



Surface Reactions of Ethylene Carbonate and Propylene Carbonate on the Li(001) Surface



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ABSTRACT

Controlling the formation of the solid electrolyte interphase (SEI) layer of the future generation of lithium metal batteries is critical in optimising both their safety and performance. Unfortunately, lithium and lithiated anode materials are inherently susceptible to unwanted side-reactions including lithium metal dendrite formation, which compromises cell safety. This aberrant lithium re-deposition process occurring on the lithium anode originates at the electrode surface, with few considering the initial adsorption of electrolyte components onto lithium metal, and the effect this has on the formative stages of SEI layer development. In this work, density functional theory calculations and *ab initio* molecular dynamics simulations are used to determine the preferred adsorption sites and orientations of two common battery electrolytes, ethylene carbonate (EC) and propylene carbonate (PC) on a Li(001) surface. Three types of orientations were found for both EC and PC each consisting of O atoms ionically bonded to surface Li atoms. Both molecules were found to weakly chemisorb with a similar stability to each other. *Ab initio* molecular dynamics simulations were used to determine the dissociation mechanism of both molecules on the surface. EC was shown to decompose within 7 ps of simulation time by first accepting an electron from the Li surface and breaking the bond between the carbonyl C and ring O. It then accepted another electron from the Li surface and the bond between the carbonyl C and the other ring O breaks. PC decomposition proceeded via a similar pathway over a longer timescale by accepting an electron from the Li surface and breaking the bond between the carbonyl C and a ring O atom. In contrast to EC, the breaking of the other carbonyl C ring O bond was not seen for PC within the 20 ps simulation, which has been ascribed to the greater stability provided by the methyl group.

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1. Introduction

Despite the widespread adoption and popularity of lithium based battery technologies, a number of significant improvements need to be made in order to improve the energy density, safety, cost and durability of rechargeable lithium (Li)-based batteries [1].

A promising avenue for improving the energy density of these batteries is to replace the commonly used graphite anodes with lithium metal anodes, which forms what is called a lithium metal battery. For this to be feasible, the repetitive deposition and

stripping of lithium or “cycling” during the normal service life of the battery must be reversible, without significant interfacial degradation occurring during charge/discharge cycling. Unfortunately, aberrant lithium deposition in lithium metal batteries often results in the formation of dendritic lithium structures which are capable of piercing separator materials, reducing cycling efficiency, and more critically, leading to internal short circuits which can cause the battery to catch fire or burst [2].

During lithium metal battery cycling, the electrolyte materials (salts and solvents) decompose forming thin films on the electrode surfaces, which are known as the solid electrolyte interphase (SEI). The physical properties and inhomogeneity of the SEI significantly affect lithium deposition and battery performance. The composition and electrical properties of the SEI are determined by the combination of solvent/salt used and the electrode chemistry in the cell. It is thought that the right combination of solvent/salt can

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lead to a more homogeneous SEI and thus improve lithium deposition and therefore cycling efficiency [3], as the salt can be preferentially reduced during the initial charge process, producing precipitates that prevent further decomposition of other electrolyte components [4].

Two organic compounds commonly used together as a solvent in lithium metal batteries are the non-aqueous organic carbonates: ethylene carbonate (EC) and propylene carbonate (PC) (Fig. 1). There have been a number of studies using both experimental and theoretical techniques that have examined the effects and formation of the SEI between a lithium metal electrode and the EC/PC electrolytes.

Aurbach *et al.* [5] found experimentally that EC is more reactive towards lithium than PC. Previous *ab initio* calculations have shown that the Li stabilised radical anions of EC were more stable than those of PC. It was concluded that a combination of the electron donating properties of the methyl group and steric effects reduced the reactivity of PC [5]. They found experimentally that Li cycling efficiency in EC and PC based electrolytes was greatly influenced by the composition of the solvent system and by contaminants such as CO₂ at the ppm level and suggested this to be due to the SEI composition [5]. The composition of the SEI formed on a lithium metal surface after it had been submerged in solutions of EC and PC was examined using Fourier transform infra-red (FTIR) spectroscopy and it was found that it consisted mainly of ROCO₂Li compounds [6].

To investigate how these ROCO₂Li compounds are formed, Wang *et al.* [7] used density functional theory calculations and determined a number of reductive decomposition mechanisms of EC leading to different dicarbonate products. Calculations were carried out for an isolated EC molecule and for the supermolecules Li⁺(EC)_n (n = 1–4). It was found that the presence of the Li cation considerably stabilised the EC reduction intermediates and the reaction products showed a weak dependence on the EC concentration.

The EC and PC decomposition mechanisms were further examined by Tasaki *et al.* [8] using *ab initio* calculations, this time in the presence of a lithium electrode. They used a cluster of 15 lithium atoms to model the electrode and found activation energies for the reductive decomposition reactions of EC and PC to be 24.9 and 26.4 kcal mol⁻¹, respectively. The reaction enthalpies were found to be -142.0 and -138.4 kcal mol⁻¹, respectively. Generally speaking, the lower the activation energy and the more negative the reaction enthalpy, the more likely the reaction was to occur. These findings support the preference for EC reduction over PC reduction found experimentally [5].

More recently, *ab initio* molecular dynamics simulations have been utilised to examine the reductive decomposition of EC and PC

in the presence Li ions and in the presence of a Li electrode. Leung *et al.* [9] have performed a number of these studies, initially simulating reactions of EC and PC on C=O, C—OH and C—H terminated LiC₆ interfaces analogous to a fully charged graphite anode. This is also analogous to the conditions for SEI growth on Li metal as has been demonstrated previously [6,10]. Two major decomposition mechanisms were found for EC. Either C_E—O_E cleavage occurred yielding CO₃²⁻ + C₂H₄ or C_C—O_E cleavage occurred yielding CO + OC₂H₄O²⁻. OC₂H₄O²⁻ could then react with CO₂ or CO₃²⁻ at longer time scales to form (CH₂CO₃Li)₂, the main SEI component in an EC electrolyte.

Leung *et al.* [11] then performed simulations of EC in the presence of Li electrodes. They modelled 32 EC molecules between two Li slabs at 350 K. Within 15 ps, the 12 molecules adjacent to the Li metal had decomposed. Eleven out of the 12 molecules decomposed via the breaking of C_C—O_E bonds to form CO + OC₂H₄O²⁻. Only one molecule decomposed via the breaking of C_E—O_E bonds to form CO₃²⁻ + C₂H₄ which had been widely accepted in the literature as the prominent pathway. Energy profiles at 0 K were produced of the two modes of excess electron-induced EC break down on Li metal and showed that breaking the C_C—O_E was thermodynamically less favourable than breaking the C_E—O_E bond by 1.53 eV. Energy barriers associated with both types of bond breaking were found to be extremely small, hence speculating that the kinetic pre-factor favours the route which forms CO making it the predominant product in the simulations.

To date, no studies have determined more than one possible adsorption site and orientation of EC and PC on a Li surface prior to reductive decomposition. Nor have *ab initio* molecular dynamics simulations been used to establish the mechanism of PC decomposition in the presence of a Li electrode. While the entire battery system includes more components, by understanding how individual components react in the first instance, one is better positioned to understand the more complex interactions when lithium salts, or other components, for example, are introduced later. This work uses DFT calculations and *ab initio* molecular dynamics simulations to model the reaction of EC and PC on the Li (001) surface which is used to represent the lithium metal electrode. The preferred adsorption sites, orientations, and vibrational frequencies of EC and PC are presented. The effect of temperature is also examined and it is determined whether the molecules dissociate and by what mechanism, as it is the reactions occurring between EC and PC directly with the Li that form the basis of the SEI layer. Such information is needed to help guide research into new additives, electrolytes or electrode surface coatings which can help control the formation of a better SEI, leading to the development of next generation batteries.

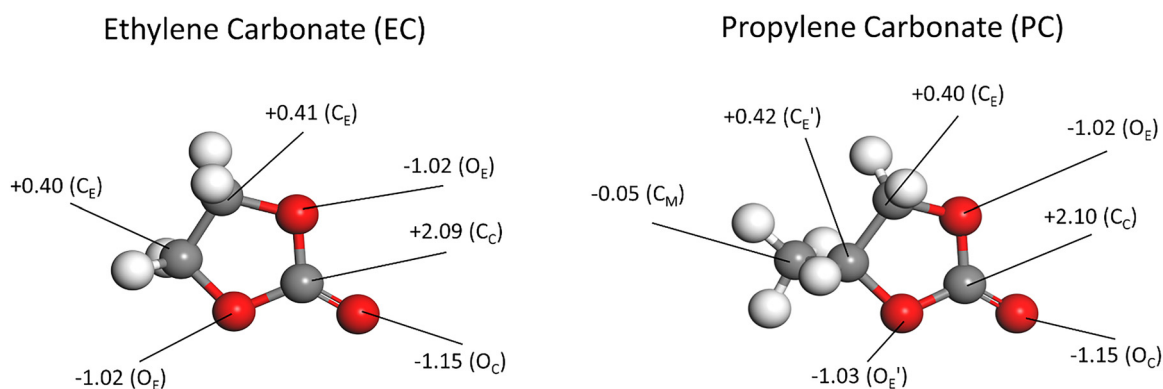


Fig. 1. Optimised EC and PC molecules with atomic partial charges.

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