# Computational screening of solid electrolyte interphase forming additives in lithium-ion batteries

Young-Kyu Han [a,*], Kunjoon Lee [a], Sung Chul Jung [a], Yun Suk Huh [b,*]

[a] Department of Energy and Materials Engineering and Advanced Energy and Electronic Materials Research Center, Dongguk University-Seoul, Seoul 100-715, Republic of Korea
[b] Department of Biological Engineering, College of Engineering, Inha University, Incheon 402-751, Republic of Korea

A B S T R A C T

Computational screening is the cornerstone of in silico material discovery, as computational evaluation is faster and much less expensive than experimental trial-and-error testing. Calculations were made of the highest-occupied and lowest-unoccupied molecular orbitals and binding energy with a $Li^+$(ethylene carbonate) ion for 33 organic molecules, which are electrolyte additives for solid electrolyte interphase (SEI) formation in lithium-ion batteries. This work supports the utility of $Li^+$ binding affinity values calculated from a more simple $Li^+$(additive) model. We suggest five promising SEI-forming additives with high anodic stability comparable to fluoropropane sultone on the basis of our calculations.

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## 1. Introduction

For lithium-ion batteries (LIBs), the electrolyte typically consists of one or more lithium salts dissolved in an aprotic solvent, often with at least one additive. Additives are included in electrolyte formulation to perform specific functions. A common function is to enhance electrode stability by facilitating the formation of the solid electrolyte interphase (SEI) layer. In LIBs using a graphite anode, various simple organic molecules act as anode SEI additives. The additives are selected to control the chemistry at the anode/electrolyte interface. The SEI plays a vital role in the battery reactions of LIBs and is also a key material for cycle life, lifetime, power capability, and even safety. The initial step toward anode SEI formation is electron transfer to the SEI-forming species, resulting in a single- or multi-step decomposition reaction that produces the passivating SEI layer at the graphite–electrolyte interface [1–3].

A higher reduction potential than the solvent would therefore be an important requirement for electrolyte additives selected to protect the electrolyte solvent from decomposition. The lowest-unoccupied molecular orbital (LUMO) energy or electron affinity values have been used as a key screening factor for the development of SEI-forming additives in LIBs [4]. Computational screening is the cornerstone of in silico material discovery, as it allows

researchers to identify promising structures efficiently. Computational evaluation is faster and much less expensive than experimental trial-and-error testing when effective screening factors are known [5]. Despite the importance of computational screening, there have been few exploratory studies exist on screening for electrolytes [4,6].

Han et al. [6] showed that a low binding energy with a $Li^+$ ion ($BE(Li^+)$) value is a predominant characteristic of SEI-forming additives; the authors calculated the LUMO, $\eta$, $\mu$, and $BE(Li^+)$ for 32 SEI-forming additives and proposed that the LUMO and $BE(Li^+)$ values can be critical indicators of suitable SEI formation. Leggesse and Jiang [7,8] supported low $Li^+$ binding affinities of SEI-forming additives from the density function theory (DFT) calculations of their additives.

Recently, Han and his coworkers [9] demonstrated that fluorine-substituted propane sulfone (FPS) outperforms vinylene carbonate (VC), the most widely used SEI-forming additive, because of its higher anodic stability and its excellent SEI-forming ability. Interestingly, the $Li^+$ binding affinity of FPS is smaller than those of even the widely used additives, VC and propane sultone (PS).

In this work, we examine the $Li^+$ binding affinity of 33 SEI-forming additives [9,13–43], employing a more realistic $Li^+$(ethylene carbonate)(additive) model than the $Li^+$(additive) model employed in our previous work [6]. We aim to show that $Li^+$-ion binding affinity values are critical indicators of suitable SEI formation via calculations employing the more realistic model. We suggest promising SEI-forming additives with high anodic stability comparable to FPS on the basis of our highest-occupied molecular orbital

* Corresponding authors. Tel.: +82 2 2260 4975 (Y.-K. Han).
  E-mail addresses: ykenergy@dongguk.edu (Y.-K. Han), yunsuk.huh@inha.ac.kr (Y.S. Huh).

(HOMO) energies. More elaborate models would be possible for estimating a very complex property, SEI formation ability. Actually, Xing and Borodin [10] reported that at least two EC molecules should be considered to accurately predict oxidation potential and reaction products of EC oxidative decomposition. Yoshitake [11,12] indicated that HOMO trends often did not agree with the experimentally measured oxidation potentials of electrolytes. Nevertheless, the use of molecular orbital energy and Li$^+$ binding affinity is still a useful choice because simple models are necessary for practical and cost-effective screening. The molecular structures of 33 SEI-forming additives are included in Fig. S1 of the Supporting Information.

## 2. Computational details

Kohn–Sham DFT has become a popular method for calculating molecular properties for a vast array of organic molecules used in LIBs [44–48]. The ground-state structures of the molecules have been fully optimized within C1 symmetry by means of DFT methods. The Kohn–Sham equation was calculated with the B3PW91 functional and 6-311G(d,p) basis sets of triple-$\zeta$ quality. The functional includes a three-parameter adiabatic connection exchange term [49]: a linear combination of the exact Hartree–Fock exchange, Slater exchange [50], and B88 gradient-corrected exchange [51].

This study employs the conductor-variant polarized continuum model (CPCM) [52], which places the solute in a molecular-shaped cavity imbedded in a continuum dielectric medium. In the CPCM, the variation of the free energy when going from vacuum to solution is composed of the work required to build a cavity in

the solvent (cavitation energy) together with the electrostatic (solute–solvent interaction and solute polarization) and non-electrostatic (dispersion and repulsion energy) work. A dielectric constant of 31.9 was adopted as a weighted average value between the dielectric constants of ethylene carbonate (EC: 89.2) and ethyl methyl carbonate (EMC: 2.9), because an EC:EMC = 1:2 solution is widely used as the solvent in LIBs [1,53]. Our group has previously demonstrated that the CPCM is very effective for evaluating various electrochemical properties in the battery electrolyte [6,9,54–57]. All of the DFT and CPCM calculations were performed with the program package Gaussian 03 [58].

## 3. Results and discussion

The HOMO, LUMO, BE(Li$^+$)$_{gas}$, and BE(Li$^+$)$_{sol}$ values of 33 additives are listed in Table 1, along with the EC and propylene carbon-

**Table 2**
Calculated BE(Li$^+$)$_{sol}$ values (in eV) using different dielectric constants for the Li$^+$(EC)(additive) systems.

| $\varepsilon$ | BE(Li$^+$)$_{sol}$ | | |
|---|---|---|---|
| | **16** | **33** | EC |
| 10.0 | 0.17 | 0.08 | 0.43 |
| 20.0 | 0.09 | 0.00 | 0.36 |
| 31.9 | 0.06 | −0.02 | 0.33 |
| 40.0 | 0.05 | −0.03 | 0.32 |
| 50.0 | 0.04 | −0.04 | 0.31 |

Propane sultone (**16**), Fluoro propane sultone (**33**), and ethylene carbonate (EC).

**Table 1**
Highest occupied molecular orbital (HOMO), Lowest unoccupied molecular orbital (LUMO), and Li$^+$ binding energy (BE(Li$^+$)) of 33 SEI-forming additives. The results for EC and PC are included for comparison.

| Material | HOMO (eV) | LUMO (eV) | BE(Li$^+$) (eV) | | Ref. |
|---|---|---|---|---|---|
| | | | Gas | Solvent | |
| (1) Vinylene carbonate | −7.19 | −0.26 | 1.55 | 0.27 | [13–15] |
| (2) Vinylethylene carbonate | −8.04 | −0.84 | 1.74 | 0.32 | [16,17] |
| (3) Phenylethylene carbonate | −7.42 | −0.96 | 1.76 | 0.32 | [18] |
| (4) Fluoroethylene carbonate | −8.72 | 0.37 | 1.53 | 0.27 | [19–21] |
| (5) Trifluoromethyl propylene carbonate | −8.76 | 0.36 | 1.53 | 0.27 | [22,23] |
| (6) Succinic anhydride | −8.01 | −1.03 | 1.42 | 0.23 | [24] |
| (7) Maleic anhydride | −8.38 | −3.41 | 1.31 | 0.19 | [25] |
| (8) Phthalic anhydride | −8.17 | −2.86 | 1.49 | 0.19 | [26] |
| (9) 1,3-Benzodioxol-2-one | −7.08 | −1.09 | 1.54 | 0.22 | [27] |
| (10) Methyl benzoate | −7.33 | −1.48 | 1.61 | 0.25 | [27] |
| (11) **α**-Bromo-$\gamma$-butyrolactone | −7.76 | −1.10 | 1.65 | 0.18 | [28] |
| (12) Methyl chloroformate | −8.53 | −0.40 | 1.27 | 0.17 | [28] |
| (13) Vinyl acetate | −7.09 | −0.53 | 1.46 | 0.25 | [29] |
| (14) Allyl methyl carbonate | −7.64 | −0.24 | 1.51 | 0.24 | [29] |
| (15) Ethylene sulfite | −8.00 | −0.77 | 1.55 | 0.27 | [30] |
| (16) Propane sultone | −8.29 | 0.37 | 1.53 | 0.06 | [31] |
| (17) Propene sultone | −8.12 | −1.55 | 1.53 | 0.06 | [32] |
| (18) Butane sultone | −8.57 | 0.71 | 1.54 | 0.02 | [33] |
| (19) Propylene sulfite | −7.96 | −0.71 | 1.60 | 0.28 | [34] |
| (20) Butylene sulfite | −7.81 | −0.61 | 1.65 | 0.28 | [35] |
| (21) Dimethyl sulfite | −7.63 | −0.32 | 1.53 | 0.24 | [36,37] |
| (22) Diethyl sulfite | −7.39 | −0.27 | 1.79 | 0.32 | [36,37] |
| (23) Glycolide | −8.15 | −0.83 | 1.38 | 0.26 | [38] |
| (24) Dimethyl glycolide | −7.91 | −0.75 | 1.46 | 0.25 | [39] |
| (25) Tetramethyl glycolide | −7.67 | −0.58 | 1.55 | 0.26 | [40] |
| (26) N-acetyl caprolactam | −7.21 | −0.81 | 1.57 | 0.22 | [41] |
| (27) Succimide | −7.35 | −0.80 | 1.51 | 0.29 | [27] |
| (28) 2-Vinylpyridine | −6.70 | −1.47 | 1.56 | 0.19 | [27] |
| (29) 2-Cyanofuran | −7.19 | −1.57 | 1.53 | 0.23 | [42] |
| (30) Methyl cinnamate | −6.69 | −2.03 | 1.70 | 0.27 | [27] |
| (31) Vinyl ethylene sulfite | −7.83 | −0.96 | 1.59 | 0.27 | [43] |
| (32) Chloroethylene carbonate | −8.79 | −0.43 | 1.51 | 0.25 | [27] |
| (33) Fluoro propane sultone | −8.75 | 0.29 | 1.37 | −0.02 | [9] |
| Ethylene carbonate (EC) | −8.25 | 0.81 | 1.70 | 0.33 | |
| Propylene carbonate (PC) | −8.16 | 0.83 | 1.68 | 0.33 | |