The DFT-ReaxFF Hybrid ~~Molecular~~ Reactive Dynamics Method with application to the Reductive Decomposition Reaction of the TFSI and DOL Electrolyte at a Lithium-Metal Anode Surface

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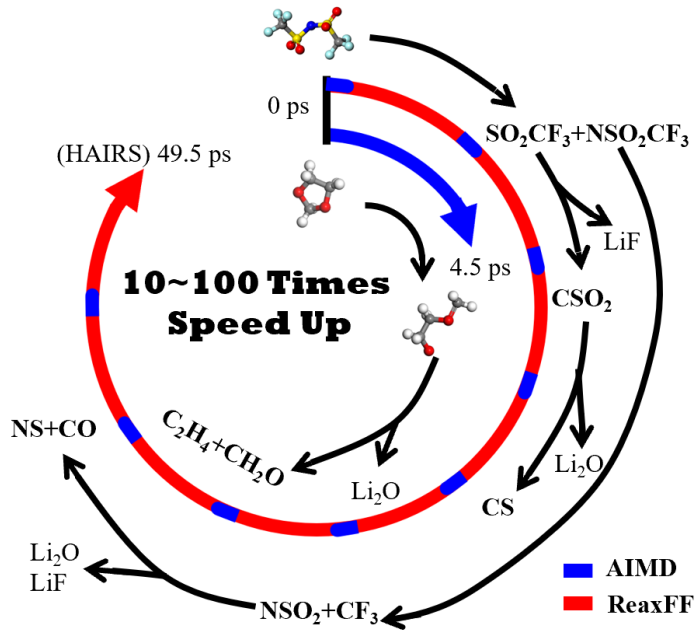
Abstract: The high energy density and suitable operating voltage make rechargeable lithium-ion batteries (LIB's) promising candidates to replace such conventional energy storage devices as non-rechargeable batteries. However, large-scale commercialization of LIB's is impeded significantly by degradation of the electrolyte, which reacts with the highly reactive lithium metal anode. Hence, to improve battery performance, it is of great importance to understand the reaction mechanisms responsible for degradation and formation of the solid-electrolyte interphase (SEI). In this work, we develop a hybrid computational scheme, **Hybrid *ab initio* molecular dynamics combined with reactive force fields**, denoted **HAIR**, to accelerate Quantum Mechanics based reaction dynamics (QM-RD or AIMD, for *ab initio* RD) simulations. The HAIR scheme extends the time scale accessible to AIMD by a factor of 10 times through interspersing ReaxFF simulations between the AIMD parts. This enables simulations of the initial chemical reactions of SEI formation, which may take 1 ns, far too long for AIMD.

We apply the HAIR method to the bis(trifluoromethanesulfonyl)imide (TFSI) electrolyte in 1,3-dioxolane (DOL) solvent at the Li metal electrode, demonstrating that HAIR reproduces the initial reactions of the electrolyte (decomposition of TFSI) previously observed in AIMD simulation while also capturing solvent reactions (DOL) that initiate by ring-opening to form such stable products as CO, CH_2O, and C_2H_4, as observed experimentally. These results demonstrate that the HAIR scheme can significantly increase the time scale for reactive MD simulations while retaining the accuracy of AIMD simulations. This enables a full atomistic description of the formation and evolution of SEI.

TOC GRAPHICS



Keywords: Hybrid reactive dynamics, Reactive force field, Lithium-ion batteries, Reductive Decomposition, Bis(trifluoromethanesulfonyl)imide electrolyte.

The global population explosion with the concomitant demand for energy and environmental sustainability, requires renewable energy technologies based on energy storage with batteries playing an essential part.[1] The high energy density and operating voltage characteristics of rechargeable lithium-ion batteries (LIB's) make them most promising candidates to facilitate high energy density storage.[2,3] Typical LIB's combine positive and negative electrodes (the anode and cathode respectively) with an electrolyte solution containing dissolved lithium salts, which leads to possible reactions and degradation.[4]

Rechargeable lithium-ion batteries are widely used for energy storage, but critical obstacles, such as irreversible capacity, safety, and cycle life, have prevented applications of LIB's to such large-scale applications as electric vehicles and aircraft at commercially feasible costs.[5,6] For example, Li metal, which is most reactive, leads to spontaneous reactions with such electrolytes as TFSI. These electrolyte degradation reduction reactions lead to the formation of a solid-electrolyte interphase (SEI) layer that limits retention of capacity and decreases battery lifecycles.[7,8] To facilitate optimization toward commercial Li-ion battery performance, it is crucial to gain a comprehensive atomistic mechanistic understanding of the SEI formation process and degradation of the electrolyte.[9]

During the charge-discharge cycles of a Li-ion battery, SEI films are formed with both inorganic and organic layers, which isolate the electrolyte and electrode by formation of a passivation layer that prevents further reactions.[10] To elucidate the formation and composition of the SEI layer, numerous experimental and theoretical studies have been reported.[11-14] Since the discovery of the passivation layer by Dey[11] in the 1970's, efforts have been made to clarify the nature of SEI from the experiment. In 1985, Nazri[15] identified Li_2CO_3 as a major component of the SEI by combining

IR spectroscopy, low angle X-ray diffraction, and scanning electron microscope (SEM) methods. These experiments identified LiF and Li_2O as major inorganic components, while organic carbonates were identified as major organic components.[16] Based on these analyses, Ramos-Sanchez concluded that the composition of electrolyte and solvent determines the nature of the SEI layer produced.[17,18]

Unfortunately, the components and detailed reaction mechanism of formating the SEI layer remain far from clear, with experimental resolution of the atomic structure continuing to be a challenge. However, atomic-scale simulation have improved to the point where they can provide an effective alternative tool to explore complex reaction processes by tracking the reactive events along the RD trajectories. This provides the means to develop a fundamental understanding of the initial reactions involved in SEI formation and electrolyte degradation. [19] For example, Wang[20] calculated the potential energy surface (PES) of the reaction between Li cation and solvent ethylene carbonate (EC) using density functional theory (DFT) methods. Moreover, molecular dynamics (MD)-assisted simulation has been widely used to investigate the reduction of electrolyte and SEI formation.[21-23] Camacho-Forero[22] constructed theoretical models of the lithium-metal anode surface with such electrolyte solvents as EC, dimethoxyethane (DME), and dioxolane (DOL). Initial reactions were simulated with *ab initio* molecular dynamics (AIMD) to describe the Li-salts: lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) or lithium bis(fluorosulfonyl)imide (LiFSI). They observed that the Li-salts in contact with Li-surface react quickly, even before the degradation reduction of solvents.[24-26]

Although AIMD simulations have been demonstrated to be useful in understanding the initial steps of reactions, the computational expense limits the time scale for AIMD simulation to 10's of picosecond (ps), which is not sufficient to explore the SEI film formation process, which may require nanoseconds (ns) or longer. An alternative is to use empirical methods for reactive simulations, such as the ReaxFF reactive force field, derived to fit quantum mechanics (QM) calculations and practical up to millions of atoms for ns and beyond. This can extend the time scale of SEI formation to sufficient time scales to observe the final SEI.[27,28] For example, Bedrov and co-workers[29] developed ReaxFF parameters for singly-reduced EC while including Li cations. They investigated the reduction reactions in both the gas phase and solution phase to propose reaction mechanisms.

However, ReaxFF has two problems in simulating batteries. First, sufficiently accurate force field parameters for battery-related systems may not be available. Thus, ReaxFF force field parameters are not available for the two most widely used experimental electrolytes: TFSI and FSI (bis(fluorosulfonyl)imide).[23] This explains why few simulations have been reported for these systems, despite their importance. Second, the current framework of ReaxFF does not include explicit consideration of the electron, which may impede describing electrochemical reactions that involve electron (e^-) transfer. Strategies, that explicitly include electrons, such as the electron force field (eFF) and eReaxFF,[30] have not yet been shown to be adequate for the above two systems.

In this work, we develop an alternative hybrid scheme: **Hybrid *ab initio* and reactive force field reactive dynamics (HAIR),** which combines AIMD and ReaxFF Reactive dynamics. The

advantage of the HAIR method is that AIMD simulations can describe accurately the localized electrochemical reactions while the ReaxFF MD can describe the longer range and longer time chemical reactions in the electrolyte along with the mass transfer. This HAIR scheme also alleviates the burden of fitting the ReaxFF force field parameters to describe every local bond-breaking barrier accurately, because this is handled by the AIMD steps.

In this work, we started with the ReaxFF parameters developed by Islam et al[31] , which we optimized further using training data from our accurate QM calculations that in turn was combined with the Monte Carlo simulated annealing (MC) force field optimization method[32,33] The final ReaxFF parameters are in the SI. We then apply HAIR reactive dynamics to simulate the degradation reactions at the Li-metal surface for 1 M LiTFSI in DOL, [34-36] a typical electrolyte used in batteries.

To provide a training set of QM data to train the ReaxFF for LiTFSI, we use the B3LYP[37] hybrid flavor of density functional method with the 6-311+G(d,p) basis set. All QM calculations were conducted using Jaguar 8.8. During the HAIR simulations, the forces and dynamics for the AIMD lithium-electrolyte model were calculated using the Vienna *ab Initio* Simulation Package (VASP 5.4.4) while the ReaxFF simulations used the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS 2018) software.

The AIMD simulation used the Perdew-Burke-Ernzerhof (PBE) functional to describe the electron exchange and correction energies within the generalized gradient approximation (GGA). To describe the London dispersion integrations, we added the Grimme D3 correction. The projector augmented wave (PAW) method as implemented in VASP was utilized. A 1 × 1 × 1 Monkhorst-Pack k-point mesh was used to sample the Brillouin zone integration, and we chose a 400-eV energy cutoff for plane-wave basis expansion. We used a Gaussian smearing width of 0.2 eV. The threshold for the electronic structure convergence of the self-consistent field was set to 10^{-4} eV.

In the HAIR procedure, the AIMD and ReaxFF MD simulations are conducted alternatively using the NVT ensemble at 300 K, which fixes the molecule numbers (N), volume (V), and temperature (T). Moreover, the timesteps for AIMD and ReaxFF were set at 1 fs and 0.25 fs respectively to guarantee good energy conservation during the HAIR simulations while ensuring efficient converge for collisions and smooth reactions. All HAIR simulations were conducted for 110 cycles (660 ps). In this work, we focus on the liquid electrolyte, in which diffusion is fast. So we consider a10-time acceleration to be sufficient. Our future work will move forward to a solid electrolyte, for which 10-time acceleration is likely not enough, perhaps requiring 100 times.

For the purpose of describing the lithium-electrolyte system accurately, ReaxFF parameters were extended to describe Li-TFSI. In the training set, we bond a hydrogen atom to the TFSI radical to obtain a neutral molecule. Table 1 exhibits the main decomposition reaction energies from QM and ReaxFF simulations. The gas-phase bond dissociation energies for C-S, N-S, and C-F bond cleavages are 104.4, 53.1, and 49.8 kcal/mol with ReaxFF, which are similar and in the same order as the QM values, 114.9, 50.3, and 50.2 kcal/mol respectively. This indicates that C-S and N-S bond breaking are the most plausible initial decomposition pathways, not C-F bond breaking. This

result that the Li-salt initiates breaks the C-S or N-S bonds is in good agreement with previous work.[38] Furthermore, the mean absolute deviations (MAD) between QM results and ReaxFF predictions are 0.045 Å for bond distances and 3 degrees for bond angles (Figure 1). More details about the fitting force field parameters and bond dissociation curves are in the SI

Table 1. The relative reaction energies (in kcal/mol) for QM and ReaxFF calculations.

Reaction	**Relative Reaction Energies (kcal/mol)**	
	QM(B3LYP/6-311+g(d,p))	**ReaxFF**
$HN(SO_2CF_3)_2$=$HN(SO_2CF_3)SO_2CF_2$+F	114.9	104.4
$HN(SO_2CF_3)_2$= $HN(SO_2CF_3)SO_2$+CF_3	50.3	53.1
$HN(SO_2CF_3)_2$= $HNSO_2CF_3$+SO_2CF_3	50.2	49.8

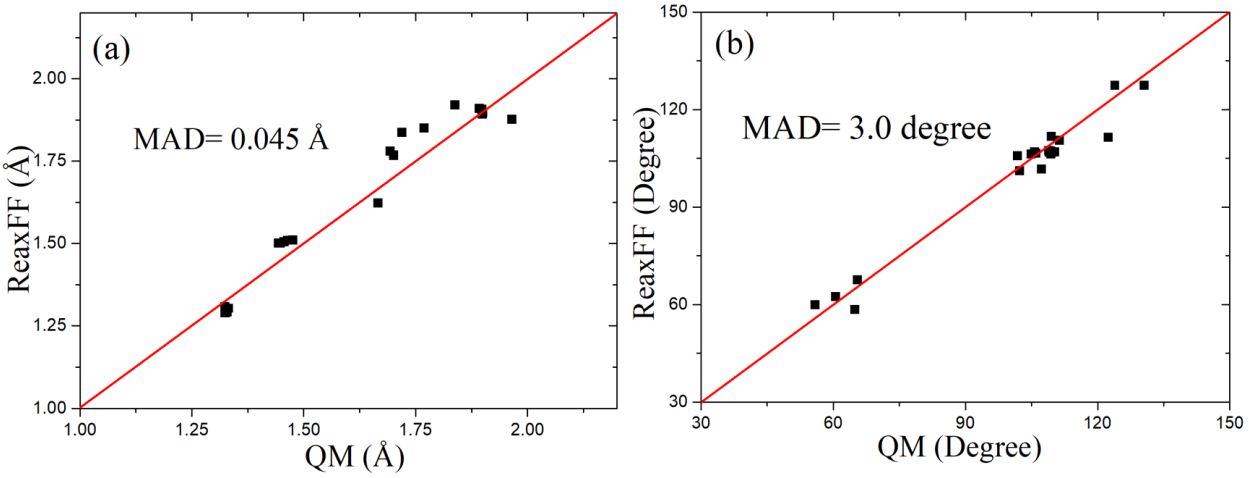


Figure 1. Comparison of training set geometries predicted by QM and ReaxFF methods. (a) Bond distances; (b) Bond angles.

Reactive dynamics simulations were conducted using the HAIR method with the NVT canonical ensemble at T=300K. Figure 2(a) and 2(b) show the temperatures (T) for AIMD and ReaxFF during HAIR simulations. This shows a smooth transition between the AIMD and ReaxFF periods, suggesting continuous and smooth molecular dynamics simulations.

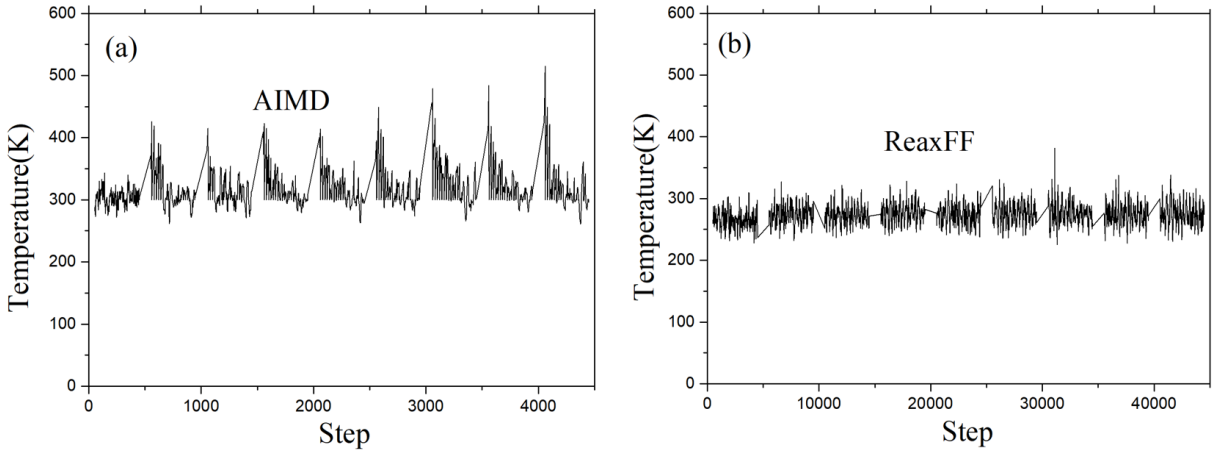


Figure 2. Temperatures for (a) AIMD and (b) ReaxFF during HAIR simulations.

In order to explore the initial mechanism for degradative reduction of the lithium-electrolyte system, we monitored MD trajectories during HAIR simulations. As exhibited in Figure 3, the degradation reaction initiates by breaking the N-S bond of TFSI, forming two fragments at around 6.0 ps. This decomposition process is consistent with previous theoretical and experimental results.[23,38,39] During the 6.0-11.0 ps period, the SO_2CF_3 fragment was reduced by Li^0 to form LiF, which has been regarded as an important component of the SEI layer investigated by experimental method.[40,41]

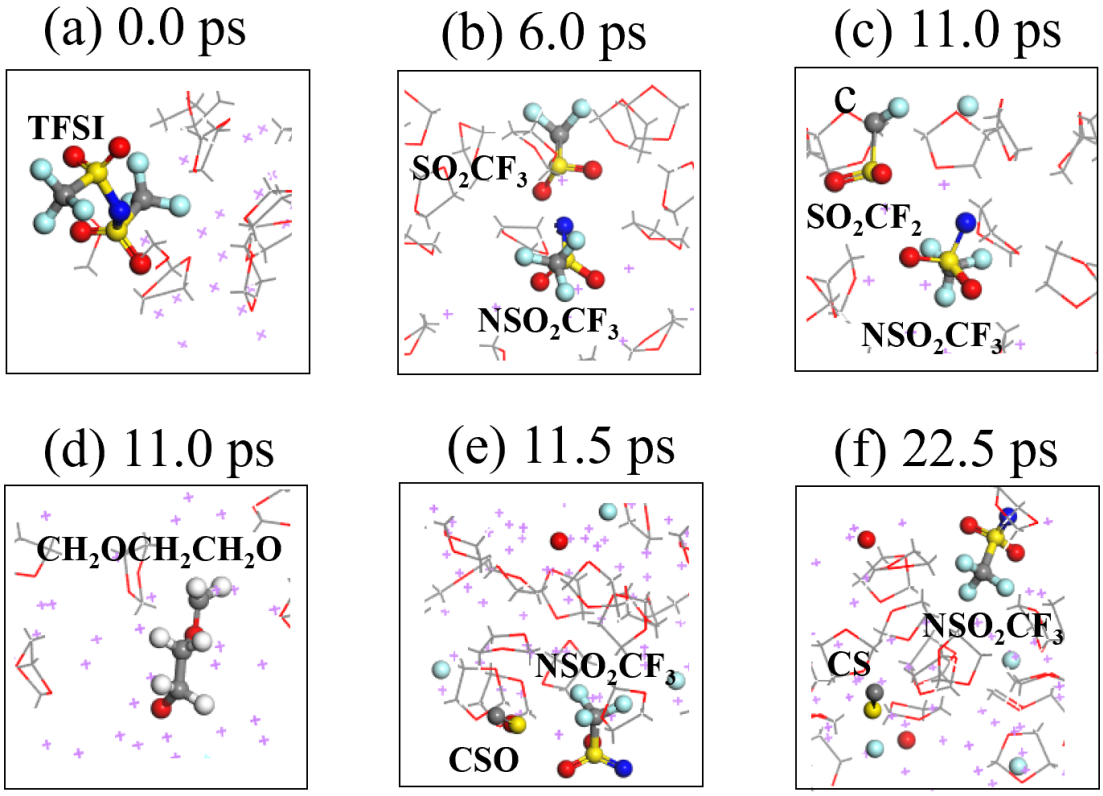


Figure 3. Sequence of TFSI and DOL decompositions obtained from HAIR simulations for the DOL/LiTFSI mixture between 0-22.5 ps. (a) 0.0 ps; (b) 6.0 ps; (c) 11.0 ps; (d) 11.0 ps; (e) 11.5 ps; (f) 22.5 ps. Color code: lithium, purple; oxygen, red; carbon, gray; fluorine, cyan; sulfur, yellow, nitrogen, blue; hydrogen, white. Furthermore, lithium induced the ring of the DOL electrolyte to open, forming $CH_2OCH_2CH_2O$, as observed by Camacho-Forero[42] using AIMD.

In Figure 4, the NSO_2CF_3 fragment decomposes into CF_3 and NSO_2 via C-S bond cleavage at 27.6 ps, just as in the QM trajectory, which was predicted to be the possible reaction pathway.[43] Subsequently, the decomposition fragments CF_3 and NSO_2 also undergo reduction reactions from Li_2O and LiF. Moreover, we also observed C_2H_4 and CH_2O at 33.0 ps, from $CH_2OCH_2CH_2O$ degradative reduction via C-O bond breaking.

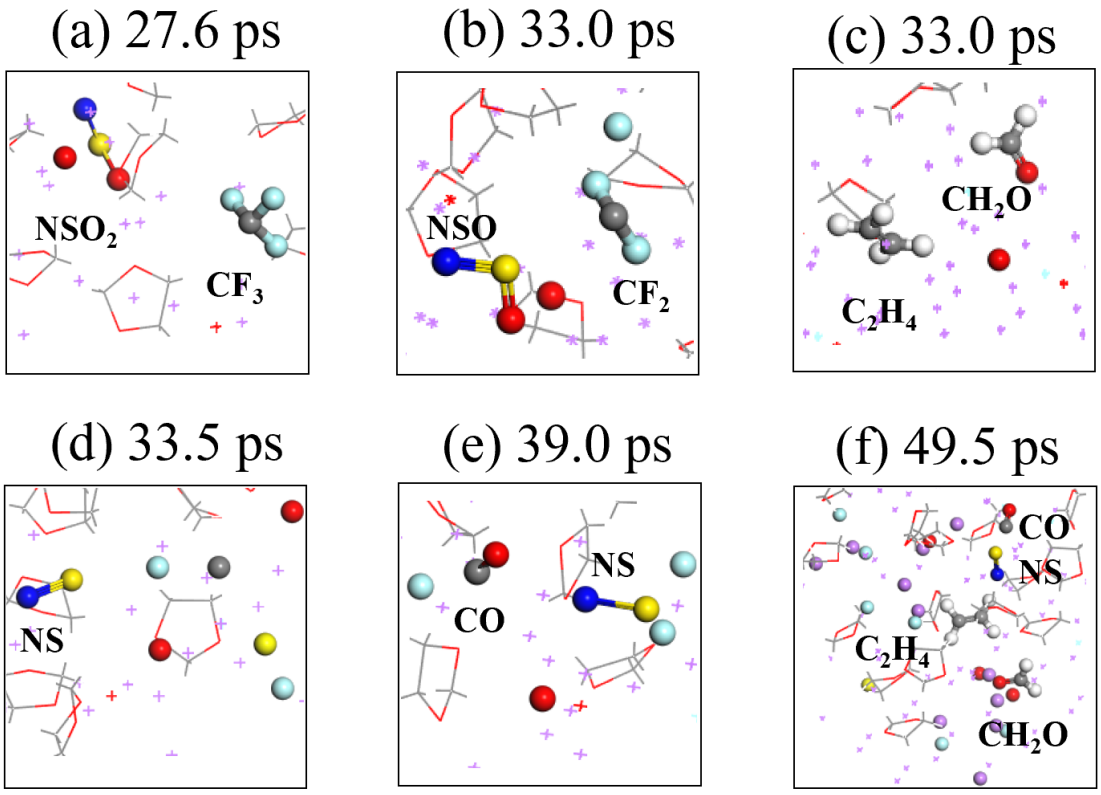


Figure 4. Sequence of NSO_2CF_3 and DOL decomposition obtained from HAIR simulations for DOL/LiTFSI mixture between 27.6-49.5 ps. (a) 27.6 ps; (b) 33.0 ps; (c) 33.0 ps; (d) 33.5 ps; (e) 39.0 ps; (f) 49.5 ps. Color code as in Figure 3.

Camacho-Forero[42] proposed this decomposition reaction mechanism for DOL and calculated the reaction pathway of DOL decomposition. In addition, Zhang ref investigated the detailed PES pathway of DOL decomposition using QM calculations, finding that DOL experienced a ring-opening process followed by conversion into C_2H_4 and CH_2O_2 fragments. the C_2H_4 has been mentioned as an important product during the reduction of electrolyte DOL.[44] Additionally, similar ring-opening and C_2H_4 emission mechanisms have been reported by Yun[45] using the ReaxFF method to clarify the EC decomposition reaction mechanism. Thus, these experimental and

theoretical results all indicate the reliability of the reduction reaction mechanism explored using the HAIR method.

The detailed MD simulation trajectories were monitored and the reaction mechanism clarified within 49.5 ps as illustrated in Figure 5. The decomposition reaction for TFSI was initiated by N-S bond breaking to form NSO_2CF_3 and SO_2CF_3 fragments. The initial reactions of the Li-salts are supported by QM calculations and by high accuracy AIMD simulations and experimental results. Subsequently, these fragments undergo multiple reduction reactions along with the removal of fluorine or oxygen atoms. The main products, including Li_2O and LiF, were verified as the components of the SEI layer according to previous experimental results. [ref] In the degradation reactions of the DOL electrolyte, both ring-opening and C_2H_4 elimination processes were observed during the RD simulations, which are consistent with both QM calculations and experimental observations. Therefore, the proposed HAIR method retains the accuracy of AIMD simulations with a low computational cost, with simulation results supported by experimental. [44,45]

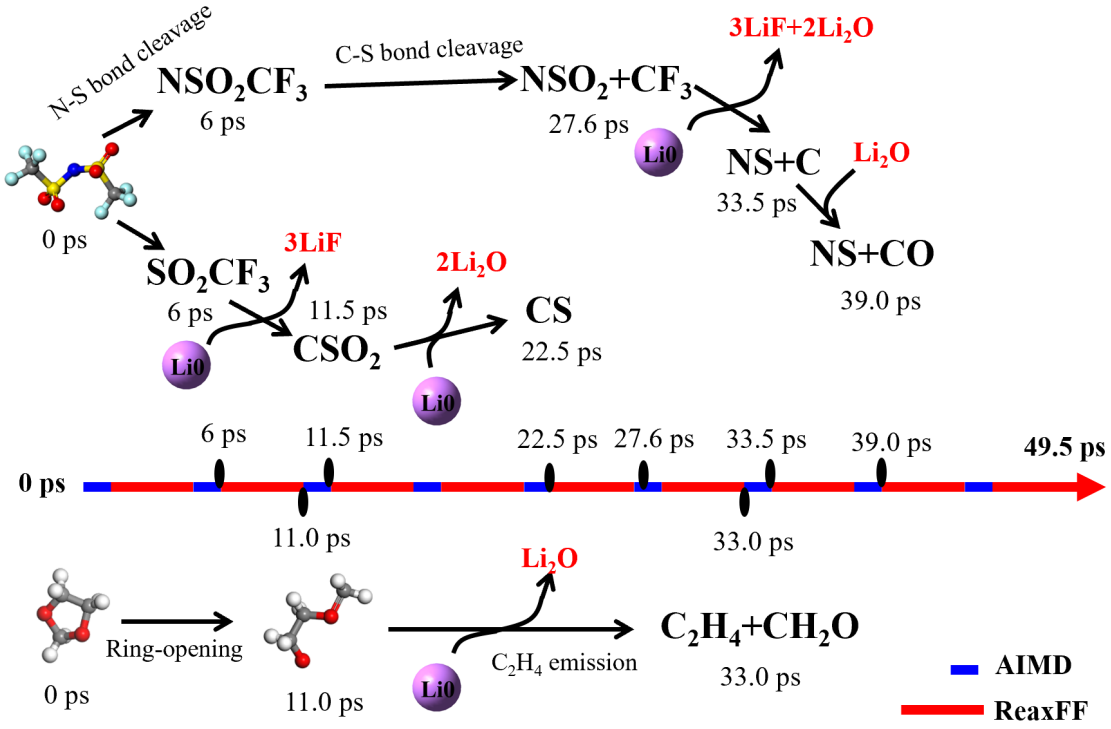


Figure 5. Reaction pathway obtained from HAIR simulations for LiTFSI and DOL.

Figure 6(a)-(c) exhibit the radial distribution function from the HAIR MD simulations at 22 ps and 660 ps. A sharp peak arises at 2 Å for Li-F and Li-O, indicating additional products (LiF and Li_2O) produced at 660 ps. The snapshots from RD simulations in Figure 6(d) and 6(e), how significant differences that clarify the main products or fragments at 22 ps and 660 ps. As shown in Table 2, the products and fragments at 22 ps form mainly by direct decomposition of TFSI, leading to Li_2O, LiF, NSO_2CF_3, CSO, and a ring-opened molecule of DOL (by Li^0) to form $CH_2OCH_2CH_2OLi$.

At to 660 ps, Further reactions are observed to form stable products, including C_2H_4, CH_2O, LiF, Li_2O, CO, CO_2.

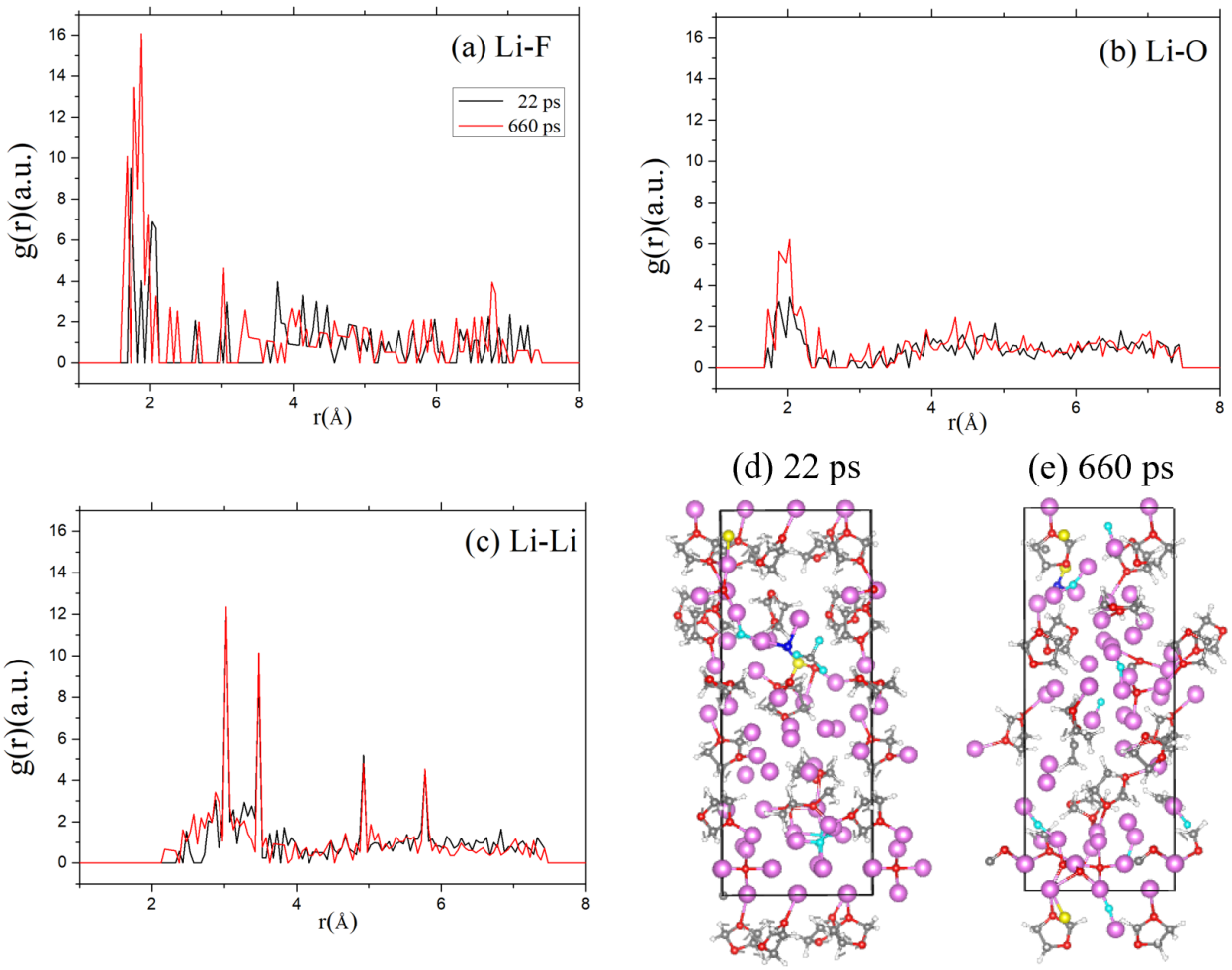


Figure 6. Radial distribution function for (a) Li-F; (b) Li-O; (c) Li-Li and snapshots from MD simulation at (d) 20 ps and (e) 660 ps.

Table 2. The products and fragments obtained from HAIR MD simulation at 22 ps and 660 ps.

Simulation Time	Products or fragments
20 ps	Li_2O, LiF, NSO_2CF_3, CSO, $CH_2OCH_2CH_2OLi$
660 ps	C_2H_4, CH_2O, LiF, Li_2O, CO, CO_2, CS, NS, LiH, C_2H_3Li

In summary, we introduce here a new Hybrid AIMD-ReaxFF Scheme (HAIR) that combines QM and MM reactive dynamics, and we apply it to investigate the degradation reduction reactions of the lithium-electrolyte system. The HAIR simulation is implemented by alternating between AIMD and ReaxFF RD with a smooth connection. The ReaxFF parameters for LiTFSI were optimized using the MC force field optimization method. We found that the predictions of the ReaxFF method exhibit good agreement with QM results, which implies suitable descriptions for Li-salt containing system.

In order to explore the reaction mechanism of the degradation of the electrolyte on the lithium electrode, we performed RD simulations using the HAIR method for 660 ps. Our RD simulation trajectories show that TFSI decomposition is initiated by N-S bond cleavage to form NSO_2CF_3 and SO_2CF_3. Subsequently, fluorine and oxygen atoms break off from NSO_2CF_3 and SO_2CF_3 step by step to form stable products Li_2O and LiF.

For the DOL electrolyte, we observed ring-opening and C_2H_4 emission processes similar to the predictions by Yun. Ref Our RD using the HAIR method are in accordance with QM and experimental results. But the computational efficiency of the HAIR method increases the total time covered by a factor of 10 to 660 ps, far too long for AIMD but with the same accuracy as AIMD simulations.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Details of the Hybrid AIMD-ReaxFF scheme, reactive force field parameters optimization and force field parameters, model of the lithium-electrolyte system and XRD patterns from MD simulations at 22 ps and 660 ps.

Notes

The authors declare no competing financial interests.

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References

(1) Bilgen, S. Structure and Environmental Impact of Global Energy Consumption. *Renewable Sustainable Energy Rev.* **2014**, 38, 890−902.

(2) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, 414, 359−367.

(3) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, 334, 928−935.

(4) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, 135, 1167–1176.

(5) Lin, D.; Liu, Y.; Cui, Y. Reviving the Lithium Metal Anode for High-Energy Batteries. *Nat. Nanotechnol.* **2017**, 12, 194-206.

(6) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. Li-O_2 and Li-S Batteries with High Energy Storage. *Nat. Mater.* **2012**, 11, 19–29.

(7) Huang, C.; Xiao, J.; Shao, Y.; Zheng, J.; Bennett, W. D.; Lu, D.; Saraf, L. V.; Engelhard, M.; Ji, L.; Zhang, J.; et al. Manipulating Surface Reactions in Lithium-Sulphur Batteries Using Hybrid Anode Structures. *Nat. Commun.* **2014**, 5, 3015.

(8) Shi, F.; Pei, A.; Boyle, D. T.; Xie, J.; Yu, X.; Zhang, X.; Cui, Y. Lithium Metal Stripping Beneath the Solid Electrolyte Interphase. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, 115, 8529−8534.

(9) Scheers, J.; Fantini, S.; Johansson, P. A Review of Electrolytes for Lithium–Sulphur Batteries. *J. Power Sources* **2014**, 255, 204–218.

(10) Barghamadi, M.; Kapoor, A.; Wen, C. A Review on Li-S Batteries as a High Efficiency Rechargeable Lithium Battery. *J. Electrochem. Soc.* **2013**, 160, A1256-A1263.

(11) Dey, A. N. Film Formation on Lithium Anode in Propylene Carbonate. *J. Electrochem. Soc.* **1970**, 117, C248.

(12) Peled, E., Golodnitsky, D.; Ardel, G. Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and Polymer Electrolytes. *J. Electrochem. Soc.* **1997**, 144, L208–L210.

(13) Aurbach, D. et al. New Insights into the Interactions between Electrode Materials and Electrolyte Solutions for Advanced Nonaqueous Batteries. *J. Power Sources* **1999**, 81, 95–111.

(14) Verma, P., Maire, P.; Novak, P. A Review of the Features and Analyses of the Solid Electrolyte Interphase in Li-ion Batteries. *Electrochim. Acta* **2010**, 55, 6332–6341.

(15) Nazri, G.; Muller, R. H. Composition of Surface Layers on Li Electrodes in PC, $LiClO_4$ of Very Low Water Content. *J. Electrochem. Soc.* **1985**, 132, 2050–2054.

(16) Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* **2014**, 114, 11503–11618.

(17) Agubra, V. A.; Fergus, J. W. The Formation and Stability of the Solid Electrolyte Interface on the Graphite Anode. *J. Power Sources* **2014**, 268, 153–162.

(18) Ramos-Sanchez, G. et al. Computational studies of interfacial reactions at anode materials: initial stages of the solid-electrolyte-interphase layer formation. *J. Electrochem. En. Conv. Stor.* **2016**, 13, 031002.

(19) Aurbach, D.; Daroux, M. L.; Faguy, P. W.; Yeager, E. Identification of Surface Films Formed on Lithium in Propylene Carbonate Solutions. *J. Electrochem. Soc.* **1987**, 134, 1611–1620.

(20) Wang, Y.; Liu, Y.; Tu, Y.; Wang, Q. Reductive Decomposition of Solvents and Additives toward Solid Electrolyte Interphase Formation in Lithium-Ion Battery. *J. Phys. Chem. C* **2020**, 124, 9099−9108.

(21) Wang, A.; Kadam, S.; Li, L.; Shi, S.; Qi, Y. Review on Modeling of the Anode Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries. *npj Computational Materials* **2018**, 4: 15.

(22) Camacho-Forero, L. E.; Smith, T. W.; S Bertolini, S.; Balbuena, P. B. Reactivity at the Lithium−Metal Anode Surface of Lithium−Sulfur Batteries. *J. Phys. Chem. C* **2015**, 119, 26828−26839.

(23) Kamphaus, E. P.; Angarita-Gomez, S.; Qin, X.; Shao, M.; Engelhard, M.; Mueller, K. T.; Murugesan, V.; Balbuena, P. B. Role of Inorganic Surface Layer on Solid Electrolyte Interphase Evolution at Li-Metal Anodes. *ACS Appl. Mater. Interfaces* **2019**, 11, 31467−31476.

(24) Bertolini, S.; Balbuena, P. B. Buildup of the Solid Electrolyte Interphase on Lithium-Metal Anodes: Reactive Molecular Dynamics Study. *J. Phys. Chem. C* **2018**, 122, 10783−10791.

(25) Camacho-Forero, L. E. Smith, T. W. Balbuena P. B. Effects of High and Low Salt Concentration in Electrolytes at Lithium−Metal Anode Surfaces. *J. Phys. Chem. C* **2017**, 121, 182−194.

(26) Ospina-Acevedo, F.; Guo, N.; Balbuena, P. B. Lithium Oxidation and Electrolyte Decomposition at Li-Metal/Liquid Electrolyte Interfaces. *J. Mater. Chem. A* **2020**, 8, 17036–17055.

(27) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. ReaxFF: A Reactive Force Field for Hydrocarbons, *J. Phys. Chem. A* **2001**, 105, 9396–9409.

(28) Chenoweth, K.; van Duin, A. C. T.; Goddard, W. A. ReaxFF Reactive Force Field for Molecular Dynamics Simulations of Hydrocarbon Oxidation. *J. Phys. Chem. A* **2008**, 112, 1040–1053.

(29) Bedrov, D.; Smith, G. D.; van Duin A. C. T. Reactions of Singly-Reduced Ethylene Carbonate in Lithium Battery Electrolytes: A Molecular Dynamics Simulation Study Using the ReaxFF. *J. Phys. Chem. A* **2012**, 116, 2978−2985.

(30) Islam,M. M.; Kolesov, G.; Verstraelen, T.; Kaxiras, E.; van Duin A. C. T. eReaxFF: A Pseudoclassical Treatment of Explicit Electrons within Reactive Force Field Simulations. *J. Chem. Theory Comput.* **2016**, 12, 3463−3472.

(31) Islam, M. M.; Bryantsev, S. V.; van Duin A. C. T. ReaxFF Reactive Force Field Simulations on the Influence of Teflon on Electrolyte Decomposition During Li/SWCNT Anode Discharge in Lithium-Sulfur Batteries. *J. Electrochem. Soc.* **2014**, 161(8), E3009-E3014.

(32) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N. Teller, A. H.; Teller, E. Equation of State Calculations by Fast Computing Machines. *J. Chem. Phys.* **1953**, 21 1087–1092.

(33) Kirkpatrick, S.; Gelatt, C. D.; Vecchi, M. P. Optimization by Simulated Annealing, *Science* **1983**, 220, 671.

(34) Mikhaylik, Y. V.; Akridge, J. R. Low Temperature Performance of Li/S Batteries. *J. Electrochem. Soc.* **2003**, 150 (3), A306−A311.

(35) Agostini, M.; Scrosati, B.; Hassoun, J. An Advanced Lithium-Ion Sulfur Battery for High Energy Storage. *Adv. Energy Mater.* **2015**, 5(16), 1500481.

(36) Chen, X.; Hou, T. Z.; Li, B.; Yan, C.; Zhu, L.; Guan, C.; Cheng, X. B.; Peng, H. J.; Huang, J. Q.; Zhang, Q. Towards Stable Lithium-Sulfur Batteries: Mechanistic Insights into Electrolyte Decomposition on Lithium Metal Anode. *Energy Storage Mater.* **2017**, 8, 194–201.

(37) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, 98, 5648−5652.

(38) Sodeyama, K.; Yamada, Y.; Aikawa, K.; Yamada, A.; Tateyama, Y. Sacrificial Anion Reduction Mechanism for Electrochemical Stability Improvement in Highly Concentrated Li-Salt Electrolyte. *J. Phys. Chem. C* **2014**, 118, 14091−14097.

(39) Merinov, B. V.; Zybin, S. V.; Naserifar, S.; Morozov, S.; Oppenheim, J.; Goddard, W. A.; Lee, J.; Lee, J. H.; Han, H. E.; Choi, Y. C. Interface Structure in Li-Metal/[Pyr_{14}][TFSI]-Ionic Liquid System from *ab initio* Molecular Dynamics Simulations. *J. Phys. Chem. Lett.* **2019**, 10, 4577−4586.

(40) Li, N.-W.; Yin, Y.-X.; Yang, C.-P.; Guo, Y.-G. An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Adv. Mater.* **2016**, 28, 1853−1858.

(41) Menkin, S.; Golodnitsky, D.; Peled, E. Artificial Solid-Electrolyte Interphase (SEI) for Improved Cycleability and Safety of Lithium−Ion Cells for EV Applications. *Electrochem. Commun.* **2009**, 11, 1789−1791.

(42) Camacho-Forero, L. E.; Balbuena, P. B. Effects of Charged Interfaces on Electrolyte Decomposition at the Lithium Metal Anode. *Journal of Power Sources* **2020**, 472, 228449.

(43) Haskins, J. B.; Yildirim, H.; Bauschlicher, Jr. C. W.; Lawson, J. W. Decomposition of Ionic Liquids at Lithium Interfaces. 2. Gas Phase Computations. *J. Phys. Chem. C* **2017**, 121, 28235−28248.

(44) Chen, X.; Hou, T.-Z.; Li, B.; Yan, C.; Zhu, L.; Guan, C.; Cheng, X. B.; Peng, H.-J.; Huang, J.-Q.; Zhang, Q. Towards Stable Lithium-Sulfur Batteries: Mechanistic Insights into Electrolyte Decomposition on Lithium Metal Anode. *Energy Storage Materials* **2017**, 8, 194–201.

(45) Yun, K.-S.; Pai, S. J.; Yeo, B. C.; Lee, K.-R.; Kim, S.-J. Simulation Protocol for Prediction of a Solid-Electrolyte Interphase on the Silicon-Based Anodes of a Lithium-Ion Battery: ReaxFF Reactive Force Field. *J. Phys. Chem. Lett.* **2017**, 8, 2812−2818.