Solubility of Lithium Salts Formed on the Lithium-Ion Battery Negative Electrode Surface in Organic Solvents

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The solubility of lithium salts in dimethyl carbonate (DMC) found in solid electrolyte interface (SEI) films was determined. The salt–DMC solutions evaporated, and the salts were transferred into water for ion conductivity measurements. The salts examined included lithium carbonate (Li$_2$CO$_3$), lithium oxide ([Li$_2$O]$_2$), lithium fluoride (LiF), lithium hydroxide (LiOH), lithium methyl carbonate (LiOCO$_2$CH$_3$), and lithium ethyl carbonate (LiOCO$_2$CH$_3$H$_2$). The salt molarity in DMC ranged from 9.6 × 10$^{-4}$ mol L$^{-1}$ (Li$_2$CO$_3$CH$_3$H$_2$) to 9 × 10$^{-3}$ mol L$^{-1}$ (Li$_2$CO$_3$) in the order of Li$_2$CO$_3$CH$_3$H$_2$ > Li$_2$CO$_3$H$_3$ > LiOH > LiF > (Li$_2$CO$_3$)$_2$ > Li$_2$O. X-ray photoelectron spectroscopy measurements on SEI films on the surface of the negative electrode taken from a commercial battery after soaking in DMC for 1 h suggested that the films can dissolve. Separately, the heat of dissolution of the salts was calculated from computer simulations for the same salts, including lithium methoxycarbonyl (LiOCH$_3$), and dilithium ethylene glycol dicarbonate ([CH$_2$OCO$_2$Li]$_2$LiEDC) in both DMC and ethylene carbonate (EC). The results from the computer simulations suggested that the order in which the salt was likely to dissolve in both DMC and EC was LiEDC > Li$_2$CO$_3$CH$_3$H$_2$ > LiOH > Li$_2$CO$_3$H$_3$ > LiOCH$_3$ > LiF > (Li$_2$CO$_3$)$_2$ > Li$_2$O. This order agreed with the experiment in DMC within the experimental error. Both experiment and computer simulations showed that the organic salts are more likely to dissolve in DMC than in the inorganic salts. The calculations also predicted that the salts dissolve more likely in EC than in DMC in general. Moreover, the results from the study were used to discuss the capacity fading mechanism during the storage of lithium-ion batteries.

The solubility of this study is to examine the solubility of a series of SEI film components. The lithium salts studied here included lithium fluoride (LiF), lithium hydroxide (LiOH), lithium carbonate (Li$_2$CO$_3$), lithium oxide ([Li$_2$O]$_2$), lithium methyl carbonate (LiOCO$_2$CH$_3$), and lithium ethyl carbonate (LiOCO$_2$CH$_3$H$_2$). Their solubility was measured in DMC. Because the characteristics of SEI films, including their compositions, vary depending on the active materials and the electrolyte, it is our hope that measurements of the solubility of individual lithium salts would apply to a wide range of SEI film compositions. Computational tools were used not only to interpret the experimental data, but also to supplement the data by analyzing other salts such as lithium oxide (Li$_2$O), lithium methoxycarbonyl (LiOCH$_3$), and dilithium ethylene glycol dicarbonate ([CH$_2$OCO$_2$Li]$_2$, referred to as LiEDC). The heat of dissolution for each salt in DMC was calculated by molecular dynamics

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(MD) simulations and was compared with the experimental results from the solubility measurements where possible. The heat of dissolution for each salt in ethylene carbonate (EC) was also calculated for comparison.

All of the lithium salts studied here have been experimentally observed, and the reactions to produce the salts have been proposed. The reactions associated with the production of lithium salts are summarized below, where LiPF₆ is used as the initial lithium salt:

\[
\begin{align*}
\text{LiPF}_6 & \rightarrow \text{LiF} + \text{PF}_3 \\
\text{LiPF}_6 + \text{H}_2\text{O} & \rightarrow \text{LiF} + \text{POF}_3 + 2\text{HF} \\
(\text{CH}_2\text{O})_2\text{C} = \text{O} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{CH}_2 = \text{CH}_2 \\
\text{Li}_2\text{CO}_3 + \text{LiPF}_6 & \rightarrow 3\text{LiF} + \text{POF}_3 + \text{CO}_2 \\
\text{Li}_2\text{CO}_3 + 2\text{HF} & \rightarrow 2\text{LiF} + \text{CO}_2 + \text{H}_2\text{O} \\
2\text{CO}_2 + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{CO} \\
\text{H}_2\text{O} + \text{Li}^+ + \text{e}^- & \rightarrow \text{LiOH} + \frac{1}{2}\text{H}_2 \\
\text{LiOH} + \text{Li}^+ + \text{e}^- & \rightarrow \text{Li}_2\text{O} + \frac{1}{2}\text{H}_2 \\
\text{Li}_2\text{CO}_3 + 2\text{HF} & \rightarrow 2\text{LiF} + \text{CO}_2 + \text{H}_2\text{O} \\
\text{ROCO}_2\text{R} + \text{Li}^+ + \text{e}^- & \rightarrow \text{LiROCO}_2\text{R} + \frac{1}{2}\text{R}_2 \\
2\text{LiOCHO}_2\text{R} + \text{H}_2\text{O} & \rightarrow \text{Li}_2\text{CO}_3 + 2\text{ROH} + \text{CO}_2 \\
\text{ROCO}_2\text{R} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow \text{Li}_2\text{CO}_3 + \text{R}_2 \\
\text{LiO}_2\text{CO}_2\text{R} + \text{HF} & \rightarrow \text{LiF} + \text{ROH} + \text{CO}_2 \\
\text{ROCO}_2\text{R} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow 2\text{LiOR} + \text{CO} \\
2(\text{CH}_2\text{O})_2\text{C} = \text{O} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow (\text{CH}_2\text{O}_2\text{C}_2\text{Li})_2 + \text{CH}_2 = \text{CH}_2 \\
(\text{CH}_2\text{O}_2\text{C}_2\text{Li})_2 & \rightarrow \text{Li}_2\text{CO}_3 + \text{CH}_2 = \text{CH}_2 + \text{CO}_2 + \frac{1}{2}\text{O}_2 \\
\text{Li}_2\text{CO}_3 & \rightarrow \text{Li}_2\text{O} + \text{CO}_2 \\
\text{O}_2 + 4\text{Li}^+ + 4\text{e}^- & \rightarrow 2\text{Li}_2\text{O} \\
(\text{CH}_2\text{O}_2\text{C}_2\text{Li})_2 & \rightarrow 2\text{Li}^+ + 2\text{e}^- \rightarrow (\text{LiCO}_2\text{Li})_2 + (\text{CH}_2\text{O}_2\text{Li})_2 \\
2\text{CH}_2\text{O}_2\text{CO}_2\text{Li} + 2\text{Li}^+ + 2\text{e}^- & \rightarrow (\text{LiCO}_2\text{Li})_2 + 2\text{Li}_2\text{OCH}_3
\end{align*}
\]

where R is either CH₃ or CH₂H₅; thus, R₂ can be either CH₃H₄ or C₄H₈O₂, respectively. As can be seen in the above reactions, some lithium salts are products of direct reductions of organic solvents, while the others are decomposition products, often further consuming lithium. Some reactions produce water, which can set off additional salt decomposition steps. Many of the above reactions are interdependent, mostly in equilibrium. This suggests a complex series of cascading reactions at the SEI during storage. We attempt to address the role of the salt dissolution in the SEI film formation reactions and the SEI film components and the compositions as a whole.

### Experimental

LiF, Li₂CO₃, Li₂C₂O₄, and LiOH were purchased from Aldrich, while LiOCO₂CH₃ and LiOCO₂C₂H₅ were purchased from Organoem (Coventry, RI), which synthesized them according to the procedure of Dedryvère et al. DMC was purchased from Ferro Corp. (Cleveland, OH). The chemicals were used as received. Initially, we attempted to measure the solubility of the salts by dissolving them in DMC and measuring the Li concentration with an inductively coupled plasma (ICP) or with flame ionization. However, a weak Ar line that overlapped the Li line in the ICP interfered with the ICP measurement, while the flame ionization measurements were not sufficiently reproducible. Instead, solubilities of the salts in DMC were determined by measuring ion conductivities using a temperature-compensated Oakton Acorn CON-6 conductivity meter from Oakton Instruments (Vernon Hills, IL). This device is designed for water solutions, not DMC solutions, so we followed the following procedure. All chemical operations were carried out in a glove box filled with high quality Ar gas. Excess salt was put in a 10 mL vial that was then filled with DMC. The vial was sealed, removed from the glove box, and shaken for 10 h at ambient temperature under ambient pressure to ensure that the salt–DMC solution was saturated. Shaking the vial was extended to 1 week, but no difference in the final results was observed. The vial was transferred back into the glove box where it was unsealed. The supernatant liquid was then drawn through a 2 μm filter, trapping any undissolved salt. The saturated solution that passed through the filter was left to evaporate, leaving behind the salt that had been dissolved. This recovered salt was then removed from the glove box and dissolved in a measured volume of distilled and deionized water, in which all of the salts were highly soluble. The concentration of the salt was determined by measuring the ionic conductivity of the salt aqueous solution and comparing that result to a set of calibration curves. The calibration curves were generated by dissolving a known mass of the same salt into distilled and deionized water and measuring the resulting conductivity. We then successively diluted the salt aqueous solution by factors of 2 until the conductivity meter reading was about 1 μS cm⁻¹, near the lower limit for the meter. We repeated three measurements for each salt to present the mean solubility and one standard deviation from the mean. The temperature was maintained at 25°C during the measurements. The concentration in water was then converted to the original concentration in DMC. Measurements for Li₂O and LiOCH₃ could not be carried out because they reacted chemically with water. To examine a possibility that highly soluble impurities in the salts could have been responsible for the conductivity signals, separate experiments were run. First, each salt was presoaked and shaken in excess DMC for about 10 h. The supernatant liquid with possible impurities was then discarded, and the remaining undissolved salt was used for the solubility measurements according to the above procedure. The results with and without the presoaking procedure agreed to within experimental error.

XPS is a common tool for the electrode surface chemistry analysis; yet, the findings vary among research groups. It is plausible that ex situ electrode treatments before examination such as rinsing with a solvent may have altered the surface characteristics in some cases. Therefore, we examined negative electrode surfaces before and after soaking for 1 h in DMC to search for this effect. To avoid using a laboratory-specific SEI film, we examined negative electrodes taken out of a disassembled LM40 laptop battery pack manufactured by LGChem, model LR1865AH without any surface pretreatment. Details of the material components used in the cell are not known though we suspect that the artificial graphite was used for the negative electrode. After being fully charged, the battery cell was disassembled in a glove box under Ar atmosphere to extract the negative electrode. It was carried under argon to a Kratos Axis Ultra spectrometer with a monochromatized Al Kα radiation (hv = 1486 eV). The spectrometer was calibrated using the photoemission line Ag 3d₅/₂. The core spectra were recorded with a 20 eV constant pass energy. No charge neutralization was used. Peak assignments were made according to the previous studies. We repeated this procedure several times starting from different batteries and analyzed representative spectra. All measurements were conducted at ambient temperature.

### Computational

The lithium salt examined by computational simulations included, in addition to the salts subjected to the experimental mea-
The chemical structures of all molecules studied: (a) lithium fluoride, (b) lithium oxide, (c) lithium hydroxide, (d) lithium methoxide, (e) lithium carbonate, (f) lithium methyl (R = CH₃) or ethyl carbamate (R = C₂H₅), (g) di lithium ethylene glycol dicarbonate, (h) lithium oxalate, (i) lithium methyl carbonate, or ethyl carbonate, (j) EC.

Figure 1. The chemical structures of all molecules studied: (a) lithium fluoride, (b) lithium oxide, (c) lithium hydroxide, (d) lithium methoxide, (e) lithium carbonate, (f) lithium methyl (R = CH₃) or ethyl carbamate (R = C₂H₅), (g) diliethylyl ethylene glycol dicarbonate, (h) lithium oxalate, (i) lithium methoxide, or ethyl carbonate, (j) EC.

Figure 2. The thermodynamic cycle used for the calculations of the heat of sublimation ($\Delta H_{\text{sub}}$), the heat of solution ($\Delta H_{\text{sol}}$), and the heat of dissolution ($\Delta H_{\text{diss}}$).

Figure 3. (Color online) The atomic charges for the salts, not shown for the hydrogen atoms, used in computer modeling. (a)–(j) show the same molecules as those in Fig. 1. The structures displayed were taken from the optimized structures by energy minimization by DFT calculations. See the text for details.
which required longer simulations, 2 ns, especially in solid, due to its larger molecular size. The average value from several runs was taken for the potential energy used for the heat calculations. The long range interactions, both van der Waals and electrostatic interactions, were treated by the Ewald summation.39 The crystal structures were used for the solids when the crystallographic data were available. For LiOH,51 LiF,52 LiCl,53 Li2CO3,54 and Li2O,55 the crystal structure was used, while amorphous structures were generated for the others using the Amorphous Cell software package.56

Results and Discussion

Figure 4 shows a log–log plot of the calibration curves for each salt in water used to determine the salt concentration from the ion conductivity measurements. The average slope for all of the curves was plotted against the logarithm of the salt concentration for each salt. The unit for the conductivity was mS cm−1. The unit for the concentration was mg salt per 20 mL water. All the measurements were conducted at 25°C.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** The calibration curves used for the determination of the salt concentration in water: LiOH (●), Li2CO3 (○), LiF (■), (LiCO2)2 (△), LiC2H4CO3 (●), and LiCH3CO3 (◊). The logarithm of the ion conductivity was plotted against the logarithm of the salt concentration for each salt. The unit for the conductivity was mS cm−1. The unit for the concentration was mg salt per 20 mL water. All the measurements were conducted at 25°C.

The increased peaks both around 290 eV in the C 1s spectrum and at 533 eV in the O 1s spectrum,34 and organic salts at around 531 eV in the O 1s spectrum.34 After soaking in DMC, the C 1s peak at around 285 eV, due to the graphite carbon, was enhanced, suggesting that the SEI film dissolution exposed the graphite surface.

Table I summarizes the results from the solubility measurements for the salts in DMC. In the table, the solubility is expressed in terms of both ppm (mass/mass) and molarity M (mol L−1) of each salt in DMC. It is well accepted that the solubility of a solute in a solvent is related to the similarity between their molecular structures.56 As expected, the two organic salts, LiOCO2CH3 and LiOCO2C2H5, dissolved more than other salts. The former was more soluble than the latter in DMC because of the closer structural similarity of the former to DMC than the latter. The dilithium salts, Li2CO3 and (LiCO2)2, were the least soluble among them. The salts were likely to dissolve in the order of LiOOCO2C2H5 > LiOOCO2C2H5 > LiOH > LiF > (LiCO2)2 > Li2CO3 in terms of M. Assuming that a salt constitutes 10% of a 50 mm thick SEI film having a total of 1 cm² of surface area, a somewhat arbitrary assumption, the volume of pure DMC required to dissolve Li2CO3 is only 77.5 μL. This simple estimate is consistent to the finding by Abraham et al.11 and Du Pasquier et al.6 though the individual components in the SEI film were not reported in their work. Still, the above estimate is based on a very rough assumption. Kang et al.53 and West et al.58 suggested that the SEI can also be induced to dissolve via an electrochemical process.

Table I. The solubility of various lithium salts in DMC. The measurements were conducted at 25°C.

<table>
<thead>
<tr>
<th>Salt</th>
<th>ppm</th>
<th>M (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2CO3</td>
<td>6 ± 1</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>(LiCO2)2</td>
<td>9 ± 5</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>LiF</td>
<td>4 ± 1</td>
<td>1.7 ± 0.4</td>
</tr>
<tr>
<td>LiOH</td>
<td>14 ± 8</td>
<td>6.8 ± 3.6</td>
</tr>
<tr>
<td>LiOOCO2C2H5</td>
<td>47 ± 9</td>
<td>5.3 ± 1.0</td>
</tr>
<tr>
<td>LiOCO2CH3</td>
<td>73 ± 30</td>
<td>9.6 ± 3.9</td>
</tr>
</tbody>
</table>

Table II lists the heat of dissolution for each salt obtained from MD simulations, along with the heat of sublimation and the heat of solution in DMC and EC. LiEDC has a large exothermic heat of dissolution, while LiOOCO2C2H5 shows a moderately exothermic heat. Our previous work predicted the heat of dissolution for LiEDC...
to be endothermic. However, the force field used in the previous work was different from the current one and never compared against any experimental data. The heat of dissolution for the rest is either exothermic or endothermic, depending on the salt or the solvent. The salts tend to dissolve somewhat more in EC than in DMC, in general, due to the higher polarity of EC than DMC. The order in which the heat of dissolution becomes more endothermic in DMC coincides well with the order of solubility in terms of the molarity obtained from the experiment, at least for those for which the experimental data were obtained. An exception is LiOH, which is predicted to be more soluble than LiOCO₂C₂H₅ though a qualitative experimental data were obtained from the experiment, at least for those for which the experimental data were obtained. An exception is LiOH, which is predicted to be more soluble than LiOCO₂C₂H₅ though a qualitative agreement is still met within the experimental errors, as shown below.

Figure 6 plots the ratio of the molarity in the natural logarithmic scale (∆ln(M₁/Mₙ)) against the difference in the heat of dissolution between the salts divided by RT(∆Hₒ élevé₁ - ∆Hₒ élevéₙ)/RT, where 1 and n refer to LiOCO₂C₂H₅ and any other salt, respectively. ∆ln(M₁/Mₙ) is expressed by a bar including the experimental errors in the figure. The relative positions of -[∆Hₒ élevé₁ - ∆Hₒ élevéₙ])/RT with the statistical errors shown by the horizontal line fall within the experimental errors of the corresponding ∆ln(M₁/Mₙ), demonstrating the relative solubility of the experimental data reasonably reproduced by the calculations. Both experiments and calculations show Li₂CO₃ as the least soluble salt in DMC. A thin film of sputtered Li₂CO₃ has been used as a passivation film on the negative electrode surface to prevent electrolyte decompositions. Crystal structures were not used for all the salts in the simulations because crystallographic data were available only for LiOH, LiF, (LiCO₂)₂, Li₂CO₃, and Li₂O. Instead, amorphous structure forms were used for other salts. The effect of not using a crystal structure on the heat of dissolution was examined for those salts for which the crystal structure is known. For amorphous simulations, to avoid having a system stuck in a shallow potential energy well, the cell was first heated to 600 K and then gradually cooled to 298 K; this was followed by a 1–2 ns simulation at the same temperature. For LiOH, LiF, (LiCO₂)₂, Li₂CO₃, and Li₂O, the values of the heat of dissolution obtained from such amorphous simulations were 1.24, 7.45, 8.49, 23.94, and 80.02 kcal mol⁻¹, respectively. The differences from those obtained from the crystal simulations ranged from 0.14 kcal mol⁻¹ for LiOH to 37.38 kcal mol⁻¹ for Li₂O. Yet, the order in the heat of dissolution either in DMC or EC was not altered. Some studies have found amorphous regions in SEI films.

Experimental data for a direct comparison to the calculations are limited. Table III summarizes the comparison with the available literature values, the heat of vaporization for DMC and EC,

### Table II. The Heat of Sublimation, the Heat of Solution, and the Heat of Dissolution for Various Lithium Salts (kcal mol⁻¹) (obtained as average over 1 ns MD simulations at 25°C).

<table>
<thead>
<tr>
<th>Salt</th>
<th>ΔHₛₒᵇ</th>
<th>ΔHₜₒ</th>
<th>ΔHₒᵈₚ</th>
<th>ΔHₛₒᵇ</th>
<th>ΔHₜₒ</th>
<th>ΔHₒᵈₚ</th>
<th>LiO⁻</th>
<th>LiCHO₃</th>
<th>LiOH⁺</th>
<th>LiOCO₂C₂H₅</th>
<th>LiOCO₂CH₃</th>
<th>LiEDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>98.97</td>
<td>79.57</td>
<td>83.01</td>
<td>62.26</td>
<td>50.47</td>
<td>95.50</td>
<td>52.24</td>
<td>49.02</td>
<td>148.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>-55.72</td>
<td>-66.06</td>
<td>-71.26</td>
<td>-51.74</td>
<td>-45.94</td>
<td>-93.82</td>
<td>-50.44</td>
<td>-52.38</td>
<td>-169.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LiCO₂)₂</td>
<td>42.66</td>
<td>12.93</td>
<td>11.16</td>
<td>9.92</td>
<td>3.94</td>
<td>1.10</td>
<td>1.21</td>
<td>-3.95</td>
<td>-21.65</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The crystal structure was used for the simulations. See Ref. 51-55.
also the heat of sublimation for LiF,61 all of which are reasonably reproduced by the calculations. One can argue that the errors associated with both the heat of sublimation and the heat of solution by our calculations may be canceled out because the heat of dissolution is a summation of $\Delta H_{\text{sub}}$ and $\Delta H_{\text{sol}}$. However, the comparison of $\Delta H_{\text{sub}}$ with the experimental data does not support the claim, at least for LiF. Still, the calculations are only meant to be compared to the experiments qualitatively because they only give the heat of dissolution and the entropy is difficult to calculate for the systems studied. We believe, however, that the relative discussion among the salts studied is still relevant, judging from the plots in Fig. 4.

Lithium diffusion in each salt solid was also examined using the results from computer simulations. The self-diffusion coefficient, $D$, of the lithium ion can be calculated by the following equation

$$D = \lim_{t \to \infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t}$$  \hspace{1cm} \text{[25]}$$

Figure 6. (Color online) The natural logarithm of $M_i/M_0$, $\ln(M_i/M_0)$, the lower axis, plotted against $-\left(\Delta H_{\text{diss}}(1) - \Delta H_{\text{diss}}(n)/RT\right)$, the upper axis, for the salts where 1 refers to LiOCOCH$_3$, while $n$ refers to any other salt. The wide bar represents $\ln(M_i/M_0)$ with the experimental error, while the perpendicular line shows $-\left(\Delta H_{\text{diss}}(1) - \Delta H_{\text{diss}}(n)/RT\right)$, with the statistical error shown by a thin horizontal line.

Table III. Comparisons of calculations and experimental data. The experimental data are in the parentheses. The temperatures measured and calculated for DMC, EC, and LiF were 25, 150, and 25°C, respectively.

<table>
<thead>
<tr>
<th></th>
<th>DMC</th>
<th>EC</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of vaporization, kcal mol$^{-1}$</td>
<td>9.47 ± 0.48 (9.26°)</td>
<td>12.04 ± 0.42 (13.45°)</td>
<td>—</td>
</tr>
<tr>
<td>Heat of sublimation, kcal mol$^{-1}$</td>
<td>—</td>
<td>—</td>
<td>62.26 (64.59°)</td>
</tr>
</tbody>
</table>

$^a$ Reference 59.
$^b$ Reference 60.
$^c$ Reference 61.

Table IV. The self-diffusion coefficient for the lithium salt solid (obtained from mean-square displacements of the lithium ion calculated from MD simulations performed at 25°C, according to Eq. 25).

<table>
<thead>
<tr>
<th>Salt</th>
<th>$D \times 10^5$ cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O</td>
<td>1.6 × 10$^{-5}$</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>9.0 × 10$^{-4}$</td>
</tr>
<tr>
<td>(LiCO$_2$)$_2$</td>
<td>4.6 × 10$^{-3}$</td>
</tr>
<tr>
<td>LiF</td>
<td>3.5 × 10$^{-5}$</td>
</tr>
<tr>
<td>LiOH</td>
<td>1.1</td>
</tr>
<tr>
<td>LiOOC$_2$CH$_3$</td>
<td>1.3 × 10$^{-3}$</td>
</tr>
<tr>
<td>LiOOC$_2$CH$_3$</td>
<td>0.3</td>
</tr>
<tr>
<td>LiEDC</td>
<td>0.7</td>
</tr>
<tr>
<td>LiF</td>
<td>0.8</td>
</tr>
</tbody>
</table>

$^a$ The crystal structure was used for the simulations. See the text for the references.
During storage or cycling, some components studied here have been proposed that LiEDC can be decomposed into Li$_2$CO$_3$ as well. During storage, the reduction reactions may produce more organic salts under a very low current, which further promotes dissolution into the electrolyte, triggering more reactions with the electrolyte. It follows that during storage, the SEI film undergoes cycles of dissolution into the electrolyte and formation of the film on the graphite surface through further reactions with the electrolyte. The increased impedance from the SEI during aging has been reported. This model, however, is not meant to describe anything on the film thickness, but rather on the film composition.

Because the SEI film is likely to be phase-separated between the crystal and the amorphous phases and also because it undergoes a continuous transformation of the compositions through salt dissolutions, reductions, and decompositions, the film may lack a fundamental thermodynamic stability. The increased impedance from the SEI during aging has been reported.

Figure 7 summarizes the reactions comprising some of Eq. 1-20, which may occur at the active material surface or in the SEI film during the first charge cycle and the subsequent storage. Not all equations are included due to the space limitation. Figure 7 is not intended to accurately describe the reactions in the SEI film. Rather, it is to illustrate schematically the cascading reactions of lithium salts set off by the reduction reactions of the electrolyte while consuming more lithium ions, going further down the successive reactions. Most of the cascading lithium salt reactions end at LiF, Li$_2$O, and (Li$_2$CO$_3$)$_2$, with many reactions leading to LiF. LiF crystallites have been found on the graphite surface in the LiPF$_6$ electrolyte after storage.

In the absence of these decomposition reactions of lithium salts, the lithium ions would be simply recycled through the dissolution of lithium salts into the electrolyte, and capacity loss would not occur through this mechanism. Likewise, without dissolution of the salts into the electrolyte, the succession of salt decompositions would eventually come to cease, as the availability of reactants becomes less, thus reducing the rate of capacity fading. Yet, the capacity fade rate does not decline and may even grow in some cases during storage, though a loss of integrity of the cells is a possibility. Furthermore, the growth of SEI films has also been observed by XPS, scanning electron microscopy analysis, and other means. We propose that it is the dissolution of some of the salts and the subsequent reduction of the electrolyte that drive the cascade decomposition reactions to a significant degree by supplying the reactants for the salt decompositions, consuming lithium continuously, and contributing to more SEI film growth.

During storage, the reduction reactions may produce more organic salts under a very low current, which further promotes dissolution into the electrolyte, triggering more reactions with the electrolyte. It follows that during storage, the SEI film undergoes cycles of dissolution into the electrolyte and formation of the film on the graphite surface through further reactions with the electrolyte. The increased impedance from the SEI during aging has been reported. This model, however, is not meant to describe anything on the film thickness, but rather on the film composition.

Because the SEI film is likely to be phase-separated between the crystal and the amorphous phases and also because it undergoes a continuous transformation of the compositions through salt dissolutions, reductions, and decompositions, the film may lack a fundamental thermodynamic stability. The increased impedance from the SEI during aging has been reported. This model, however, is not meant to describe anything on the film thickness, but rather on the film composition.
only based on the SEI characteristics on the anode side. The imped-
ance of the SEI on the cathode increases during storage.

Conclusion

The solubility of lithium salts, which are well-known individual SEI components, has been determined in DMC through ion conduc-
tivity measurements. Among the salts studied here, the order in
which the salt was likely to dissolve was LiOHC\textsubscript{2}CH\textsubscript{3} > LiOHC\textsubscript{2}C\textsubscript{2}H\textsubscript{4} > LiOH > LiF > (LiCO\textsubscript{2})\textsubscript{2} > Li\textsubscript{2}CO\textsubscript{3}. The or-
ganic salts were more likely to dissolve than the inorganic salts in
DMC. The heat of dissolution in both DMC and EC was also

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