

Physical Properties of SEI Films in Li-Ion Battery Electrolyte by Molecular Dynamics Simulations

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Introduction

Understanding the process of solid electrode interface (SEI) formations on the anode surface and controlling them are a major research activity among others in Li-ion secondary battery developments.

Previously, we reported a more negative energy for a second-electron reduction of vinyl carbonate (VC) than other solvents such as ethylene carbonate (EC) or propylene carbonate (PC) by Density Functional Theory calculations.¹ This VC's higher reactivity was attributed to a part of its effectiveness as an electrolyte additive. Yet, little difference between EC and PC has been observed in their reactivity.^{1,2} Recently, Aurbach has proposed a model where the cohesiveness of the SEI film between EC and PC results in the difference in the behavior during the first recharge cycle: a Li ion intercalation in EC and an exfoliation of graphite in PC.³ In this study, we examine the difference in the physical properties between the SEI film produced from an EC electrolyte and that from a PC electrolyte by molecular dynamics (MD) simulations. The interactions of the SEI films with the graphite surface will also be discussed.

Simulations

The SEI model films studied were dilithium ethylene dicarbonate (Li-EDC) for the EC-based SEI film and dilithium propylene dicarbonate (Li-PDC) for the PC-based SEI film, shown in Figure 1.

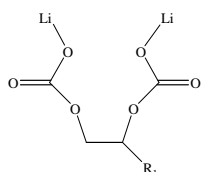


Figure 1. Dilithium ethylene dicarbonate, Li-EDC, ($R_1=H$) and dilithium propylene dicarbonate, Li-PDC, ($R_1=CH_3$).

These compounds are main components of the SEI films produced in EC and PC electrolytes, respectively.⁴ The bulk properties (the density and the cohesive energy) were calculated from 500 ps MD simulations of a box consisting of 50 molecules under NPT condition. The solubility properties were obtained from 500 ps MD simulations of a box having one solute molecule in 50 solvent molecules of either EC or PC. The force field was COMPASSTM.⁵

Results and Discussions

Table 1 lists the bulk properties of Li-EDC and Li-PDC obtained from MD simulations.

Table 1. The Bulk Properties of the SEI Films

	density g cm ⁻³	cohesive energy kcal mol ⁻¹
Li-EDC	1.36	-260.9
Li-PDC	1.19	-217.7

As is shown, the EC-based SEI film has a higher density and cohesive energy than that the PC-based film. This suggests that the EC-based SEI film is more dense and less brittle than PC-based film. It also supports the Aurbach's model based on the cohesiveness of the film. The

difference between the two films stems from the methyl group of PDC that prevents molecules from packing themselves close to each other. The solubility of the SEI films into solvent was also examined. The heat of dissolution was calculated by the following equation:

$$\Delta H_{\text{diss}} = \Delta H_{\text{sol}} - \Delta H_{\text{sub}} \quad (1)$$

where ΔH_{sol} and ΔH_{sub} are the heat of solution and the heat of sublimation, respectively.

Table 2. Heat of Dissolution for the SEI Films (kcal mol⁻¹)

	Li-EDC	Li-PDC
solvent	EC	PC
ΔH_{sol}	26.4	-68.5
ΔH_{sub}	-260.9	-217.68
ΔH_{diss}	287.3	149.3

It was found that the PC-based SEI film is more soluble in the solvent. In this study, we found a significant difference between the SEI films produced in EC and in PC, with the EC-based SEI film having more favorable characteristics in terms of the bulk properties and the solubility. This difference certainly contributes to the behavior of electrolyte during the first recharge cycle.

References

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