

To break or not to break: mechanisms of DMSO decomposition in aprotic Li-O₂ battery electrolytes

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Conclusions

Four principle breakdown mechanisms of DMSO by LiO₂^{*} are reported based on DFT calculations.

High energy barriers to reactions are found for all mechanisms, which suggest DMSO to be stable under the simulated conditions. The qualitative results hold also for reactions of DMSO with O₂⁻ and HO₂^{*}.

Low energy barriers to reactions with alternative reacting species cannot be excluded, as demonstrated by the reaction of DMSO with OH^{*}.

Stable reaction products in the liquid phase include DMSO₂, DMSO-CH₃, and decomposition products thereof. DMSO-H is not a stable product.

Surface reactions between DMSO and Li₂O₂ favor the formation of DMSO₂, as the liquid phase reactions.

Catalyzing effects at specific surface sites or other circumstances that destabilize DMSO in Li-O₂ battery electrolytes has still to be reported.

Introduction

Rechargeable Li-O₂ batteries ideally make use of oxygen (O₂) from the air as a fuel, which is reduced and combined with Li⁺ to form LiO₂ or Li₂O₂ at the cathode/electrolyte interface [1]. However, side-reactions interfere with the main reactions and limit the lifetime of practical Li-O₂ cells.

The critical goal is to prevent side-reactions by developing more stable solvents and/or stabilizing the reactive species.

This poster presents simulated energies and mechanisms of dimethyl sulfoxide (DMSO) decomposition. There is disagreement in literature if DMSO is decomposed by O₂⁻/LiO₂^{*} in solution, the Li₂O₂ surface, or if protic impurities are needed to catalyze the reaction [2-5].

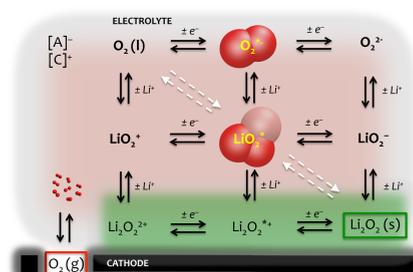
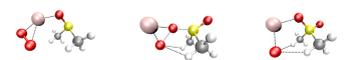


Figure Schematic of the Li-O₂ battery electrolyte/electrode interface from [6]. Oxygen enters the electrolyte via pores in the cathode, is reduced, and combined with Li⁺ to form solid Li₂O₂ on the cathode. Ideally, the solvent is just a passive medium. In practice, the solvent reacts with LiO₂^{*} and O₂⁻.

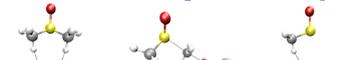
Four decomposition pathways

We report four principle reaction mechanisms of single molecules of DMSO and LiO₂^{*} based on DFT calculations. LiO₂^{*} is the most probable reactant, since it is energetically favored in solution over the solvent-separated ions (Li⁺ + O₂⁻) [6].

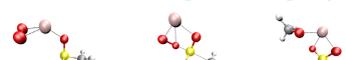
Path 1: DMSO + LiO₂^{*} → DMSO₂ + LiO^{*}



Path 2a: DMSO + LiO₂^{*} → DMSO-CH₃^{*} + LiOOCH₃



Path 2b: DMSO + LiO₂^{*} → DMSO₂-CH₃^{*} + CH₃OLi



Path 3: DMSO + LiO₂^{*} → DMSO-H^{*} + H₂O

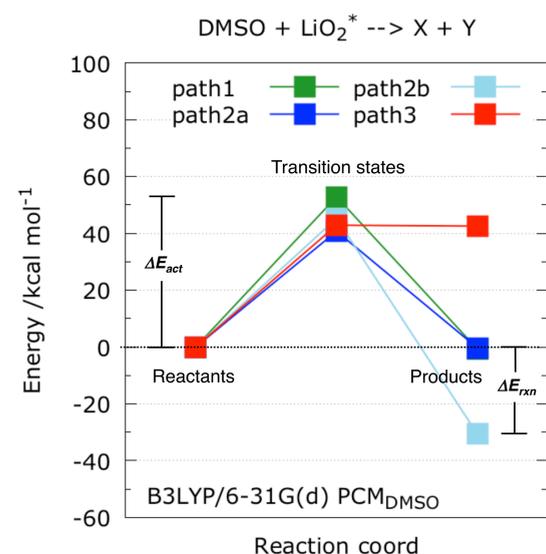
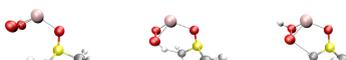


Figure Reactant, transition state, and product energies for decomposition along paths 1, 2a, 2b, and 3. The reaction barrier ΔE_{act} is the energy between the transition and reactant states. The reaction energy ΔE_{rxn} is given between the product and reactant states.

Methods and models

The reaction energies of single molecules of DMSO and O₂⁻, LiO₂^{*}, HO₂^{*}, and OH^{*} were calculated using density functional theory [DFT; B3LYP/6-31G(d)] in a polarizable continuum model (PCM), as implemented in the software Gaussian 09.

DMSO and LiO₂^{*} in the liquid phase (35DMSO + LiO₂^{*}) were simulated with DFT Molecular dynamics [DFT-MD; PBE] at 353K using the Car-Parrinello MD approach (CPMD).

The reactions of a single molecule of DMSO with Li₂O₂ surfaces (0001 and 11-20) were simulated with CPMD [DFT-MD; PBE] at a temperature of 150K.

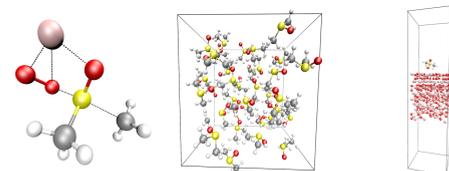


Figure Two-molecule, liquid phase, and surface models used to simulate the decomposition of DMSO in the presence of LiO₂ or Li₂O₂ (0001).

Literature cited

- [1] Z. Peng *et al.* *Science* **337** (2012) 563
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Acknowledgments

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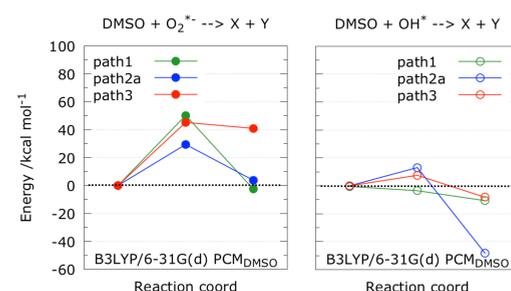
Chalmers Centre for Computational Science and Engineering (C3SE) and the supercomputer facilities at University of Tokyo and Kyushu University are gratefully acknowledged.



Reactions with O₂⁻, HO₂^{*}, and OH^{*}

For the reactions of DMSO with O₂⁻ path 2b is absent – possibly because of difficulties stabilizing the transition state in the absence of Li⁺. The barrier to path 2 is ca 10 kcal mol⁻¹ smaller for the reaction with O₂⁻, but still comparatively high [5].

The reaction energies and barriers of DMSO and HO₂^{*} (not shown) are close to identical to those with LiO₂^{*}. However, the reaction of DMSO with OH^{*} shows much lower barriers – even a barrier less path 1 – indicating the importance of the type of reactant.

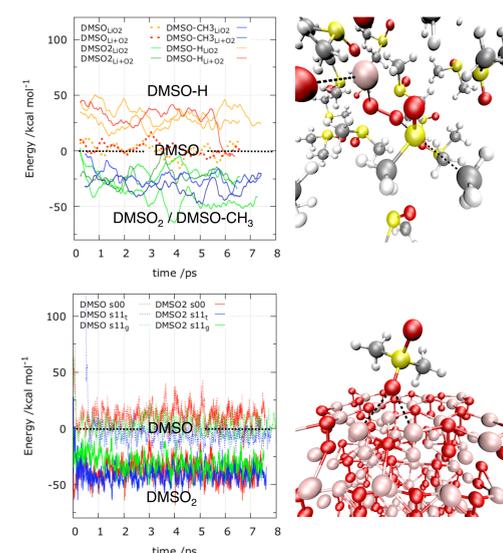


Reactions in solution and at Li₂O₂

More realistic models beyond the two molecule approach is required to take into account effects of an explicit solvent surrounding. DFT-MD simulations of reactions between DMSO and LiO₂ in solution phase show that the initial products of path 1 and 2 react spontaneously with other DMSO molecules. The DFT-MD simulations also support the result that reaction path 3, to form DMSO-H, is not energetically favored.

Decomposition of DMSO, to form DMSO₂, by the O₂ units at Li₂O₂ surfaces is energetically favored. The result holds at multiple surfaces and sites. Simulations of energy barriers to decomposition in solution and at Li₂O₂ surfaces is in progress to search for conditions that could explain the experimentally observed decomposition of DMSO in Li-O₂ battery electrolytes [3].

Figure Energy trajectories and snapshots from DFT-MD of solutions of DMSO, intact or where one DMSO molecule is decomposed (top), and for a surface system where DMSO or DMSO₂ is adsorbed at three different Li₂O₂ surface sites (0001, 11-20_g, or 11-20_l).



Work in progress