Effect of 1,3-Propane Sultone on the Formation of Solid Electrolyte Interphase at Li-Ion Battery Anode Surface: A First-Principles Study

Fan-Wei Lin, Ngoc Thanh Thuy Tran, and Wen-Dung Hsu*

ABSTRACT: Density functional theory is applied to investigate the reductive reactions of reductive-type additive, 1,3-propane sultone (PS), on the formation of solid electrolyte interphase (SEI) near the lithium-ion battery anode surface. Different from the studies that mostly focus on the reduction dissociation of a specific molecule, we adopt an iterative method that systematically considered most possible reactants from the environment in every round of the reaction. The thermodynamically favorable reaction in each round was chosen. Its products then proceed to the following step. At least four iterations of reactions were calculated. The favorable products in each round were then analyzed to understand the trend of the series reactions. With the iterative method, the compounds in every reaction round can be inspected in detail. The method not only predicted the compounds that are consistent with those observed in the experiments but also provide insights into how PS forms an effective SEI. In the solvent state, the most stable reduction states of PS and electrolyte ethylene carbonate (EC) are confirmed as the initial reactants further interact with the environment supplies. First, with the addition of PS, the reduction of PS is prior to EC, which would suppress the reduction of EC and decrease the generation of ethene gas. Second, the compounds from the initial reaction round of PS are lithiated ones and show higher reduction ability than that of EC, while the latter show lower reduction ability than that of the EC, which terminated the reactions. This would be the critical properties for reductive-type additive to form an effective SEI film.

INTRODUCTION

Lithium-ion batteries (LIBs) possess high energy density and capacity, which make them superior to the existing secondary batteries. A typical LIB consists of a graphic carbon as the anode, a transition metal oxide as the cathode, and a mixture of organic electrolyte solvents and lithium salts. During the first charging process, the electrolyte undergoes a reduction at the anode surface. The reduction reactions then result in the formation of a passivating layer called the solid electrolyte interphase (SEI) on the graphite surface. The SEI film is comprised of inorganic and organic electrolyte decomposition byproducts. This significantly determines the important properties of LIBs, such as safety, cycling life, and specific capacities. Therefore, the study of SEI film formation mechanism and morphology has become very important to develop high-performance LIBs. Adding additives that can facilitate the formation of SEI film is one of the efficient ways to improve performance.

Studies have reported several reductive additives that are very effective in the formation of high-quality SEI film. Experiment data have shown that high-quality SEI film is dense and thin. Ideally, this layer prevents further electrolyte degradation by blocking the transport of electrons, while allowing Li ions to pass through during cycling, leading to a long cycle life. Common reductive additives are vinylene carbonate (VC), ethylene sulite (ES), fluoroethylene carbonate (FEC), and 1,3-propane sultone (PS). In this study, the additive 1,3-propane sultone (PS) was chosen because it is commonly used in commercial LIBs and has proven to be very effective in improving the performance of LIBs. Moreover, PS can decrease the gas generation and suppress the swelling of the cell. In recent years, some theoretical calculations were carried out for electrolytes and PS. The reductive decomposition mechanism for ethylene carbonate (EC) was studied. In the bulk solvent, EC is likely to undergo one- or two-electron reduction process. The possible termination products show that the formation of Li2CO3 is slightly more favorable at low EC concentrations, whereas (CH3OCO2Li)2 is favored at high EC concentration. In the propylene carbonate (PC)-based electrolytes, it has been reported that PS is reduced prior to PC to form a stable reduction intermediate. The products from the termination reactions of the primary radical are Li2SO3, (CH−CH1−CH2−OSO2Li)2, and (PC−Li(O2S)O(CH2)3)2, which would build...
up the effective SEI film. Moreover, PS is shown to not only enhance the formation of SEI on the graphite anode case but also other types of electrodes such as silicone-based SiOx anode. Among different types of additives including PS, VC, and ES, the SEI formed in the presence of PS was found to have the best one with low irreversible capacity and good cycle performance.

Through previous works, the basic properties of additive and electrolyte, as well as the possible components of SEI film, were studied. However, the detailed mechanisms that are responsible for the formation of high-quality SEI film by reductive-type additives, like PS, are still unclear. Besides, understanding the mechanisms would also help in developing or screening new additives. In this paper, the systematic method was applied to understand the role of PS and its reduction products compared with that of EC. The density functional theory (DFT) calculation has been carried out for analyzing the effect of 1,3-propane sultone (PS) on the modification of SEI formation. The details of the systematic method are described in the next sections.

RESULTS AND DISCUSSION

Scheme of Calculation. The iterative method is presented in Figure 1. First, the most stable reduction states of PS or EC were confirmed, since those initial states are important for the further intermediates as well as the final products which will form the SEI film on the anode surface. Then succeeding reactions with the environment supplies such as Li⁺, EC, and PS itself are considered. The reaction Gibbs free energy is the criterion for the selection of a thermodynamically favorable reaction. The most possible products then proceed to the next round of reactions. In the case of EC, the environment supplies considered were Li⁺, EC, and CO3²⁻. The reduction abilities of the products of each round reaction were analyzed. The adiabatic electron affinity (EAad) is defined as the free energy difference between a neutral molecule and its negative ion at their optimized geometry and evaluated using the following expression (eq 1)\(^{16}\)

\[
EA = G(\text{optimized anion}) - G(\text{optimized neut.})
\]

where \(G(\text{optimized neut.})\) and \(G(\text{optimized anion})\) are the Gibbs free energies of the optimized neutral system and its negative ion form after gaining an electron, respectively.

The reaction Gibbs free energy, \(\Delta G\), is defined as the Gibbs free energy difference between the products and the reactants, which is evaluated using the following expression (eq 2)

\[
\Delta G = G(\text{products}) - G(\text{reactants})
\]

where \(G(\text{reactants})\) and \(G(\text{products})\) are the Gibbs free energies of the reactants and products, respectively.

Reduction Reactions of EC and PS. Abe et al. have proven that the energy barrier for lithium ion to intercalate into an anode is around 0.5 eV, which results in a very reductive environment at the anode surface during charging. The electrolyte molecules close to the anode surface are then easily reduced.\(^{17}\) Therefore, reduction-induced reactions are the main mechanisms for the formation of SEI. The optimized structures and charge distributions of EC and PS in different reduction states in the solvent state are shown in Figure 2. For EC, the neutral EC is the cyclic structure while reduced EC is the ring-opening structure via the cleavage of the C−O bond.\(^{13}\)

Two-electron reduction products of EC decomposed into two parts, which are C₂H₄ and CO₃²⁻. Through the charge analysis, the charge is concentrated on the oxygen atoms of the CO₃²⁻ part rather than C₂H₄.\(^{18,19}\) In the case of PS, the neutral PS is the cyclic structure, while the reduced PS is the ring-opening structure via the cleavage of the S−O bond.\(^{14}\) However, there is no decomposition during the two-electron reduction process of PS, which only results in a longer S−O bond length. The charge distribution of PS is more uniform than EC, which may imply that the structural stability undercharging for PS is superior to that for EC.

EAad values and the molecular orbital energies of EC and PS are shown in Table 1. The deviations between our results and refs 13, 20 are due to different calculation methods. The negative EAad of EC and PS implies that both molecules can be reduced in the solvent state. The EAad value owing to the first electron reduction of PS is lower than that of EC (−3.29 vs −2.95 eV), which implies that PS has a higher probability to gain one electron and get reduced than EC initially. However, the EAad value owing to the second electron reduction of EC is much lower than that of PS (−5.28 vs −4.46 eV). In addition, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) are also included in the calculation, in which the former is an important value to evaluate the reduction probability. As shown in Table 1, the LUMO energy of PS is lower than that of EC (−0.43 vs 0.002 eV), indicating that the reduction of PS is prior to EC. Under the consideration that EC and PS gain one electron from the graphite, the ability of PS to gain the first electron in the solvent is superior to that of EC.

Reaction Paths of PS and Environment Supplies. With the addition of PS additive in the EC-based electrolytes, the reduction of PS is superior to that of EC as mentioned above so first consider the reaction of PS⁻ with the environment supplies, such as electrolyte, EC, and Li ions (Li⁺) from lithium...
salts. The results of the optimized structures after the reactions are presented in Figure 3. The reaction Gibbs free energy, $\Delta G$, is defined by eq 2, which is a criterion for the selection of favorable reactions. Possible reaction sites were tested in each reaction and here only showed the results of the most negative value of reaction energies.

The compounds PS$^-$ (EC) and Li$^+$/PS$^-$ were formed after the reactions of PS$^-$ with EC and Li$^+$, respectively. The positive/negative $\Delta G$ of PS$^-$ (EC)/Li$^+$/PS$^-$ implies that PS$^-$ do not easily react with EC but can react with Li$^+$ to form a stable compound in which the oxygen atoms of PS$^-$ are favorite sites for Li$^+$ to react and the distances between Li$^+$ and two oxygens are 1.93 and 1.99 Å. In the next reaction round, the reduction ability of Li$^+$/PS$^-$ was calculated and (Li$^+$/PS$^-$)$^-$ was formed after gaining one more electron. Consider Li$^+$/PS$^-$ as a reactant reacting with the environment supplies, such as EC, Li$^+$, and PS, then Li$^+$/PS$^-$ (EC), (Li$^+$/PS$^-$)$^-$, and Li$^+$/PS$^-$ (PS) are formed. The negative $\Delta G$ values of Li$^+$/PS$^-$ (EC) and Li$^+$/PS$^-$ (PS) imply that the complex-lithiated compounds can be stably formed, while the positive $\Delta G$ values of (Li$^+$/PS$^-$)$^-$ implies that Li$^+$/PS$^-$ has a weaker tendency to solvate additional Li$^+$. Comparing the values of $\text{EA}_{\text{ad}}$ and $\Delta G$, (Li$^+$/PS$^-$)$^-$ has the biggest possibility to be formed from Li$^+$/PS$^-$ ($\text{EA}_{\text{ad}} = -4.90$ eV). Besides, the $\text{EA}_{\text{ad}}$ value of the Li$^+$/PS$^-$ is more negative than the $\text{EA}_{\text{ad}}$ value of PS$^-$ ($-4.90$ vs $-4.46$ eV), which implies that Li$^+$/PS$^-$ exhibits a higher reduction ability than PS$^-$ to suppress the further reduction of PS$^-$. In the next reaction round, the reduction ability of (Li$^+$/PS$^-$)$^-$ was calculated and (Li$^+$/PS$^-$)$^-$ was formed after gaining one more electron. It is also worth noting that the $\text{EA}_{\text{ad}}$ value of (Li$^+$/PS$^-$)$^-$ is much less negative than that of Li$^+$/PS$^-$ ($-0.53$ vs $-4.90$ eV), which shows a weaker reduction ability. Similarly, (Li$^+$/PS$^-$)$^-$ was considered as a reactant that reacted with EC, Li$^+$, and PS and created (Li$^+$/PS$^-$)$^-$ EC, Li$^+$PS, and (Li$^+$/PS$^-$)$^-$ PS, respectively, with more negative $\Delta G$ values ($-4.83$, $-5.33$, and $-4.53$ eV) compared to the reactant one. Among products in this reaction round, (Li$^+$/PS$^-$)$^-$ shows the highest tendency to solvate additional Li$^+$ with different oxygen atoms and form Li$_2$PS ($\Delta G = -5.33$ eV). As discussed so far, it is suggested that PS formed further products with the aid of the solvation of Li$^+$ on the oxygen atoms during the SEI formation: PS$^-$ $\rightarrow$ Li$^+$/PS$^-$ (PPS$_2$) $\rightarrow$ (Li$^+$/PS$^-$)$^-$ (PPS$_3$) $\rightarrow$ Li$_2$PS (PPS$_4$).

In the next reaction round, Li$_2$PS can be reduced to (Li$_2$PS)$^-$ after gaining one more electron. The positive value of $\text{EA}_{\text{ad}}$ of Li$_2$PS ($\text{EA}_{\text{ad}} = 0.33$ eV) implies that the reduction reaction of Li$_2$PS can be terminated. In addition, since there is no reaction site for more Li ions in Li$_2$PS, hence, Li$_2$PS is considered to react with EC and PS to form Li$_2$PS$^-$EC and Li$_2$PS$^-$PS, respectively. The negative values of $\Delta G$ of Li$_2$PS$^-$EC and Li$_2$PS$^-$PS ($-4.89$ and $-4.72$ eV) show that Li$^+$ in Li$_2$PS is a good reaction site to react with the solvent molecules. Comparing the value of $\text{EA}_{\text{ad}}$ and $\Delta G$ of products (Li$^+$/PS$^-$)$^-$, Li$_2$PS$^-$EC, and Li$_2$PS$^-$PS, the second compound has the biggest possibility to be formed with $\Delta G = -4.89$ eV. Similarly, Li$_2$PS$^-$EC can get reduced to (Li$_2$PS$^-$EC)$^-$ after gaining one more electron. The positive $\text{EA}_{\text{ad}}$ value of Li$_2$PS$^-$EC implies that the reduction reaction can hereby be terminated.

In summary, Li$^+$ is the reaction site for the oxygen atoms of EC and PS, and the lithiated compounds are formed and stable in all possible reactions. In the first three reaction rounds, PS, Li$_2$PS$^-$ (PPS$_2$), and (Li$^+$/PS$^-$)$^-$ (PPS$_3$) show a higher reduction ability ($-3.29$, $-4.90$, and $-0.53$ eV) than that of Li$_2$PS$^-$(PPS$_4$) and Li$_2$PS$^-$EC (PPS$_5$) ($0.33$ and $0.11$ eV) in the fourth and fifth reaction rounds. This implies the reaction path can be terminated shortly by adding PS to the electrolyte. This finding is consistent with the behavior of PS additive investigated in PC$^-$-based electrolyte of LIB.14

**Reaction Path of EC and Environment Supplies.** Without the addition of the additive PS, the electrolyte EC will be reduced to the opening-ring EC$^-$ so EC$^-$ is considered to react with the environment supplies (EC and Li$^+$). The results of optimized structures after reactions are presented in Figure 4. EC$^-$ reacted with EC and Li$^+$ and formed C$_3$H$_4$O$_3$EC and C$_3$H$_5$O$_5$Li$^+$, respectively. The positive

Table 1. Adiabatic Electron Affinity (eV) and Molecular Orbitals of the EC and PS in the Solvent State

| electron affinities | molecular orbitals energies |
|--------------------|-----------------------------|
| $\text{EA}_{1\text{ad}}$ | $\text{EA}_{2\text{ad}}$ | LUMO | $\text{EA}_{\text{ad}}$ | HOMO | $\text{EA}_{\text{ad}}$ | reference | reference |
| EC | -2.95 | -2.11 [13] | -5.28 | 0.002 | 0.81 [20] | -8.413 | -8.25 [20] |
| PS | -3.29 | -3.27 [14] | -4.46 | -0.043 | 0.37 [20] | -8.286 | -8.29 [20] |

Figure 2. Optimized structures and charge distributions of EC and PS in different reduction states in the solvent state.
values $\Delta G$ of $\text{C}_3\text{H}_4\text{O}_3^-$ $\text{EC}$ and $\text{C}_3\text{H}_4\text{O}_3^-$ $\text{Li}^+$ imply that $\text{EC}^-$ is not easy to form new compounds with the environment supplies. However, $\text{EC}^-$ has a high tendency to be reduced to $\text{EC}^2-$, which are decomposed into $\text{CO}_3^{2-}$ and $\text{C}_2\text{H}_4$. Consequently, the reactions of $\text{C}_2\text{H}_4$ and $\text{CO}_3^{2-}$ with the environment supplies (EC and Li$^+$) were taken into account. $\text{C}_2\text{H}_4$ reacts with EC and Li$^+$, leading to $\text{C}_2\text{H}_4\text{EC}$ and $\text{C}_2\text{H}_4\text{Li}^+$, respectively, in which their positive $\Delta G$ values imply that $\text{C}_2\text{H}_4$ is not an active reactant and the generation of gas $\text{C}_2\text{H}_4$ will increase with the reduction of $\text{EC}$. In contrast, $\text{CO}_3^{2-}$ is rather active to form $\text{CO}_3^{2-}\text{EC}$, $\text{LiCO}_3^-$, and $\text{CO}_3^{2-}\text{CO}_3^{2-}$ after reacting with $\text{EC}$, $\text{Li}^+$, and $\text{CO}_3^{2-}$, respectively. The positive values $\Delta G$ of $\text{CO}_3^{2-}\text{EC}$ and $\text{CO}_3^{2-}\text{CO}_3^{2-}$ imply that it is not easy to form further products, while the negative value of $\Delta G$ ($-0.54$ eV) of $\text{LiCO}_3^-$ means that $\text{CO}_3^{2-}$ can form the lithiated compound. $\text{LiCO}_3^-$ can gain one electron and get reduced to $\text{LiCO}_3^{2-}$. On the other hand, we consider $\text{LiCO}_3^-$ as a reactant that reacts with EC, $\text{Li}^+$, and $\text{CO}_3^{2-}$ and creates $\text{LiCO}_3^-\text{EC}$, $\text{LiCO}_3^-\text{CO}_3^{2-}$, and $\text{Li}_2\text{CO}_3$ ($\Delta G = -0.20$, $-0.33$, and $-0.90$ eV, respectively). A comparison of the values of $\text{EA}_{\text{ad}}$ and $\Delta G$ in this reaction round shows that $\text{Li}_2\text{CO}_3$ has the highest possibility to be formed.

In the next reaction round, the reduction abilities of $\text{Li}_2\text{CO}_3$ were calculated and form $\text{Li}_2\text{CO}_3^-$ after gaining one more electron. The negative value of $\text{EA}$ ($-0.53$ eV) implies that the reduction reaction of $\text{Li}_2\text{CO}_3^-$ can be continuous. Then, we consider $\text{Li}_2\text{CO}_3$ as a reactant reacting with EC and $\text{CO}_3^{2-}$ to form $\text{Li}_2\text{CO}_3^-(\text{EC})$ and $\text{Li}_2\text{CO}_3^-(\text{CO}_3^{2-})$, respectively. The further lithiated compounds can be produced with negative $\Delta G$ values. Within this reaction round, $\text{Li}_2\text{CO}_3^-(\text{CO}_3^{2-})$
PEC_4 has the biggest possibility to be formed. Similarly, Li₂CO₃^−(CO₃²−) can get reduced to become (Li₂CO₃−(CO₃²−))^− with a negative value for EA_{ad}, indicating that further reduction reactions for the latter products of EC can be continuous.

In summary, the two-electron reduction of EC has a higher possibility than its one-electron reduction process. With the presence of Li-ion from lithium salt, the lithiated compounds are formed and stable in all possible reactions. In the first and second reaction rounds, EC and LiCO₃^− (PEC_2) show weaker reduction abilities than that of PS and Li^+PS^− (PPS_2). However, in the third and fourth reaction rounds, the EA_{ad} values of PEC_3 and PEC_4 are still negative, which implies that the reduction reactions are continuous.

Reduction Ability of Reactants and Products. Based on the aforementioned discussion, the dominant products in each reaction round with PS additive are PS, PS^−, PPS_2, PPS_4, and PPS_5, whereas the dominant products are EC, C₂H₄, CO₃²−, PEC_2, PEC_3, and PEC_4 in the case without PS, as shown in Figure 5. The reduction abilities of the dominant products in each reaction round are shown in Table 2, in which PS shows a higher reduction ability than that of EC (−3.29 vs −2.95 eV). The former lithiated products from PS show higher reduction abilities (−4.90 vs −0.46 eV), while the latter products show lower reduction abilities (0.33 vs −0.58 eV and 0.11 vs −0.53 eV) compared to the EC case. The negative EA_{ad} value of the products from EC implies that the reduction reactions of EC can continue, while the positive EA value of the latter products from PS implies that the reduction reaction can be terminated. From this viewpoint, compared with that of the electrolyte EC, the reductive-type additive PS would have higher reduction ability initially but lower reduction ability lately and can be terminated. These results would be the critical properties for reductive-type additive PS to form a thin and stable SEI film.

The effect of PS on the SEI formation at the anode could be examined by experimental measurements. It is worth noting that the structural analysis of the SEI layer and the electrochemical performance could be examined by ex situ surface analysis, followed by Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), and electron-
dispersive spectroscopy (EDS). In addition, NMR spectroscopy is recently considered as a powerful technique for the structural elucidation in the SEI layer. Differential capacity plots and ex situ surface analysis have confirmed that PS is reduced prior to EC and alter the structure of the anode SEI.\(^{21,22}\) Moreover, the formation of \(\text{C}_4\text{H}_8\), \(\text{Li}_2\text{CO}_3\), and \((\text{CH}_2\text{OCO}_2\text{Li})_2\) due to EC reduction have been confirmed by FTR, XPS, and NMR analysis.\(^{23-25}\) On the other hand, with the PS additive, there results in the production of \(\text{ROSO}_2\text{Li}\) compound as verified by XPS, EDS, and NMR.\(^{21,25,26}\)

### CONCLUSIONS

The iterative method by the use of DFT calculations has been applied to comprehend the effect of reductive-type additive PS on the mechanism of SEI formation. In the solvent state, with the addition of additive PS, the reduction of PS occurs faster than that of EC and the most stable reduction state is PS\(^-\). Without the addition of additive PS, the most stable reduction state is EC\(^2-\), which is decomposed to \(\text{C}_2\text{H}_4\) and \(\text{CO}_2\)^\(^{2-}\). Therefore, with the addition of PS, the generation of \(\text{C}_2\text{H}_4\) is decreased, which means the swelling of the cell can be alleviated.

An inspection of the products in each reaction round shows that they are all composed of lithiated compounds with or without the addition of PS. PS is a reductive-type additive. The reduction abilities of PS and its initial products are high, while those of its latter products are low, which implies that the reduction reaction can be terminated. However, the products from EC show continuous reduction reactions in all reaction rounds. In this way, compared with the electrolyte EC, the reductive-type additive PS has a higher reduction ability in the initial stage but a lower reduction ability in further product steps. Further experimental examinations involving XPS, FTR, NMR, and EDS are necessary for verifying the products from the reduction and termination reactions with and without PS additive. These results would be the critical properties for a reductive-type additive to form a thin and stable SEI film.

### COMPUTATIONAL METHOD

The theoretical investigations of the reduction state and the reaction processes have been carried out using DFT with B3LYP methods\(^{27-30}\) using 6-311++G(d,p) basis set as presented in the Gaussian 03 package.\(^{31}\) The relative energies including zero-point energy (ZPE) correction, Gibbs free energy, and enthalpies are calculated at 298.15 K. Mulliken population analysis\(^{32}\) with the same basis set was also performed in the Gaussian 03 package. The study employs the conductor-variant polarized continuum model (CPCM),\(^{33}\) which considers the solute in a molecular cavity presented in a continuum dielectric medium. The dielectric constant of the solvent was set to 31.6 to mimic the EC/EMC = 1:2 solution, which is commonly used as LIB’s electrolyte.\(^{18}\) However, in this work, only EC is considered for the reaction path calculation since EMC does not affect the SEI layer formation.\(^{20}\)

### AUTHOR INFORMATION

**Corresponding Author**

Wen-Dung Hsu — Department of Materials Science and Engineering and Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan 701, Taiwan; orcid.org/0000-0002-4634-8059;

Phone: +886-6-2757575; Email: wendung@mail.ncku.edu.tw; Fax: +886-6-2346290

**Authors**

Fan-Wei Lin — Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan

Ngoc Thanh Thuy Tran — Hierarchical Green-Energy Materials (Hi-GEM) Research Center, National Cheng Kung University, Tainan 701, Taiwan; orcid.org/0000-0001-6419-3655

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04447

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was financially supported by the Hierarchical Green-Energy Materials (Hi-GEM) Research Center, from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) and the Ministry of Science and Technology (MOST 109-2634-F-006-020) in Taiwan.

**REFERENCES**

1. Aurbach, D.; Talyosef, Y.; Markovsky, B.; Markevich, E.; Zinigrad, E.; Asraf, L.; Gnanaaraj, J. S.; Kim, H. J. Design of electrolyte solutions for Li and Li-ion batteries: a review. Electrochim. Acta 2004, 50, 247–254.
2. Pole, E. The electrochemical behavior of alkali and alkaline earth metals in nonaqueous battery systems—the solid electrolyte interphase model. J. Electrochem. Soc. 1979, 126, 2047–2051.
3. Verma, P.; Mairle, P.; Novák, P. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. Electrochim. Acta 2010, 55, 6332–6341.
4. Zhang, S. S. A review on electrolyte additives for lithium-ion batteries. J. Power Sources 2006, 162, 1379–1394.
5. Han, G.; Li, B.; Ye, Z.; Cao, C.; Guan, S. The cooperative effect of Vinylene Carbonate and 3-Propane Sultone on the Elevated Temperature Performance of Lithium Ion Batteries. Int. J. Electrochem. Sci. 2012, 7, 12963–12973.
6. Sasaki, T.; Abe, T.; Iriyama, Y.; Inaba, M.; Ogumi, Z. Suppression of an alkyl dicarbonate formation in Li-ion cells. J. Electrochem. Soc. 2005, 152, A2046–A2050.
7. Wrodnigg, G. H.; Besenhard, J. O.; Winter, M. Ethylene Sulfite as Electrolyte Additive for Lithium-Ion Cells with Graphitic Anodes. J. Electrochem. Soc. 1999, 146, 470–472.
8. Choi, N. S.; Yew, K. H.; Lee, K. Y.; Sung, M.; Kim, H.; Kim, S. S. Effect of fluoroethylene carbonate additive on interfacial properties of silicon thin-film electrode. J. Power Sources 2006, 161, 1254–1259.
9. Park, G.; Nakamura, H.; Lee, Y.; Yoshio, M. The important role of additives for improved lithium ion battery safety. J. Power Sources 2009, 189, 602–606.
10. Yim, T.; Kim, S. H.; Woo, S. G.; Lee, K.; Song, J. H.; Cho, W.; Kim, K. J.; Kim, J.; Kim, Y. J. 3-Propanesulfonate as an effective functional additive to enhance the electrochemical performance of over-lithiated layered oxides. RSC Adv. 2014, 4, 19172–19176.
11. Zao, X.; Xu, M.; Li, W.; Su, D.; Liu, J. Electrochemical reduction of 1, 3-propane sultone on graphite electrodes and its application in Li-ion batteries. Electrochem. Solid-State Lett. 2006, 9, A196–A199.
12. Yongxing, G.; Zhenguo, Y.; Zhiyong, T.; Xinhai, L.; Zhixing, W. Functional additive to enhance the electrochemical performance of over-lithiated layered oxides. J. Power Sources 2009, 184, 513–516.
(13) Wang, Y.; Nakamura, S.; Ue, M.; Balbuena, P. B. Theoretical studies to understand surface chemistry on carbon anodes for lithium-ion batteries: reduction mechanisms of ethylene carbonate. J. Am. Chem. Soc. 2001, 123, 11708–11718.

(14) Leg gesse, E. G.; Jiang, J. C. Theoretical study of the reductive decomposition of 1, 3-propane sultone: SEI forming additive in lithium-ion batteries. RSC Adv. 2012, 2, 5439–5446.

(15) Yoon, S. R.; Jeong, S. K. Effects of Organic Additives on Electrochemical Properties of SiOx Electrodes in Lithium Secondary Batteries. Appl. Mech. Mater. 2016, 835, 121–125.

(16) Rienstra-Kiracofe, J. C.; Tschumper, G. S.; Schaefer, H. F.; Nandi, S.; Ellison, G. B. Atomic and molecular electron affinities: photoelectron experiments and theoretical computations. Chem. Rev. 2002, 102, 231–282.

(17) Abe, T.; Fukuda, H.; Iriyama, Y.; Ogumi, Z. Solvated Li-ion transfer at interface between graphite and electrolyte. J. Electrochem. Soc. 2004, 151, A1120–A1123.

(18) Mosallanejad, B. Phthalimide Derivatives: New Promising Additives for Functional Electrolyte in Lithium-ion Batteries. Chem. Methodol. 2019, 3, 145–275.

(19) Leung, K. Two-electron reduction of ethylene carbonate: A quantum chemistry re-examination of mechanisms. Chem. Phys. Lett. 2013, 568–569, 1–8.

(20) Wang, F. M.; Yu, M. H.; Hsiao, Y. J.; Tsai, Y.; Hwang, B. J. Aging effects to solid electrolyte interface (SEI) membrane formation and the performance analysis of lithium ion batteries. Int. J. Electrochem. Sci. 2011, 6, No. e1026.

(21) Zhang, B.; Metzger, M.; Solchenbach, S.; Payne, M.; Meini, S.; Gasteiger, H. A.; Garsuch, A.; Lucht, B. L. Role of 1, 3-propane sultone and vinylene carbonate in solid electrolyte interface formation and gas generation. J. Phys. Chem. C 2015, 119, 11337–11348.

(22) Delp, S. A.; Borodin, O.; Olguin, M.; Eisner, C. G.; Allen, J. L.; Jow, T. R. Importance of reduction and oxidation stability of high voltage electrolytes and additives. Electrochim. Acta 2016, 209, 498–510.

(23) Lin, L.; Yang, K.; Tan, R.; Li, M.; Fu, S.; Liu, T.; Chen, H.; Pan, F. Effect of sulfur containing additives on the formation of a solid-electrolyte interphase evaluated by in situ AFM and ex situ characterizations. J. Mater. Chem. A 2017, 5, 19364–19370.

(24) Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S. Analysis of vinylene carbonate derived SEI layers on graphite anode. J. Electrochem. Soc. 2004, 151, A1659–A1669.

(25) Xu, M.; Li, W.; Lucht, B. L. Effect of propane sultone on elevated temperature performance of anode and cathode materials in lithium-ion batteries. J. Power Sources 2009, 193, 804–809.

(26) Zuo, X.; Xu, M.; Li, W.; Su, D.; Liu, T. Electrochemical reduction of 1, 3-propane sultone on graphite electrodes and its application in Li-ion batteries. Electrochem. Solid-State Lett. 2006, 9, A196–A199.

(27) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 1988, 37, 785.

(28) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652.

(29) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F. N.; Frisch, M. J. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem. A 1994, 98, 11623–11627.

(30) Vosko, S.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys. 1980, 58, 1200–1211.

(31) Frisch, M. J. T. G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; et al. Gaussian 03, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

(32) Mulliken, R. S. Electronic population analysis on LCAO–MO molecular wave functions. J. Chem. Phys. 1955, 23, 1833–1840.