

Lithium-air batteries: a DFT-MD study of $\text{Li}^+ + \text{O}_2^{*-}$ and LiO_2^* in DMSO and PC electrolytesJohan Scheers^{1,2}, Keitaro Sodeyama^{2,3}, Zdeněk Futera², Yoshitaka Tateyama^{2,3}¹Department of Applied Physics, Chalmers University of Technology, SE-41296, Gothenburg, Sweden.²International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.³Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Goryo-Ohara, Kyoto 615-8245, Japan.

The lithium-air battery combines the benefits of a non-locally stored fuel (O_2 from air) with the very electropositive lithium metal. In theory, the combination enables a battery with a storage capacity comparable to that of gasoline. However, there are vast challenges involved to fulfil a practical lithium-air battery.

Research activities are focused on identifying materials; solvents, salts, binders, etc that will provide reversible electrochemistry, initially with pure oxygen as a fuel (Li- O_2 battery). A main obstacle is the poor electrolyte stability in the presence of the reduction products of O_2 . Therefore, much effort has been devoted to study the reactivity and decomposition mechanisms of a first generation of solvents for Li- O_2 batteries, in particular propylene carbonate (PC).

Computationally, DFT calculations have been used to identify possible decomposition mechanisms for a variety of electrolyte solvents and to quantify the energy barriers to decomposition – in order to suggest alternatives [1–3]. In addition, *ab initio* Molecular Dynamics (DFT-MD) has been implemented for more detailed studies of single solvent decomposition, in bulk or in the presence of a Li_2O_2 surface [4,5].

Here we will present results from DFT-MD simulations of the radicals O_2^{*-} and LiO_2^* in PC and dimethyl sulfoxide (DMSO) with the aim of identifying electrolyte properties that could be used to *a priori* address the compatibility of electrolyte solvents and oxygen reduction products in Li- O_2 batteries.

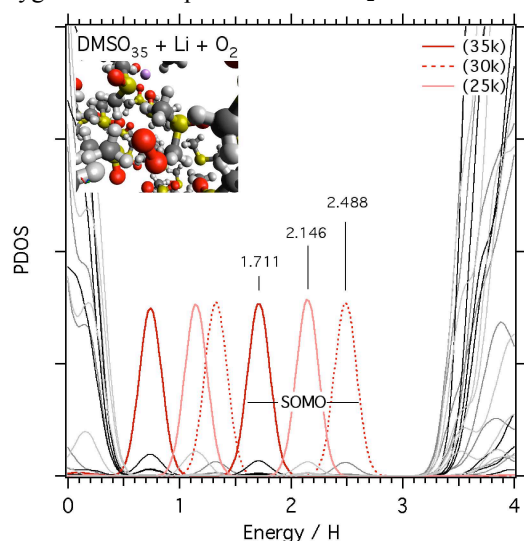


Figure Energy levels of the single occupied orbitals (SOMO) in three states of $\text{DMSO}_{35} + \text{Li}^+ + \text{O}_2^{*-}$.

1. V.S. Bryantsev et al. J Phys Chem A 115 (2011) 12399.
2. V.S. Bryantsev et al. J Phys Chem A 116 (2012) 7128.
3. V.S. Bryantsev, Chem Phys Lett 558 (2013) 42.
4. T. Laino et al. Chemistry - A Eur J 18 (2012) 3510.
5. R.S. Assary et al. J Phys Chem C 117 (2013) 8041.