the organic solvents and their mixtures [28,36–38], as well as ionic diffusion and conductivity in dilute electrolytes in the respective pure (one-component) solvents [39]. With these we demonstrate their applicability for a wide range of electrolyte–solvent compositions. As a first practical demonstration at hand of the state-of-the-art electrolyte solvent for Li/S batteries, we calculate and discuss the detailed composition of the first lithium solvation shell, the temperature dependence of lithium diffusion, as well as the electrolyte conductivities and lithium transference numbers. We complement this with new experimental measurements on viscosity and conductivity. Our validated model will thus serve as a basis for efficient future predictions of electrolyte structure and transport in complex electrode confinements for the optimization of modern Li/S batteries (and related devices).

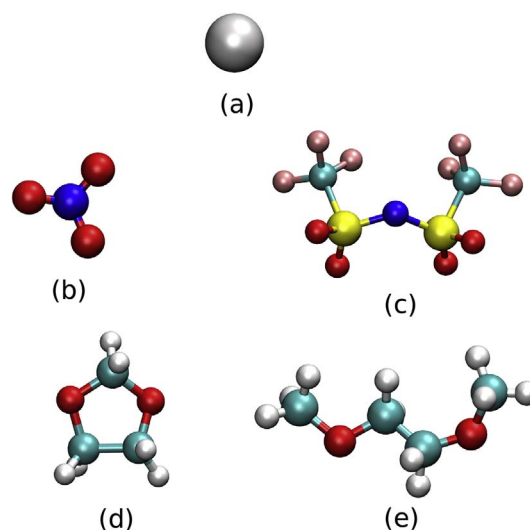


Fig. 1. Exemplary illustrations of the ions and solvent molecules involved in our simulation study: Ions: (a) Li^+ , (b) NO_3^- , (c) TFSI $^-$ and organic solvent molecules: (d) DOL and (e) DME. The sizes of Li^+ and NO_3^- are scaled up for aesthetic reason.

This paper is organized as follows: we first describe in detail the used simulation model and underlying analyzing numerical methods for evaluations of relevant quantities. In Section 3 we describe experimental settings. We then present and discuss the results in Section 4, followed by concluding remarks in Section 5.

2. Computer simulations and analysis methods

2.1. Simulation details

We perform all-atom MD computer simulations of bulk electrolytes in mixed organic solvents constituted of the molecules displayed in Fig. 1 employing the GROMACS 5.1 simulation package [40]. The production simulations are performed in the NpT ensemble at constant pressure and constant temperature in a cubic box with periodic boundary conditions in all three Cartesian directions. The temperature is maintained by the Berendsen thermostat at 304 K in system III (defined further below) and 298 K for all other systems with a time constant of 0.1 ps [41]. A constant pressure of 1 bar is controlled by the Parrinello–Rahman barostat [42,43] with a coupling constant of 2 ps. Electrostatic interactions are treated using the Particle-Mesh-Ewald (PME) method [44,45] with the Fourier spacing of 0.12 nm and 1 nm real-space cut-off. For non-neutral systems, we apply uniform neutralizing background charge in the PME. The molecules are represented by non-polarizable models, i.e., explicit electronic polarization effects are neglected. We consider the polarization implicitly as discussed in the force-field subsection below. All non-bonded non-electrostatic interatomic interactions are based on the Lennard-Jones (LJ) potential with a cut-off at 1 nm and shifted to zero there, together with the geometric combination rules [27] $\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}$ and $\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}$ for the LJ size and energy parameters, respectively. The LINCS algorithm [46,47] is employed for all bond constraints. The integration time step is 2 fs. In order to facilitate the equilibration of solvent conformers, we first perform a simulated annealing approach where we heat the systems to 440 K or 500 K and then cool them down to 298 K within a time interval of 2 ns in the NVT ensemble.

2.2. Force fields

Due to the multi-component nature and the many degrees of freedom in our rather low dielectric systems, the parametrization of the model to reproduce a wide range of properties is notoriously difficult.

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