Reconsideration of SEI stability: reversible lithium intercalation into graphite electrodes in *trans*-2,3-butylene carbonate

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Abstract

Lithium ion batteries with graphitic carbon anodes and $LiCoO_2$ cathodes are cycled reversibly in electrolytes based on *trans*-2,3-butylene carbonate (*t*-BC), even in the absence of ethylene carbonate. While the poor interfacial film (the solid electrolyte interface (SEI)) on the lithium electrode can be readily explained in terms of previous models of its stability, this highly reversible behavior of graphite is hard to account for. To explain this profound difference in the SEI stability of the two electrodes, we have taken into account the influence that the nature of the electrode (lithium metal versus graphite) and the type of the reaction site (basal plane versus edge sites) exert on the solvent reduction pathways. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium ion batteries with graphitic carbon anodes have achieved not only commercial success, but have also given rise to a proliferation of research on the interfacial behavior of graphitic carbon electrodes. The stability of the interfacial film, also called the solid electrolyte interface (SEI), is critical for the effective utilization of highly crystalline graphitic carbons, because a stable SEI prevents a rapid decline in the performance that arises from a continuous decomposition of the electrolyte. Therefore, it is important to understand the factors that control the stability of the SEI and its formation mechanism.

It has been claimed [1–4] that the main constituent of the SEI layer is the solvent-decomposition product, and that the stability of the SEI is controlled primarily by its solubility toward the native solvents. A number of solvent reduction pathways are proposed on the basis of compositional analysis using a variety of spectroscopic tools, e.g. Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), to understand the structure of the SEI and its formation mechanisms [1,2,4–7]. For example, Aurbach et al. [2] have concluded, using the FTIR results, that lithium alkyl carbonates are the major reduction product of cyclic carbonates whose stability toward the

native solvents determines the reversibility of lithium intercalation behavior of graphite. Ein-Eli [3] has developed this idea further to propose a new model that lays down criteria for the SEI stability. The vastly different SEI stability of ethylene carbonate (EC) and propylene carbonate (PC) has been attributed to the loose methyl tail of PC that prevents the formation of a compact SEI. As a consequence of the poor passivation property of the SEI, PC-based electrolytes are decomposed continuously on the graphite surface [2,3,8].

Although the models of Aurbach et al. [2] and Ein-Eli [3] can elegantly explain a wide range of experimental observations, they seem to underestimate the role of the solvent co-intercalation, while over-emphasizing the role of the solvent-decomposition products in the overall interface formation. For example, it is assumed that the solvent decomposition is strictly a surface reaction, and that the stability of the product determines not only the reversibility of lithium intercalation but also the graphite exfoliation behavior [2,3]. In other studies [9], we have shown a number of experimental observations that contradict these postulates. These experimental results could be best explained in a unified fashion by assuming that the co-intercalation of cyclic carbonates is the primary step of graphite exfoliation and the interface formation. For example, in electrolytes based on a structural analogue of PC, namely *trans*-2, 3-butylene carbonate (*t*-BC), that is expected to be decomposed similarly to a corresponding lithium alkyl carbonate

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containing two methyl tails, quite a large amount of lithium can be intercalated without causing extensive graphite exfoliation [9,10]. Furthermore, the capability for lithium insertion also depends sensitively on the structure of the graphite, which would be counter-intuitive if the SEI formation is strictly a surface reaction.

This apparent conflict between our results and those of Aurbach et al. [2] may arise from different reaction environments at the edge sites and the basal plane of graphite, because the average SEI composition can be dominated by the reduction products on the basal surface, while the graphite exfoliation is dominated by the reaction at the edge sites. Recent analysis [5] on the surface film of HOPG (highly oriented pyrolytic graphite) suggests that the SEI composition differs significantly between the basal and prismatic planes, which is consistent with the possibility of different film-formation mechanisms at the basal planes and edge sites. This might be related to the two distinct reaction stages reported by Naji et al. [6], where EC is reduced mainly to Li_2CO_3 and to lithium alkyl carbonate above and below 0.8 V, respectively. The two distinct solvent-decomposition processes may arise from different reaction environments at the edge and the basal planes, since the reduction of electrolyte takes place initially at the edge sites and then throughout the electrode surface [11–13]. If such direct formation of Li_2CO_3 from EC above 0.8 V as proposed by Naji et al. [6] is due to the unique reaction properties of the edge sites of graphite, then other cyclic carbonates can similarly give rise to a stable SEI which is comprised mainly of Li_2CO_3.

However, reversible lithium intercalation behavior is rarely observed from PC and most cyclic carbonates other than EC. This can be attributed to extensive graphite exfoliation that destroys the surface structure continuously, which also eliminates the decomposition product deposited on the graphite surface regardless of its intrinsic stability. Therefore, t-BC in which graphite exfoliation is found to be largely suppressed can be used to test the hypothesis that cyclic carbonate may undergo direct Li_2CO_3 formation at the edge sites in general. An objective of this work is to provide experimental results on the interfacial stability of graphite in t-BC-based electrolytes. With these results, solvent-decomposition mechanisms can be proposed that take into account the different reaction environments of the edge sites and the basal planes.

2. Experimental

The t-BC (4,5-dimethyl-1,3-dioxolan-2-one) was synthesized as described previously [10]. The chemical structure and purity were confirmed by nuclear magnetic resonance (NMR) spectroscopy and gas chromatograph mass spectroscopy (GC–MS). The GC purity was over 99.95%, and the moisture content was less than 50 ppm (Karl Fischer Coulometric titration). The majority of the impurity (0.035%) of t-BC

was identified as c-BC, and the rest of the impurities were residual glycols at a level of less than 0.005%. Commercial electrolyte grade PC also contained residual alcohols and glycols in similar quantities. The electrochemical tests were conducted using 1 M $LiPF_6$ solution. All other solvents (Mitsubishi Chemicals, battery grade) and the $LiPF_6$ salt (Stella Chemicals) were used as received.

The graphitic carbon electrodes were prepared and tested as previously described [14]. The graphitic carbon used in this work was mesophase microbead from Osaka Gas, Japan (MCMB-25), an artificial graphite from Nippon Carbon, Japan (P15BG), and a flaky graphite from Timcal, Swiss (SFG6). Charge–discharge cycling was conducted using 2016 size coin cells with lithium or $LiCoO_2$ counter electrodes. Both the graphite anode and $LiCoO_2$ cathode were prepared to the uniform sizes of 1.77 and 1.5 cm^2, respectively, and the reversible capacity of the C‖$LiCoO_2$ cells was roughly 4.0 mAh. A current density at the 20 h rate (C/20, 0.25 mA) was used for C‖lithium half-cell tests between 0.01 and 1.5 V, and a higher current density at the 2 h rate (C/2, 2 mA) was used for C‖$LiCoO_2$ cells between 3.0 and 4.2 V.

3. Results

We have recently reported that graphite anode half-cells containing lithium metal counter electrode generally show poor reversibility in t-BC/diethyl carbonate (DEC) 1 M $LiPF_6$, although they do not show such extensive graphite exfoliation as in PC/DEC [10]. The initial efficiency improves substantially when DEC is replaced with ethyl methyl carbonate (EMC) (Fig. 1), in accordance with the superior SEI stability of EMC to that of DEC [4]. The capacity drops below 80% only after three cycles however, and this is even worse than the results obtained using EMC alone, which implies that t-BC has adverse effect on the formation of a stable SEI.

The reversibility of lithium intercalation depends acutely on which graphite is used. Almost 100% capacity is obtained
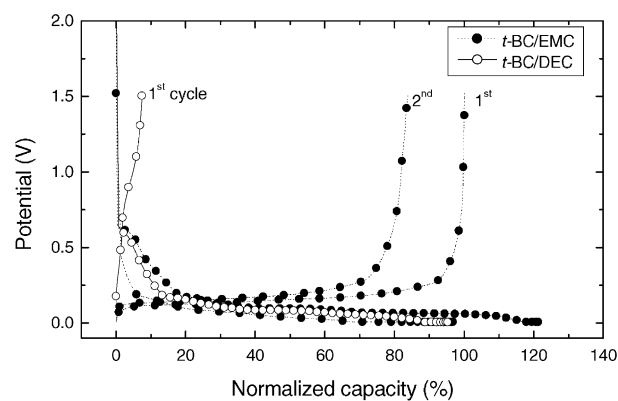

Fig. 1. Initial voltage profiles obtained using (50/50) t-BC/DEC and t-BC/EMC for MCMB25‖Li half-cells. Capacity is normalized by the reversible capacity obtained using 1 M $LiPF_6$ (50/50) EC/DEC (310 mAh g^{-1}).
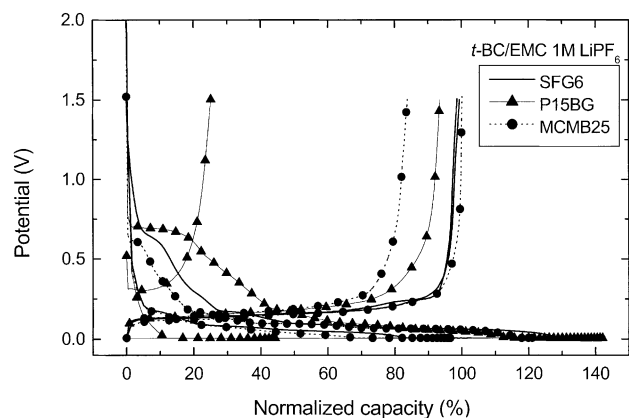
Fig. 2. Voltage profiles of first two cycles obtained using (50/50) *t*-BC/EMC for three graphite electrodes. The capacity is normalized by the reversible capacity obtained using 1 M LiPF$_6$ (50/50) EC/DEC for each sample.

Fig. 3. Voltage profiles of a Li‖Li cell obtained using (50/50) *t*-BC/DEC at a current density of 0.14 mA cm^{-2}. The internal resistance and the overpotential increase rapidly as charge–discharge continues.

repeatedly from SFG6, while the capacity of P15BO declines much more rapidly than that of MCMB25 (Fig. 2). Close examination of the data indicates that such a rapid decline in the capacity is usually accompanied by an increase in the internal resistance of the cell. Since a thin electrode made of SFG6 (1.12 mAh cm^{-2}) shows remarkable reversibility compared with the other two electrodes which are significantly thicker (i.e. 3.14 and 3.10 mAh cm^{-2} for P15BO and MCMB25, respectively), it is possible that the depth of charge–discharge of the lithium metal electrode has a strong influence on this difference. Therefore, the degradation of the lithium metal electrode has been examined using a Li‖Li coin cell. The rapid increase in the interfacial resistance with cycling is clearly observed from the voltage profiles obtained at a current density of 0.14 mA cm^{-2} between +0.5 and −0.5 V (Fig. 3). The overpotential generally decreases during the initial cycles because of an increase in the surface area, when the passive film has reasonable stability. The lithium metal electrodes
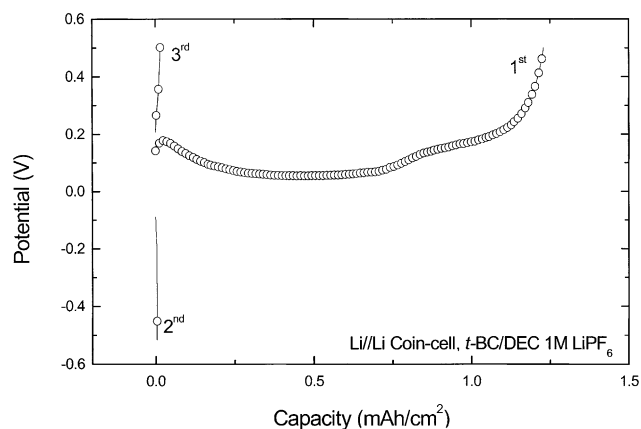
were found to be coated with a thick brown film when the cell was disassembled after the cycling. This suggests that the poor SEI of *t*-BC electrolyte on the lithium metal electrode has a strong influence on the reversibility of the graphite half-cells.

In contrast, lithium ion batteries with graphite anodes and LiCoO$_2$ cathodes have a remarkable reversibility even in *t*-BC/DEC (Fig. 4). The cells were charged at the *C*/10 rate (0.4 mA) and discharged at the *C*/5 rate (0.8 mA) during the first cycle, and then cycled at the *C*/2 rate (2 mA) between 3.0 and 4.2 V after the second cycle. The first charge cycle in *t*-BC/DEC is almost identical to that in EC/DEC, except for the larger irreversible reaction observed between 3.2 and 3.7 V. The sudden increase in the overpotential on the second cycle is merely due to the higher current density. The overall cell impedance also increases gradually with cycling. A similar change in overpotential is also observed for EC/DEC, although the increase due to a change in the current density is smaller due to the higher conductivity of
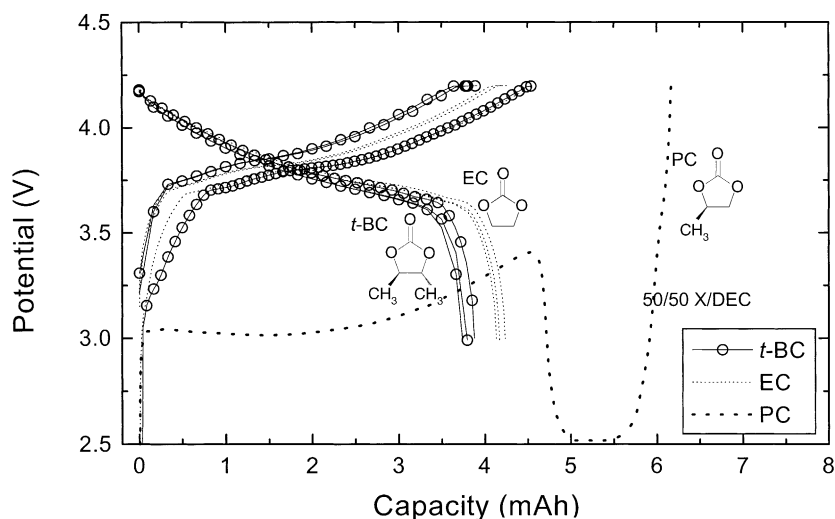

Fig. 4. First three intercalation/de-intercalation cycles of C‖LiCoO$_2$ cells with 1 M LiPF$_6$ solution of (50/50) X/DEC, where X = *t*-BC, EC, and PC.

EC/DEC compared with t-BC/DEC. After the second cycle, the capacity declines only gradually during subsequent cycling. The ratio of the tenth and the first discharge capacity is slightly smaller for t-BC/DEC (89%) than for EC/DEC (94%). The cell cannot be cycled in PC/DEC however, because the gaseous decomposition product of PC leads to cell failure.

4. Discussion

The lithium intercalation behavior of graphite‖Li half-cells in t-BC based electrolytes is usually characterized by poor reversibility and by sensitivity to the co-solvent. The poor reversibility appears to be consistent with Ein-Eli's model [3], where t-BC is decomposed to a corresponding lithium alkyl carbonate, analogous to those containing an ethyl group from EC and a propyl group from PC by a mechanism proposed by Aurbach et al. [1,2]. The lithium alkyl carbonate from t-BC would have a larger alkyl group with two loose ends, and hence is expected to be less compact and more soluble than that of EC or PC. However, the sensitivity to the linear carbonate co-solvent is not easy to explain, because the SEI of the graphite electrode is generally dominated by the decomposition of cyclic carbonates for two reasons. First, the SEI on the graphite electrode is formed by a sequence of reactions that starts with the species which are most reducible [2]. Generally, cyclic carbonates are reduced at a higher potential than linear carbonates [4]. Second, cyclic carbonate can also approach the electrode surface preferentially due to a stronger interaction with lithium ions than with linear carbonate [15]. On the other hand, the SEI of the lithium counter electrode can be affected more strongly by linear carbonates, because both linear carbonates and cyclic carbonates are extremely unstable on lithium metal. This instability of the lithium metal electrode is in agreement with our experimental observations. Therefore, we can conclude that the poor

reversibility of graphite‖Li half-cells and their sensitivity to the co-solvent are primarily due to the poor stability of the corresponding lithium alkyl carbonate that forms on the lithium metal electrode.

By contrast, a stable SEI appears to form on the graphite, independent of which co-solvent is used (Fig. 5). This is consistent with the fact that the decomposition product of cyclic carbonate controls primarily the property of the SEI on the graphite electrode. The same decomposition mechanism of lithium alkyl carbonate cannot, however, explain simultaneously the disparate role of t-BC on the SEI stability of lithium metal and the graphite electrodes. Specifically, the reversible cycling of C‖LiCoO$_2$ cells in t-BC/DEC is hard to understand, if the SEI consisted mainly of lithium alkyl carbonate containing a butyl group, which would be highly soluble toward the electrolyte.

This remarkable SEI stability on the graphite electrode can be understood by generalizing the two-step reduction of EC observed by Naji et al. [6], where direct two-electron reduction of t-BC to Li$_2$CO$_3$ takes place at a higher potential than the formation of the lithium alkyl carbonate. Since, the reduction of electrolyte initially takes place near the edge sites, Li$_2$CO$_3$ might be a dominant reduction product at the edge sites [11–13]. The resulting SEI would be comprised of a layer of lithium carbonate, which is recognized as the most stable SEI component, most close to the graphite surface particularly near the edge sites. This postulate is in good agreement with recent experimental observation that the SEI on the cross-sectional planes of HOPG has substantially higher content of lithium carbonate than that on the basal plane [5]. This two-electron reduction of a cyclic carbonate to lithium carbonate is also more consistent with the results of subtractive normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) [16] than with other indirect processes as proposed by Aurbach et al. [1,2].

Possible solvent reduction pathways are laid out in Fig. 6 to account for the plausibility of the two-electron reduction process, particularly at the edge sites of graphite electrodes. As recently substantiated by an electron spin resonance spectroscopy (ESR) observation [15], generation of a lithium-containing radical (product **1**), by electron transfer to a cyclic carbonate that is strongly solvating a lithium ion, is considered to be an initial step of the SEI formation [15]. The radical (product **1**) is likely to react further with: (i) an electron and a lithium ion; (ii) solvent molecules; or (iii) other radicals. The relative concentration of the three reactants can have a profound influence on the fate of the decomposition product. For example, at the edge sites where both the flux of lithium ions and the probability of electron transfer are particularly high, the radical can easily undergo a consecutive reduction of the radical intermediate to a simple lithium carbonate (product **2**). If such reaction mechanism is generally valid, even PC, can in principle, form a stable interface on graphite electrodes, as long as extensive exfoliation can be prohibited. Such possibility of suppressing graphite exfoliation is, in fact, demonstrated by
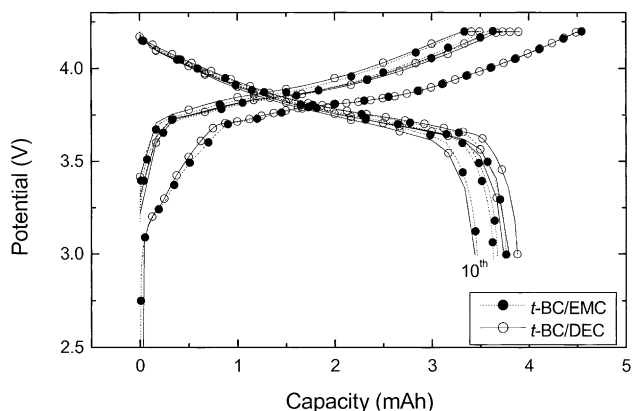

Fig. 5. First three and the tenth intercalation/de-intercalation cycles of C‖LiCoO$_2$ cells with 1 M LiPF$_6$ solution of (50/50) t-BC/DEC and t-BC/EMC. The ratio of the tenth and the first discharge capacity is 89% for t-BC/DEC and 92% for t-BC/EMC.
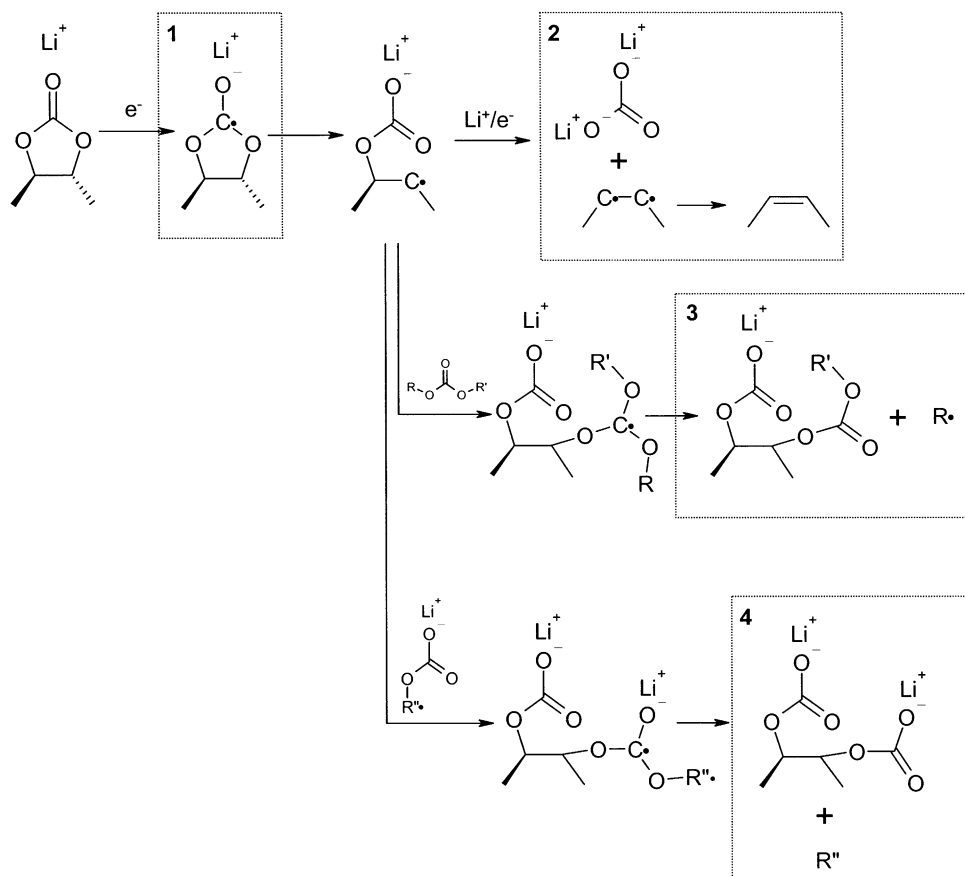
Fig. 6. Possible reduction mechanisms of *t*-BC. The radical (product **1**) is either decomposed directly to lithium carbonate or makes an electrophilic attack on the carbonyl oxygen of solvents and other carbonate radicals.

using PC/linear carbonate with less than 20% PC, and by using a graphite with a large defect density in the presence of only small amount of EC [17,18].

By contrast, such two-step reduction to lithium carbonate is less likely to occur on the basal planes or on the lithium surface because of high radical concentration (on lithium) and a low probability of a consecutive transfer of electrons and lithium ions. Thus, the radical (product **1**) makes an electrophilic attack on the carbonyl oxygen of other solvents (product **3**) or radicals (product **4**). If it reacts with a cyclic carbonate instead of a linear one, the product is again a radical and the product may become polymeric. The disproportionation reaction of the radicals, as proposed by Aurbach et al. [1,2], gives rise to product **4**. The stability of such a reduction product can be determined in light of the criteria proposed by Ein-Eli [3], which predicts that product **4** is more soluble, and hence less stable than lithium carbonates formed on the edge sites of the graphite. This product contains an alkyl group that originates from the native solvent, which is ethyl for EC, propyl for PC, and butyl for *t*-BC. Therefore, product **4** from *t*-BC tends to form a poorer SEI than similar products of EC or PC. The thick brown film formed on lithium metal after cycling appears to be a mixture of both polymeric product and the product **4**

and does not protect the lithium electrode from further reaction with the solvents.

5. Conclusions

The *t*-BC forms a stable SEI on graphite electrodes, independent of which linear carbonate co-solvent is used. By contrast, a poor interfacial film, which is significantly influenced by the co-solvent, is formed on lithium metal electrodes. Various solvent-decomposition mechanisms on the two electrodes are considered to explain this puzzling difference. At the edge sites, a two-step reduction to lithium carbonate is postulated to be predominant, which can produce a stable SEI mainly comprising of lithium carbonate. The products on lithium metal electrodes, however, are considered to be a mixture of polymeric material and organic lithium salts that are partly soluble due to a large alkyl group. In light of this result, we expect the nature of the electrode (lithium metal versus graphite) and the type of reaction site (basal plane versus edge sites) generally to exert strong influence on the solvent-decomposition mechanisms. Such site-specific decomposition mechanisms can further shed light on SEI stability as a function of electrolyte composition.

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