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The role of prop-1-ene-1,3-sultone as an additive in lithium-ion cells

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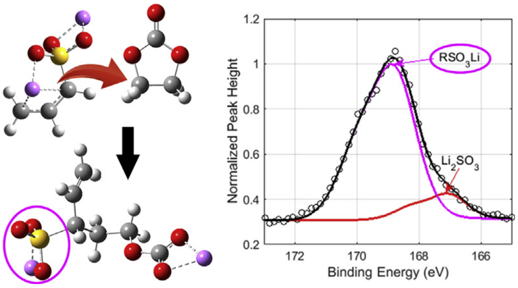
HIGHLIGHTS

- DFT was used to study the role and fate of the PES additive in a Li-ion battery.
- A “reactive electrode model” may explain decomposition to OCS at high voltage.
- The calculated potential for PES reduction matches formation cycle coulometric data.
- The reduced Li_2PES species reacts with PES and the solvent to form SEI components.
- XPS results match the predicted SEI components at the negative electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

Density functional theory (DFT) is used in conjunction with experimental results to propose decomposition pathways that describe the role and ultimate fate of the PES additive in Li-ion batteries. Oxidation of PES produces carbonyl sulfide gas and ethene at the positive electrode, both experimentally observed byproducts. However, the calculated standard potential for simple PES oxidation, E^0_{ox} ~ 6.7 V vs. Li/Li^+, is quite high, suggesting this pathway is unlikely. A “reactive electrode model” is presented, in which the positive electrode material is a reagent in the pseudo-combustion of PES (and other solvents). This spontaneous process produces carbonyl sulfide, carbon dioxide, and a rock salt surface layer, all of which are experimentally observed. At the negative electrode, the reduction of PES occurs via two one-electron steps, where $E^0_{red,1} = 0.9$ V and $E^0_{red,2} = 4.3$ V. The reduced species, Li_2PES, can react with hydrogen and methyl radicals to produce propene, methylpropene, propane and lithium sulfite. Nucleophilic Li_2PES can also react with electrophilic PES, ethylene carbonate, or ethyl methyl carbonate. Eighteen possible organic sulphate ‘building blocks’ for the solid-electrolyte interphase (SEI) are presented. X-ray photoelectron spectroscopy (XPS) measurements demonstrate that PES reduction indeed results in both lithium sulfite and organic sulphate SEI components.

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1. Introduction

One way to improve lithium-ion battery (LIB) charge–discharge cycling performance and lifetime is the use of electrolyte additives. Certain compounds added to the electrolyte solution on the order of a few weight percent can significantly extend cycling and

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calendar lifetimes, reduce detrimental gas formation in cells, and/or improve LIB safety [1–4].

The electrolyte additive studied here is prop-1-ene-1,3-sultone (PES), which has received considerable attention in recent years for its use as an individual additive and as a part of binary and ternary blends [5–12]. PES has been shown to reduce gas production at both electrodes during the first charge step, commonly called the formation cycle, and during charge–discharge cycling [4,6,13]. Moreover, PES prevents destructive exfoliation of the graphite anode [3]. This may indicate that PES is a film-forming additive that produces a stable barrier layer on the graphite surface, known as a solid-electrolyte interphase (SEI). Charge-discharge cycling experiments and surface analysis studies have provided further clues for understanding the fate of PES in cells [8,9]. However, the reactions of PES at the electrodes and the nature of the resulting SEI remain uncertain. More generally, it is a standing problem that the exact role of most electrolyte additives are unknown. Clearly developed methods to follow the decomposition of additives in a battery would be of significant benefit to the field.

In this work, several possible electrochemical and chemical reaction pathways of PES in a LIB are mapped. Computational chemistry is applied to make predictions that can be tested and compared with experimental results, many of which are already available in the published literature. The overall goal of this work is not only to understand the role and ultimate fate of PES in LIBs, but also to establish methods that may be applied to related compounds for the intelligent design of new and improved electrolyte additives.

2. Experimental

2.1. Computational methods

For the calculations in this article, the B3LYP/6-311++g(d,p) IEFPCM-UFF method was used in the Gaussian quantum chemistry software package (G09.d01) [14–16]. Except where noted, energy diagrams show the Gibbs free energy of reaction calculated in solution and at 25 °C. All geometries were tested by vibrational mode analysis. Stable and metastable geometries have only real (positive) vibrational frequencies. Transition states have one imaginary (negative) vibrational frequency. Standard potentials are all reported relative to the Li/Li$^+$ electrode in the same solution (*i.e.*, $\varepsilon = 20$, see Supplementary Information for details).

2.1.1. Functional

The B3LYP hybrid functional [14] is certainly the most popular DFT functional and it generally provides excellent speed and accuracy. However, numerous other functionals have been published, several of which are available in the Gaussian09 software package [16]. Jónsson and Johansson compared calculated the vertical ionization potentials of anions using several DFT functionals, including B3LYP, and a complete basis set (CBS) extrapolation (a very accurate but time-consuming method that combines CCSD(T) and MP2 calculations) [18]. The hybrid (B3LYP, M06-2X, PBE0, TPSSh) and double hybrid functionals (mPW2PLYP, B2PLYP) all performed similarly, whereas the non-hybrid functionals (VSXC, M06-L) gave poor results. Although M06-2X did give slightly more accurate values than the other methods, the improvements were deemed marginal enough that the authors did not endorse this functional over the others. Similarly, the heats of formation are comparable between various functionals [19]. Therefore, we concluded that the use of B3LYP is preferred, since it provides comparable accuracy to other available functionals and has the benefit of allowing freer comparison with results from other researchers.

2.1.2. Basis set

DFT calculations of the ionization potentials for Li-ion relevant species have been calculated using a variety of basis sets, including 6-31g(d,p) [20,21], 6-311+g(d) [18], 6-311++g(d) [22], 6-311+g(3df,2pd) [23]. Of these, the higher level split-valence basis set, *i.e.*, 6-311g, is becoming more common than its predecessor, *i.e.*, 6-31g, as processing speeds improve.

The inclusion of diffuse functions is especially important for anions, in which the electron–electron repulsion causes the electrons to spread out more. Diffuse functions are often not used on the hydrogen atoms because of their low electron density. However, for small molecules such as those studied here, the inclusion of these additional orbitals does not add much to the computation time and allows for the possibility of hydridic hydrogen atoms.

Polarization functions may be viewed as analogous to the traditional atomic orbitals used in Hartree-Fock theory (2s, 3p, etc.) even though, strictly, DFT uses Kohn–Sham orbitals. Because the S atom in PES is hypervalent, the inclusion of d-type functions is essential to obtain good results. For the small molecules in this work, the inclusion of p-type orbitals on the H atoms is expected to improve the accuracy slightly at a minimal computational cost. It was then considered whether additional polarization functions should be included. The oxidation of PES → PES$^+$, in solution ($\varepsilon = 20$, see below) was considered. The calculated standard potentials (see Supplementary Information) for the 6–311++G(d,p) and 6-311++G(2df,p) basis sets were 6.69 V vs. Li/Li$^+$ and 6.64 V, respectively. Although the latter is expected to be slightly more accurate, we considered this difference negligible because the precision of experimentally measured oxidation and reduction potentials is ±0.1 V. Yet the latter basis set has considerably longer calculation times. This would have posed a major obstacle for this work because of the dozens of molecular geometry optimizations, transition state optimizations, and internal reaction coordinate (IRC) calculations. Therefore, the 6-311++G(d,p) was chosen to provide a good balance between computational accuracy and cost.

2.1.3. Solvation model

The polarizable continuum model (PCM) comes standard with commercial QC software [24]. This is a simple yet robust model that represents solvents by their dielectric constant (ε). The default version of this model within Gaussian09 uses the integral equation formalism variant and a universal force field to define the solvation cavity (IEFPCM-UFF) [16]. Despite its simplicity, this method does an excellent job of modelling solvation effects for geometry and energy calculations, provided an accurate dielectric constant is known [24,25]. Dielectric constants for ethylene carbonate (EC)/ethylmethyl carbonate (EMC) solvent blends at various temperatures have recently been measured [17]. Because most experimental data is available for PES dissolved in 3:7 EC/EMC, we adopted the value $\varepsilon = 20$, which should be a good representation of this solvent blend at room temperature ($20 \leq T \leq 25$ °C).

2.2. X-ray photoelectron spectroscopy (XPS)

XPS was performed on an SPECS spectrometer equipped with a Phoibos 150 hemispherical energy analyzer and using Mg Kα radiation ($h\nu = 1253.6$ eV). To transfer air-sensitive samples from the argon-filled glove box to the spectrometer, a special transfer system was used as described in Ref. [26]. Shortly, samples were mounted onto a molybdenum holder using a copper conductive tape (3M) and placed into the transfer system under argon. The later was put under vacuum at approx. 10^{-3} mbar for 1 h and then connected to the spectrometer where samples were loaded under a pressure of

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