Electrolyte additives are a promising route to stable solution chemistries needed for improved and next-generation lithium-ion cells. Yet the underlying chemistry remains unknown for most additives and additive blends in use. This work presents possible reaction pathways for solid-electrolyte interphase formation in lithium-ion cells from ethylene sulfate (DTD), prop-1-ene-1,3-sultone (PES) and the binary PES/DTD blend. Pathways are supported by theoretical calculations (density functional theory) and experimental results (electrochemistry, gas chromatography thermal detection conductivity, X-ray photoelectron spectroscopy, isothermal microlarometry). A hypothesis to understand the synergistic chemistry of the blend is proposed: Reduction of PES, the ‘primary additive’, at the negative electrode forms a nucleophile that reacts with electrophilic DTD, the ‘secondary additive’, to produce a passive solid-electrolyte interphase that inhibits direct reduction of DTD or the solvent. The results are further discussed in the contexts of future mechanistic studies, computational additive discovery, and the development of improved lithium-ion cell chemistry.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY,http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0181714jes] All rights reserved.
computational additive discovery. Therefore, the present work utilized the PCM, although future work is encouraged to refine upon this approach and improve our capability to model solvation behaviors.

**Lithium-ion cells.**—Dry (no electrolyte), vacuum-sealed LiNi0.5Mn0.3Co0.2O2 (NMC532)/graphite cells (with a capacity, C, of 1420 mAh) were received from LiFun Technology (Tianyuan, Zhuzhou, China). The cells were cut below the heat seal, dried under vacuum at 80 °C for 14 h, and then transferred to an argon-atmosphere glove box for filling. All solutions in this work used a 3:7 solvent blend, by mass, of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), as received from BASF (≥98%), and/or PES (Lianchuang Medical Chemistry Co., ≥98%), were added no more than 24 h before cell filling. The filled cells were sealed at ∼90 kPa using a compact vacuum sealer (MSK-115A, MTI Corp.) and immediately held at 1.5 V at room temperature (21–25 °C) to prevent Cu current collector corrosion during the 24 h wetting period that followed. Cells were then loaded into temperature-controlled boxes (40.0 ± 0.1 °C) and connected to a Maccor 4000 Series automated test system (Maccor Inc.).

The water content of PES was measured using a Mettler-Toledo C20 compact Karl Fischer titrator and the D0308 drying oven accessory. The amount of water in ~0.8 g of PES samples was indistinguishable from the background signal. The limit of detection for this setup is ~8 μg per sample, corresponding to an estimated water content of ≤10 ppm. Because its thermal instability, the water content of the DTD was not successfully evaluated by this method. H NMR measurements indicate that the DTD used in this work does also have a very low H2O content, although this method is not truly quantitative.

**In situ volume measurements.**—The volume of gas produced in pouch cells was measured using the “Measuring Archimedes’ Gas Expansion” (MAGE) apparatus, as described previously. Cells were filled, immediately loaded into a 4.0 ± 0.1 °C temperature-controlled box, and held at 1.5 V for 24 h to ensure proper wetting. The same temperature was used during the wetting and charge steps because it takes several hours to fully stabilize the temperature and mass measurements. The cells were then charged at 11 mA (C/20).

**Gas chromatography.**—Following room-temperature wetting, cells were charged at 11 mA (C/20) and at 40 °C to 2.4 V, 2.7 V, or 3.0 V, as indicated in the text and on the figures. A full formation charge was not performed as only the reaction products from the reduction of the additives were of primary interest. Cells were immediately moved to a brass chamber for gas extraction (described in Reference 56), and then injected into a Bruker 436-GC equipped with a Bruker thermal conductivity detector (GC-TCD). The extraction procedure and method parameters have been described previously.

**X-ray photoelectron spectroscopy.**—Following room-temperature wetting, cells were charged at 11 mA (C/20) and at 40 °C to 2.4 V, 2.7 V, or 3.0 V, as indicated in the text and on the figures. A full formation charge was not performed as only the reaction products from the reduction of the additives were of primary interest. Cells were immediately transferred to an argon-filled glove box at open circuit for disassembly. The negative electrodes were removed and rinsed with EMC to remove dried electrolyte. Samples were then transferred via a gastight apparatus to the spectrometer’s vacuum system, as described previously. Measurements were performed with a SPECS spectrometer equipped with a non-monochromatic Mg Kα X-ray source and a Phoibos hemispherical analyzer (pass energy = 20 eV). Preliminary and final survey scans were compared to ensure that no photochemical degradation was induced during analysis.

**Results and Discussion**

**Film-forming reactions of DTD.**—The differential capacity, i.e., dQ/dV plot of SEI formation in cells containing 0.0% (0.0 mmol)–8% (0.4 mmol) DTD. The features associated with DTD and EC reduction are indicated. (b) The charge associated with the DTD reduction feature is shown as a function of the total DTD added to the cell. Because the DTD reduction feature is convoluted with an unknown background, both the maximum (i.e., the total peak charge) and the minimum (i.e., the peak charge following a conservative background subtraction) are shown. The results overlay theoretical slopes of 1.0, 1.5, and 2.0 e−/per DTD molecule (dashed gray lines).

**Isothermal microcalorimetry.**—Following filling, cells were loaded into a TAM III calorimeter (TA Instruments) for isothermal microcalorimetry (IMC) measurements. Cells were wetted for 24 h at 1.5 V, during which the calorimeter temperature fully stabilized at 40.0 °C. The SEI was formed at 2 mA (C/110) from 1.5 V to 3.5 V. A full formation charge was not performed as only the reduction of the additives, which occurs below 3.5 V, was of primary interest. Details of the instrument and procedure have been described previously. The measurement uncertainty was less than ±1 μW, the instrument noise was ∼10 nW, and the drift from baseline was <0.5 μW.
solution were filled with just 0.6 g for these experiments. This approach has been previously applied to evaluate the reduction of additives in pouch cells (namely vinyl ethylene carbonate, VEC, pyridine boron trifluoride, PBF, and pyridine phosphorus pentafluoride, PPF). Because the reduction of DTD produces gas (discussed further below), the jelly rolls were clamped using soft rubber, which improved the experimental precision.

In contrast to the previous study of PBF and PPF, the reduction of DTD is convoluted with other ‘background’ processes in the differential capacity plot (Figure 1a). This overlap is most significant at low DTD concentrations, which limits the accuracy of the slope evaluation. Therefore, the question of how best to deal with the background arises. However, it is unknown whether the reduction of DTD inhibits or shifts the onset potential of the background reduction processes. Therefore, Figure 1b shows both the total DTD reduction peak charge (i.e., without any subtraction) and this value minus the charge measured from the 0% DTD cells (i.e., following background subtraction). This particular experiment was repeated several times and various integration methods were tested, with some variability in the results, indicating low precision. Nonetheless, the results consistently suggest that either 1.5 or 2.0 electrons are required for the reduction of each DTD molecule. This information is valuable because it is inconsistent with 1.0– or 0.5-electron reduction pathways that have been proposed previously. It is, however, difficult to make any strong conclusions from this experimental data alone, regarding the exact number of electrons transferred during DTD reduction.

At higher (i.e., >1.2%) DTD concentrations, the peak area reaches a maximum. This indicates that the reduction of DTD is self-limiting, presumably due to SEI growth. However, this behavior slightly decreases but does not fully prevent the reduction of EC at any concentration tested in this work, as noted above. This indicates that DTD cannot produce a fully passivating SEI when used as a singular additive.

The addition of DTD increases the volume of gas produced during cell formation. Therefore, in situ volumetric measurements were performed during SEI formation to examine the potential (or potentials) at which gas generation occurs (Figure 2). The results reveal that the electrochemical reduction of DTD leads to gas evolution prior to the onset of EC reduction. The cell voltage at which the gas is produced decreases as the additive concentration increases. The formation of bubbles at the graphite surface explains the increased noise in the dQ/dV plots at $E_{\text{cell}} > 2.5 \text{ V}$.

The electrochemical reduction of DTD in solution was then modeled by DFT (Scheme 1). The calculations predict that the first one-electron reduction step (1a) occurs at 1.49 V vs. Li/Li$^+$ (or at a cell voltage of ~2.0 V; see Supplemental Material), followed by a consecutive reduction step (1b) at 3.95 V (Table I). The DFT-calculated value for the second reduction potential corresponds to a large negative overpotential, $\eta = E-E^\ddagger = -2.46 \text{ V}$. Therefore, the prediction is that the second electron transfer will be fast and spontaneous. This is inconsistent with a previously proposed one-electron pathway for DTD reduction.

The gas composition in the cells was then analyzed by GC-TCD (Figure 3), which reveals that both gas evolution steps primarily produce ethylene. The small hydrogen peaks are attributed to the reduction of residual moisture in the cells and impurities in the DTD. The appearance of dimethyl carbonate (DMC) and diethyl carbonate (DEC) in the chromatogram in Figure 3a–3iii indicates that transesterification of the EMC has occurred between 2.7 and 3.0 V. Although these peaks were only observed in one of two replicate cells at 3.0 V, transesterification of the solvent is typically a sign of lithium alkoxide formation from EC or EMC reduction. This further supports the hypothesis that the initial DTD reduction does not fully passivate the graphite electrode against solvent decomposition.

The electrochemical reduction of DTD in solution was then modeled by DFT (Scheme 1). The calculations predict that the first one-electron reduction step (1a) occurs at 1.49 V vs. Li/Li$^+$ (or at a cell voltage of ~2.0 V; see Supplemental Material), followed by a consecutive reduction step (1b) at 3.95 V (Table I). The DFT-calculated value for the second reduction potential corresponds to a large negative overpotential, $\eta = E-E^\ddagger = -2.46 \text{ V}$. Therefore, the prediction is that the second electron transfer will be fast and spontaneous. This is inconsistent with a previously proposed one-electron pathway for DTD reduction.

Rather, the DFT calculation predicts a two-electron reduction pathway for DTD will be favored, where the experimentally measured reduction peak is ~0.2 V from the calculated potential for DTD. The gas composition in the cells was then analyzed by GC-TCD (Figure 3), which reveals that both gas evolution steps primarily produce ethylene. The small hydrogen peaks are attributed to the reduction of residual moisture in the cells and impurities in the DTD. The appearance of dimethyl carbonate (DMC) and diethyl carbonate (DEC) in the chromatogram in Figure 3a–3iii indicates that transesterification of the EMC has occurred between 2.7 and 3.0 V. Although these peaks were only observed in one of two replicate cells at 3.0 V, transesterification of the solvent is typically a sign of lithium alkoxide formation from EC or EMC reduction. This further supports the hypothesis that the initial DTD reduction does not fully passivate the graphite electrode against solvent decomposition.

The electrochemical reduction of DTD in solution was then modeled by DFT ( Scheme 1). The calculations predict that the first one-electron reduction step (1a) occurs at 1.49 V vs. Li/Li$^+$ (or at a cell voltage of ~2.0 V; see Supplemental Material), followed by a consecutive reduction step (1b) at 3.95 V (Table I). The DFT-calculated value for the second reduction potential corresponds to a large negative overpotential, $\eta = E-E^\ddagger = -2.46 \text{ V}$. Therefore, the prediction is that the second electron transfer will be fast and spontaneous. This is inconsistent with a previously proposed one-electron pathway for DTD reduction. Rather, the DFT calculation predicts a two-electron reduction pathway for DTD will be favored, where the experimentally measured reduction peak is ~0.2 V from the calculated potential for DTD. The gas composition in the cells was then analyzed by GC-TCD (Figure 3), which reveals that both gas evolution steps primarily produce ethylene. The small hydrogen peaks are attributed to the reduction of residual moisture in the cells and impurities in the DTD. The appearance of dimethyl carbonate (DMC) and diethyl carbonate (DEC) in the chromatogram in Figure 3a–3iii indicates that transesterification of the EMC has occurred between 2.7 and 3.0 V. Although these peaks were only observed in one of two replicate cells at 3.0 V, transesterification of the solvent is typically a sign of lithium alkoxide formation from EC or EMC reduction. This further supports the hypothesis that the initial DTD reduction does not fully passivate the graphite electrode against solvent decomposition.

The electrochemical reduction of DTD in solution was then modeled by DFT (Scheme 1). The calculations predict that the first one-electron reduction step (1a) occurs at 1.49 V vs. Li/Li$^+$ (or at a cell voltage of ~2.0 V; see Supplemental Material), followed by a consecutive reduction step (1b) at 3.95 V (Table I). The DFT-calculated value for the second reduction potential corresponds to a large negative overpotential, $\eta = E-E^\ddagger = -2.46 \text{ V}$. Therefore, the prediction is that the second electron transfer will be fast and spontaneous. This is inconsistent with a previously proposed one-electron pathway for DTD reduction. Rather, the DFT calculation predicts a two-electron reduction pathway for DTD will be favored, where the experimentally measured reduction peak is ~0.2 V from the calculated potential for DTD. The gas composition in the cells was then analyzed by GC-TCD (Figure 3), which reveals that both gas evolution steps primarily produce ethylene. The small hydrogen peaks are attributed to the reduction of residual moisture in the cells and impurities in the DTD. The appearance of dimethyl carbonate (DMC) and diethyl carbonate (DEC) in the chromatogram in Figure 3a–3iii indicates that transesterification of the EMC has occurred between 2.7 and 3.0 V. Although these peaks were only observed in one of two replicate cells at 3.0 V, transesterification of the solvent is typically a sign of lithium alkoxide formation from EC or EMC reduction. This further supports the hypothesis that the initial DTD reduction does not fully passivate the graphite electrode against solvent decomposition.

The two-electron electrochemical reduction of DTD follows a two-step pathway.
Table I. Calculated and experimental reduction potentials for Scheme 1.

|          | E° (V vs. Li/Li⁺) |
|----------|------------------|
|          | Calc. a          | Expt.            |
| (1a)     | 1.49             | ~1.3 a, 1.4 b    |
| (1b)     | 3.95             | ≥ 1.3 a          |

aThis work; assumes ENMC532 ~3.5 ± 0.1 V vs. Li/Li⁺ (See Supplemental Material).
bRef. 66.

(1a). This is also consistent with the experimental results in Figure 1b, which indicate that the pathway is either 1.5 or 2.0 electrons per DTD molecule. The authors note that they were unable to propose any plausible reaction pathways that involve three electrons for every two DTD molecules, although kinetic competition with the subsequent pathway (2d) would give a deviation to less than 2.0 electrons per DTD (see below). The final product, LiO₂SOCH₂CH₂OLi, is here abbreviated Li₂DTD.

The decomposition reaction (2a) of Li₂DTD into lithium sulfate and ethylene gas was then modeled by DFT. Although the reaction is predicted to be spontaneous, the latency between the onset of DTD reduction and gas evolution in Figures 1 and 2 suggests that it does not occur during the initial stage of SEI formation, likely due to slow kinetic parameters. Therefore, the alternate reactions of Li₂DTD with EC (2b), EMC (2c), and DTD (2d) were also modeled. The chemical reaction of reduced additives with solvent components during SEI formation has been discussed previously for other additives.12,15 Many of these reactions are spontaneous, as summarized in Table II. Such thermodynamic calculations are useful to rule out those reactions that are not spontaneous, i.e., reactions (2b2), (2c3), and (2c4). However, they do not provide any insight into the kinetics of the remaining spontaneous reactions. Therefore, the DFT calculations in this article are complemented with further experimental work, to look for the proposed reaction products.

Most of the hypothetical reactions in Scheme 2 produce organic lithium sulfite esters (i.e., they contain the R-OSO₂Li functional group). Although the solubility of these compounds is unknown, they may become components of the SEI on the negative electrode. To look for the presence of these compounds, SEI formation was stopped at the three cell voltages (2.4, 2.7 and 3.0 V) indicated in Figure 1b and then XPS surface analysis of the graphite electrodes was performed (Figure 4).

Trace amounts of sulfur were measured on the graphite electrode surface as-received (Figure 4a) and from DTD-free cells charged to 2.7 V, which is just before the onset of EC reduction (Figure 4b). The position of the S 2p½ peak (169.7 eV) matches the expected binding energy for inorganic and organic sulfate species (such as DTD).60,67

In DTD-containing cells, a small amount of sulfur is observed on the graphite surface in cells charged to 2.4 V, which is before the onset of DTD reduction (Figure 4c).

Table II. Calculated reaction energies for Scheme 2.

|          | ∆G° eV | ∆G° kJ mol⁻¹ | ∆H° eV | ∆H° kJ mol⁻¹ |
|----------|--------|--------------|--------|--------------|
| (2a)     | −1.49  | −144         | −1.01  | −97          |
| (2b1)    | −0.64  | −62          | −1.04  | −101         |
| (2b2)    | 0.39   | 38           | 0.03   | 3            |
| (2c1)    | −0.82  | −79          | −0.68  | −65          |
| (2c2)    | −0.79  | −77          | −0.68  | −66          |
| (2c3)    | 0.29   | 28           | 0.43   | 42           |
| (2c4)    | 0.29   | 28           | 0.44   | 43           |
| (2d)     | −1.46  | −141         | −1.83  | −177         |

Figure 4. S 2p½ binding energy region of the X-ray photoelectron spectra (XPS) of the negative electrode surface.
of DTD reduction (Figure 4c). This sulfur is likely due to adsorbed DTD that resisted the gentle rinsing with EMC used in this work. At 2.7 V, the intensity of the sulfur peak is much greater (Figure 4d). The position of the S 2p3/2 peak (169.6 eV) is again a match for inorganic and organic sulfate species. This supports the formation of an SEI that contains one or more of the organic sulfate esters proposed in Scheme 2.

There is an additional group of weak peaks centered at ~161 eV (Figure 4d). This feature has previously been observed on the surface of graphite electrodes taken from DTD-containing cells and was attributed to Li2S.68 However, it is here suggested that this spurious feature is merely an artifact from using a non-monochromatic Mg X-ray source. The Mg Kα1 and Kα2 peaks are positioned 8.5 eV and 10.1 eV below the Mg Kα3/Kα4 peak, have 9.1% and 5.1% of the intensity of the Kα3/Kα4 peak, respectively, and have the same full-width at half maximum (FWHM) as the Kα3/Kα4 peak.69 When satellite peaks were included in the fitting procedure with these fixed parameters (Figure 4d), they were found to be a match for the experimental feature at ~161 eV. The slight baseline mismatch in the range 164–167 eV is due, in part, to the contributions of the weak Mg Kα3 emission, centered 4.6 eV below the Kα3/Kα4 peak (on the BE scale).69 Therefore, it is important to include the α3 and α4 peaks in the fitting procedure when examining this BE region if the available spectrometer is not equipped with a monochromatic source.

At 3.0 V, there is an S 2p3/2 peak at 169.9 eV, again attributed to inorganic or organic sulfate species (Figure 4e). Relative to the 2.7 V sample, the fitted peak positions are unchanged, although the peak intensities are slightly greater. This may indicate that DTD reduction continues, albeit at a slower rate, throughout the EC reduction region.

It has recently been reported how isothermal microcalorimetry (IMC) measurements and DFT calculations may be combined to evaluate proposed SEI formation reactions in lithium-ion cells.13,64 Therefore, the proposed pathways in Schemes 1 and 2 were further studied by performing concurrent electrochemical SEI formation and IMC heat flow experiments. In Figure 5, the experimentally measured heat flow of SEI formation in a DTD-containing cell is compared to the predicted heat flow for the two-electron reduction of DTD in Scheme 1, followed by the reactions in Scheme 2. The length (in mA h) of the predicted heat flow curves is a calculated value based on the amount of DTD added to the cell and the assumption of a 2 e–/DTD reaction (see Figure 1b).

Because this application for IMC and DFT is still quite new, it is prudent to assume a large uncertainty margin. Nonetheless, the results support that the dominant SEI reactions in DTD-containing cells are the decomposition of Li2DTD (2a) and the reaction of Li2DTD with EC (2b1) and/or DTD (2d). It is noted that this latter reaction would result in a smaller charge capacity because the overall pathway is 1 e–/DTD. Therefore, the most likely pathways, based on the IMC/DFT results, are (2a) and (2b1). The MAGE results suggest that gas evolution during DTD reduction is limited and, hence, that the (2b1) reaction pathway with EC is the dominant one. Future research is encouraged to more thoroughly develop the application of IMC to SEI formation and chemical pathway studies.

To further test this hypothesis, cells were prepared with 4% DTD and the amount of EC in the solvent was varied (Figure 6). With decreasing EC concentration, there is an increasing amount of gas evolution associated with the DTD reduction peak. Although it is noted that changes in the solvent properties could also affect the chemistry, it is known that the dielectric properties of 0% EC and 3% EC in EMC are very similar.42 Moreover, the onset of EMC reduction does not occur until higher cell voltages, typically Ec > 3.0 V.59 Therefore, the result supports the proposed reaction of Li2DTD with EC from solution.

**Film-forming reactions of PES.**—Having established reaction pathways for DTD, this work now considers PES, for which SEI reactions have previously been suggested.14,15 This serves as an introduction to examine the PES/DTD binary additive blend as an example of two synergistic, film-forming additives. In PES-containing cells, it has previously been proposed that SEI formation begins with the electrochemical reduction of the PES at the graphite surface (Scheme 3, Table III), followed by the reaction of the reduced Li2PES species with EC (4a), EMC (4b), or unreduced PES (4c).15,61 Unlike DTD, the initial reduction of PES greatly suppresses EC reduction (Figure 7a).
and gas evolution (Figure 7b) at higher cell voltages. The reduction peak is also well-separated from any significant background reduction processes. From the charge associated with PES reduction at various PES concentrations, it is here confirmed that SEI formation indeed follows a two-electron pathway, as proposed by Self et al. (Figure 7c). Moreover, PES reduction is self-limiting at higher concentrations. These factors offer strong evidence that the PES-derived SEI is an effective passivation layer.

It is noted that the present work re-calculated the reduction potentials of PES using a different hybrid functional (M062X rather than B3LYP) and a larger basis set (6–311++G(d,pf) rather than 6–311++G(d,p)), with slightly different results (0.75 V vs. Li/Li$^+$ cf. 0.9 V vs. Li/Li$^+$). Whereas the methods in the present work were expected to provide more accurate values, the previous results are a better match with the measured onset of PES reduction. This highlights the challenge that there is an inherent uncertainty in DFT calculations for electrochemical reactions in lithium-ion cells. Whereas a calculation error of a few hundred millivolts is quite small, by DFT standards, it poses a significant challenge for purely computational studies into electrolyte additive chemistry. However, when paired with all the available experimental data, the calculation results nonetheless support the reaction pathways posed in Ref. 15. It is therefore important that future research does not rely upon DFT calculations alone, but rather should make efforts to correlate predictions with experimental data.

From the interpretation presented here for the formation data in DTD-containing (Figure 1) and PES-containing (Figure 7) cells, one may conclude that PES is more effective at passivating the graphite electrode. However, it is thus far unclear from this discussion why cells prepared with both PES and DTD perform differently than those prepared with PES alone. The ability to understand and, ultimately, to predict the synergistic behavior of two or more additives would be very beneficial for the development of the stable solution chemistries that are needed for high-voltage and fast-charging batteries.

**Synergistic film-forming reactions of the binary PES/DTD Blend.**—From the differential capacity plots in Figure 7a, it appears that PES reduction is nearly complete before the onset of DTD reduction. Because the PES reduction leads to the formation of a passive SEI on the negative electrode surface, it also appears that the electrochemical reduction of DTD does not occur. These predictions are in agreement with the similarities of the differential capacity plots between cells that contained only PES and those that contained both additives (Figure 7a). However, this result contradicts the calculated potentials for PES and DTD reduction, 0.8 V vs. Li/Li$^+$ and 1.5 V vs. Li/Li$^+$, respectively. Two possibilities may account for this contradiction. First, the kinetics of DTD reduction may be quite slow and therefore a significant overpotential, $\eta$, could be required to obtain an appreciable current $I$:

$$E = E^0 + \eta$$  \[1\]

The predicted heat flow in Figure 5 was calculated assuming a negligible overpotential (i.e., $\eta \approx 0$) due to the small applied current. However, if this is an incorrect assumption, then the calculated heat flow would underestimate the actual amount of heat released. For example, an excess heat flow of $\sim 0.4$ mW and an applied current of 2 mA corresponds to $\sim 0.2$ V overpotential. Alternatively, it is possible that the calculated standard potential is simply incorrect. In both cases, additional work is necessary before DFT may be used to correctly predict the sequential order in which additives are reduced during SEI formation.

Nonetheless, the experimental results strongly indicate that PES reduction occurs prior to DTD reduction during formation. Given that PES has been demonstrated to passivate the graphite electrode surface, it is unlikely that the DTD reduction reactions in Scheme 2 occur in cells that contain both PES and DTD. Rather, the participation of DTD in the SEI formation reactions may occur differently than when

![Scheme 3. The two-electron electrochemical reduction pathway of PES.\textsuperscript{15}](Image 305x369 to 547x717)

**Figure 7.** (a) Differential capacity (dQ/dV) and (b) in situ volume plots showing the effect of varying the PES and DTD concentrations on the electrochemical features associated with SEI formation and the associated gas evolution during SEI formation. (c) The relationship between the charge associated with the PES reduction peak ($E_{\text{cell}} \sim 2.3–2.6$ V) and the amount of PES added to the cell follows a $2 \, e^-/\text{PES}$ slope (dashed line) up to $\sim 0.05$ mmol PES. The charge associated with the first dQ/dV peak during SEI formation ($E_{\text{cell}} \sim 2.3–2.7$ V) is also shown for variable amounts of PES with 1% DTD.

**Table III. Calculated and experimental reduction potentials for Scheme 3.**

|   | Calc\textsuperscript{a} | Expt. |
|---|-------------------|------|
| (3a) | 0.75\textsuperscript{a}, 0.9\textsuperscript{b} | 1.15\textsuperscript{a}, 1.1\textsuperscript{b} |
| (3b) | 4.39\textsuperscript{a}, 4.3\textsuperscript{b} | $\geq 1.15\textsuperscript{a}$ |

\textsuperscript{a}This work; assumes $E_{\text{NMC532}} \approx 3.5$ V vs. Li/Li$^+$ (see Supplemental Material).

\textsuperscript{b}Ref. 15.
Scheme 4. Li$_2$PES may react with EC, EMC, or PES. In the binary PES/DTD blend, these reactions compete with the newly proposed reactions (4d1) and (4d2).

Table IV. Calculated energy change for the reactions of Li$_2$PES with DTD (Scheme 4).

| Reaction | $\Delta G^0$ (eV) | $\Delta H^0$ (kJ mol$^{-1}$) |
|----------|-----------------|-----------------|
| (4d1)    | −2.44           | −235.2          |
| (4d2)    | −2.52           | −243.4          |

it is used as a single additive. From the volume of gas evolved at $E_{cell} \geq 2.9$ V, it is not apparent whether PES/DTD more effectively passivates the graphite surface than PES alone (Figure 7b). However, the maximum charge associated with SEI formation is less for the PES/DTD blend than for PES as an individual additive (Figure 7c). It is therefore hypothesized that DTD forms new SEI components by spontaneous reaction with the reduced Li$_2$PES species (Scheme 4, Table IV). In other words, PES acts as the ‘primary additive’, which is electrochemically reduced to form a nucleophile, and DTD acts as a ‘secondary additive’, which participates in SEI formation by reacting as an electrophile. The result is two new bifunctional SEI components that contain both lithium sulfonate and organic lithium sulfate ester functional groups. It is presumed that these new compounds are insoluble and have high lithium conductivity.

The proposed SEI formation reactions from the PES/DTD blend were further examined by IMC measurements (Figure 8). The initial and maximum heat flows are similar for PES- and PES/DTD-containing cells but not for DTD-containing cells. This is expected, given that the enthalpy change of the reactions of Li$_2$PES and DTD are within the same range as for the reactions of Li$_2$PES with PES, EC, and EMC (see Ref. 61). When the limiting SEI thickness is reached in PES/DTD cells, the cell voltage sharply increases and the heat flow sharply declines. This is ascribed to the rapid cessation of PES reduction and all subsequent reactions once the graphite surface is fully covered with a passivating SEI layer. Future studies are encouraged to examine the sharpness of the cell voltage increase and heat flow decrease following additive reduction as indicators of negative electrode passivation.

By classifying additives as primary and secondary, each component of the blend can be examined and, potentially, optimized individually. An effective primary additive must reduce to form a good nucleophile at a lower cell voltage than the onset of solvent or secondary additive reduction. An effective secondary additive must spontaneously react as an electrophile with this reduced primary additive to form SEI components that passivate the negative electrode.
Moreover, any additives remaining in the electrolyte solution following SEI formation must not cause excessive impedance growth\textsuperscript{5,70} and should provide benefit to the positive electrode at high potential. It is unknown whether the improved performance of the PES/DTD blend (as reported previously\textsuperscript{10}) is because a) the more effective passivation of the negative surface decreases solvent reduction or b) an increase in the amount of residual PES and/or DTD that is not consumed during negative electrode SEI formation has a beneficial effect at the positive electrode. In either case, it appears that a more passivating SEI at the negative electrode is desirable. However, the quality of the SEI has never been evaluated based on the chemical structure of its constituents. Future work is therefore encouraged to assess the value of various functional groups, such as those in Schemes 2 and 4, which include: alkanes, alkenes, esters, ethers, lithium alkoxides, lithium semicarbonates, lithium sulfate esters, lithium sulfite esters, and lithium sulfonates. Such factors as the relative solubilities, thermal stabilities, and windows of electrochemical stability associated with these functional groups may be helpful to establish criteria for what makes a good negative electrode SEI species. Such criteria may even allow a retrosynthetic route, i.e., reverse engineering, of new additive candidates. Future studies may also examine the composition of the SEI that forms in cells prepared with PES/DTD binary blends, for example by more detailed XPS surface analysis.

**Significance for computational additive discovery.**—For DFT calculations to be used for the high-throughput discovery of new electrolyte additives, the methods must be scalable in a way that is practical, in terms of project time and costs. Therefore, the present work utilizes a lightweight model that operates well on current consumer-grade computers over the timescale of 1–2 days for the largest structures in this work. In conjunction with experiments, this model was used to investigate the underlying chemistry of a binary additive blend. Yet the predictive ability of these DFT methods is presently quite limited. The methods in this article did not correctly predict the sequential order of PES and DTD reduction during SEI formation. It is unknown whether this shortcoming is from errors in the thermochemical calculations or unexamined kinetic factors. Moreover, it is unknown which chemical functional groups lead to beneficial SEI components. These considerations will impede present efforts to apply computational methods for the design and evaluation of new electrolyte additives. It is also noted that this work is focused on sacrificial film-forming additives that form a stable SEI on the negative electrode surface. Further work is still needed to understand other classes of additives, such as phosphate and borate esters, which have been suggested to act by modifying the metal oxide surface of the positive electrode.\textsuperscript{6,38}

**Conclusions**

This work proposes a scheme of the SEI formation reactions in cells prepared with DTD, PES, and the PES/DTD additive blend. Hypothetical pathways were evaluated using computational methods (DFT) and an assortment of experimental measurements (electrochemistry, MAGE, GC-TCD, XPS, IMC). Both DTD and PES form SEI components via electrochemical reduction followed by chemical reaction with the unreduced additive or with the solvent components, EC and EMC. In a binary blend, the PES may act as a primary additive that is electrochemically reduced to form a nucleophile. The DTD would therefore act as an electrophilic secondary additive by reacting with the reduced Li\textsubscript{2}PES species to form new SEI components, which are expected to include bifunctional compounds with both lithium sulfonate and organic lithium sulfate ester functional groups. One key insight from this work is that new additives may be selected to fill either the primary or secondary additive role. Future work is therefore merited to determine which chemical functional groups result in desirable SEI properties, in terms of thermal stability, electrochemical stability, ionic conductivity, and passivation of the electrode. Such work may ultimately facilitate the computer-assisted design and evaluation of new additives and additive blends.

**Acknowledgments**

This work was supported financially by the Natural Sciences and Engineering Research Council of Canada (NSERC), 3M Canada, and Tesla. The authors S.L. Glazier and L.D. Ellis acknowledge NSERC for funding under the PGS-D program and the Walter Sumner Foundation for funding under the Walter C. Sumner Memorial Fellowship program. J.P. Allen acknowledges NSERC for funding under the USRA program. Computational facilities were provided by ACENET (Atlantic Computational Excellence Network) and funded by the Canada Foundation for Innovation (CFI), the Atlantic Canada Opportunities Agency (ACOA) and the provinces of Newfoundland and Labrador, Nova Scotia, and New Brunswick.

**ORCID**

David S. Hall [https://orcid.org/0000-0001-9632-0399](https://orcid.org/0000-0001-9632-0399)

**References**

1. P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J.-M. Tarascon, *Nat. Mater.*, 11, 19 (2012).
2. N.-S. Choi et al., *Angew. Chem. Int. Ed.*, 51, 9994 (2012).
3. D. Kundu, E. Talaie, V. Duffort, and L. F. Nazar, *Angew. Chem. Int. Ed.*, 54, 3431 (2015).
4. Y. Yamada et al., *J. Am. Chem. Soc.*, 136, 5039 (2014).
5. N.-S. Choi, J.-G. Han, S.-Y. Ha, I. Park, and C.-K. Back, *RSC Adv.*, 5, 2732 (2015).
6. M. Xu et al., *Energy Environ. Sci.*, 9, 1308 (2016).
7. Z. Zhang et al., *Energy Environ. Sci.*, 6, 1806 (2013).
8. M. D. Bhatt and C. O’Dwyer, *J. Electrochem. Soc.*, 161, A1415 (2014).
9. H. Bouayad et al., *J. Phys. Chem. C*, 118, 4634 (2014).
