Poor Stability of Li$_2$CO$_3$ in the Solid Electrolyte Interphase of a Lithium-Metal Anode Revealed by Cryo-Electron Microscopy

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The solid electrolyte interphase (SEI) dictates the cycling stability of lithium-metal batteries. Here, direct atomic imaging of the SEI’s phase components and their spatial arrangement is achieved, using ultralow-dosage cryogenic transmission electron microscopy. The results show that, surprisingly, a lot of the deposited Li metal has amorphous atomic structure, likely due to carbon and oxygen impurities, and that crystalline lithium carbonate is not stable and readily decomposes when contacting the lithium metal. Lithium carbonate distributed in the outer SEI also continuously reacts with the electrolyte to produce gas, resulting in a dynamically evolving and porous SEI. Sulfur-containing additives cause the SEI to preferentially generate Li$_2$SO$_4$ and overlithiated lithium sulfate and lithium oxide, which encapsulate lithium carbonate in the middle, limiting SEI thickening and enhancing battery life by a factor of ten. The spatial mapping of the SEI gradient amorphous (polymeric $\rightarrow$ inorganic $\rightarrow$ metallic) and crystalline phase components provides guidance for designing electrolyte additives.

1. Introduction

Lithium metal in the body-centered-cubic (BCC) phase (Li$_{BCC}$) has long been regarded as the ultimate anode for rechargeable batteries, due to its high specific capacity (3860 mAh g$^{-1}$) and low redox potential ($-3.040$ V versus standard hydrogen electrode).$^{[1-9]}$ The structural, chemical, electronic, and mechanical properties of the solid electrolyte interphase (SEI) play a critical role in determining the stability of the anode.$^{[10-12]}$ The SEI is supposed to be a self-passivating layer that forms as the battery cycles, coating the anode and electronically insulating the electrolyte from the free electrons in the anode while remaining conductive to Li$^+$ cations.$^{[13,14]}$ Polyanion compounds such as lithium carbonate Li$_2$CO$_3$ and lithium sulfate Li$_2$SO$_4$ are long thought to be SEI components that directly contact Li$_{BCC}$, playing the role of the electronic insulator.$^{[15,16]}$ However, thermodynamically, the following reactions

\begin{align}
25Li_{BCC} + 6Li_2CO_3 &= LiC_6 + 18Li_2O; \quad \Delta G = -2653 \text{ kJ mol}^{-1} \\
8Li_{BCC} + Li_2SO_4 &= Li_2S + 4Li_2O; \quad \Delta G = -1362 \text{ kJ mol}^{-1}
\end{align}

have large driving forces for the decomposition of the polyanions toward the right-hand side (see Table S1 in the Supporting Information). Indeed, none of the well-known polyanion compounds, nitrate NO$_3^-$, phosphate PO$_4^{3-}$, silicate SiO$_4^{4-}$, etc. appear to be thermodynamically stable in contact with Li$_{BCC}$, either. And when considering half-cell reaction like

\begin{equation}
25Li^+ (\text{electrolyte}) + 25e^- (\text{anode U}) + 6Li_2CO_3 = LiC_6 + 18Li_2O \quad (3)
\end{equation}

as the computed equilibrium voltage is around +1 V versus Li$_{BCC}$, one has to conclude that Li$_2$CO$_3$ and Li$_2$SO$_4$ should not be stable in direct contact with the graphite anode in conventional lithium-ion batteries either.$^{[15]}$ Wherever free electrons can tunnel to from the said anodes, as Li$^+$(electrolyte) must be available right there for the charge-transfer reaction, by the definition of SEI as a nanoscale solid electrolyte.$^{[18]}$ This means the SEI, if it contains lithium polyanion compounds, must be
a nanocomposite with stable buffer phases near the Li metal. Because Li$_2$O and Li$_2$S are wide band-gap insulators, they are the more likely the “innermost” SEI components that electronically insulate the polyatomic compounds, if they exist. However, one of the decomposition products in Equation (1) and (3), LiC$_6$, or more broadly LiC$_x$ ($x = 6,12$, or other forms of lithiated carbon), are not electronically insulating, and will likely facilitate electron tunneling by tip-enhanced electron emission due to the extremely small radii of curvature of such metallic phases. So one naturally suspects that lithium carbonate Li$_2$CO$_3$ will not be a very stable SEI component, at least on the inside, compared to Li$_2$SO$_4$ since the right-hand side of Equation (1) could be electronically more conductive than the right-hand side of Equation (2). This is perhaps the reason that organic carbonate liquid electrolytes need to be supplemented by fluorine- and sulfur-containing additives, to stop the SEI from thickening indefinitely due to LiC$_6$. The 0 V reductive stability of bulk solid electrolytes has long been of concern, and the same should also be true (if not more so) for nanoscale solid electrolyte components in the SEI. Also, it is known that the SEI on the anode surface is extremely sensitive to air and moisture, and undergoes a dynamic formation and rupture-repair process with the constant consumption of electrolyte and lithium ions during battery cycling. An intrinsically unstable SEI results in electrolyte depletion and the rapid “death” of a battery.$^{[19,20]}$ For all the reasons above, we need clear atomic-scale imaging of the SEI.

Although techniques such as X-ray photoemission (spectroscopy) (XPS)$^{[21,22]}$ can readily determine the rough chemical composition of the SEI, it lacks the spatial resolution and diffraction capability to distinguish phase structures at the nano- or atomic scale to draw accurate mechanistic conclusions with regard to electrolyte additives. Indeed, by mere chemical analyses, one would find it difficult to distinguish between Li$_2$CO$_3$ and “over-lithiated Li$_2$CO$_3$,” defined to be the mixture of the right-hand side of (1) plus retained Li$_2$CO$_3$ phase. Conventional transmission electron microscopy (TEM) can easily damage the SEI due to its vulnerability to the electron beam, moisture, and oxygen during the TEM sample preparation and sample transfer. Recently, atomic-scale characterization of SEI using cryogenic TEM (cryo-TEM) can identify the chemical phases and locations of the randomly distributed inorganic and organic ingredients at the atomic scale.$^{[23–25]}$ In this work, we pushed cryo-TEM to its resolution limit with an ultralow electron-beam dosage and successfully imaged the native SEI on Li metal electrode at the atomic scale. We also conducted cryo-electron energy loss spectroscopy (cryo-EELS) mapping, giving us a comprehensive picture of the SEI’s chemistry, and vital information about the influence of the electrolyte additive on the deposited lithium-metal morphology.$^{[26–31]}$ With such high-resolution cryo-TEM (HRTEM) analysis, we reveal a clear gradient distribution of phases, including three types of amorphous phases: an outermost organic amorphous phase Poly$_{Anor}$, an amorphous oxide-sulfide phase in the middle Inorg$_{Anor}$ and a metallic L$_{Anor}$ phase in the interior, with increasing electronic conductivity as one goes from the liquid electrolyte side to the Li$_{BCC}$ side. Crystalline phases of Li$_2$CO$_3$, Li$_2$SO$_4$, Li$_2$O are dispersed within these amorphous phases. In this paper, we compare the SEI structure grown using three electrolytes—commercial pure carbonates (ethylene carbonate ((CH$_3$CH$_2$O)$_2$CO) (EC–DEC)) electrolyte without any additive, with 2% DTD (ethylene sulfate C$_4$H$_6$O$_4$S), or with 2% PS (1,3-propanesulfonate C$_3$H$_6$O$_3$S), respectively, revealing the poor stability of Li$_2$CO$_3$ as a solid electrolyte and the additives’ influence on the SEI formation. It appears that sulfur-containing electrolytes show superior performance because the “overlithiated Li$_2$SO$_4$,” Li$_2$S+4LiO, on the inside, are much more electronically insulating. Also, Li$_2$SO$_4$ formed on the exterior of SEI appear to be much more stable than Li$_2$CO$_3$, and protect the crystalline Li$_2$CO$_3$ sandwiched in the middle, similar to how some bulk solid electrolytes with a narrow electrochemical stability window are protected in solid-state batteries.

2. Results and Discussion

In the coarse-scale cryo-TEM images in Figure 1a, the as-formed lithium-metal dendrites are quite long (up to tens of micrometers), with diameters ranging from 100 nm to about 500 nm and atomic structures that can be either amorphous or crystalline. The selected area electron diffraction in Figure 1b shows the signature of bands of amorphous Li dendrites punctuated by crystalline Li$_{BCC}$ diffraction spots, as marked by the white arrows. Therefore, the as-grown Li dendrites contain a portion of disordered amorphous Li metal phase, denoted as Li$_{Amor}$. Wang et al. reported that the glassy Li-metal formation is kinetically driven and related to the battery current density and deposition time.$^{[13]}$ The high-resolution cryo-TEM image in Figure 1c shows a representative crystalline dendrite region with (01$ar{T}$)$_{Li_{BCC}}$ lattice planes. In contrast, Figure 1d shows a representative amorphous dendrite region, with little crystalline islands (3–5 nm) distributed inside, which can be indexed to small Li$_2$O crystals. High-resolution TEM (HRTEM) analysis is consistent with the overall electron diffraction analysis, proving that both crystalline Li$_{BCC}$ and amorphous Li$_{Amor}$ are present in the as-grown dendrites. The origin of the amorphous Li metal phase may be attributed to chemical impurities, as monatomic Li metal should crystallize very easily, given that the electrodeposition occurred at 2/3 of Li$_{BCC}$’s bulk melting point and Li atom diffusion is known to be facile at room temperature.$^{[1]}$ We speculate that carbon, oxygen or hydrogen on the order of 10 at% contribute to the amorphization of Li metal. These come from the in operando decomposition of the liquid electrolyte as Li$^+$ (electrolyte) + e$^-$ (anode) $\Rightarrow$ neutral Li atom is being deposited simultaneously. The crystallinity of our dendrites is seen to vary from region to region, thus such amorphization should depend on a number of factors such as deposition rates and additives. Despite the amorphous nature, Li$_{Amor}$ should still be metallic. From now on, we will use Li$_{Metal}$ to denote multiphase mixtures of Li$_{BCC}$+Li$_{Amor}$ and we speculate that the ratio of Li$_{Amor}$ in Li$_{Metal}$ likely reflects the imperfect barrier properties of the incipient SEI. Note that the SEI must spatially show “metal–insulator transition” as one scan across from the Li$_{BCC}$ side to the liquid electrolyte side, and the kinetics of forming such a gradient structure is of great consequence for liquid-electrolyte-based batteries.

Cryo-TEM enables direct atomic-scale imaging of how the morphology and atomic structures of the Li$_{Metal}$ and the SEI change when the liquid electrolyte used contains
different additives. In the presence of common carbonate electrolyte without additives, the lithium dendrite growth is more directional (Figure 1e) and the SEI layer is thick and porous (Figure 1e–h). However, in the presence of electrolyte with DTD additives, the lithium dendrite growth is more isotropic (Figure 1g) and the SEI layer is thinner, less porous and more uniform (Figure 1j). Figure 1e is a cryo-TEM image of lithium dendrites deposited in a commercial EC-based electrolyte (EC/DEC = 1:1, 1.0 mol L⁻¹ LiPF₆). The SEI shows a porous structure that is possibly caused by the CO₂ gas release during the SEI-formation process. The magnified view in Figure 1h shows that the SEI layer is quite nonuniform, with an outermost bubble-like amorphous organic layer (up to ≈30 nm in thickness) on top of a crystalline layer with dark diffraction contrast. The thickness of the inner, inorganic SEI layer ranges from ≈20 to ≈30 nm. Figure 1f–i is cryo-TEM images of lithium dendrites deposited in the PS-containing electrolyte (EC/DEC+ 2% PS). In addition, Figure 1j shows that the SEI
formed in the modified electrolyte is more uniform (Figure 1h). Further, the 35 nm thick SEI layer formed in the PS-containing and DTD-containing electrolyte shows only a very thin organic layer PolymerAmor of approximately a few nanometer on top of the dark inorganic layer on the LiMetal. The LiMetal protrusions formed in DTD are round-shaped (Figure 1g), in sharp contrast to the strip-shaped LiMetal dendrites in PS (Figure 1f). This clearly demonstrates that DTD additives can inhibit the directional growth of LiMetal. Zachman et al. reported the finding of crystalline lithium hydride in the Li dendrite.\[23\] However, we did not observe clear signature of such LiH crystalline phase based on statistical HRTEM analysis of tens of different regions at the Li dendrites in all three samples.

Because the DTD-containing electrolyte visibly contributes to a more stable SEI and suppression of lithium dendrite growth and gas bubble evolution, we hoped to correlate our structural findings with battery performance. To this end, we assembled and tested symmetric LiMetal|LiMetal cells with three kinds of electrolytes (DTD/PS/BLANK), as shown in Figure 2a. The cell with BLANK electrolyte (EC/DEC with no additives) deteriorates quickly, even within 20 h (Figure 2a,b); and the cell impedance diverged and experienced catastrophic failure after 50 h of cycling. In contrast, the LiMetal|LiMetal symmetric cell with DTD exhibited highly reversible lithium stripping/plating for over 500 h. The cycling stability and voltage polarization of the DTD cell even outperformed the PS cell, which retained stability and polarization for 350 h. It is noteworthy that cell life is the greatest at the lowest polarization, as shown in Figure 2a–c. Cryo-TEM analysis clearly demonstrates that a stable, uniform, and thin SEI layer corresponds to stable cycling performance of the lithium-metal battery. By fitting the impedance with an equivalent circuit in the EIS analysis in Figure S1 (Supporting Information), the semicircle yields a resistance of the battery of 70, 150, 250 $\Omega$ in the third cycle with DTD additive, PS additive, and blank electrolyte, respectively.

Having shown that the dendrite morphology varies significantly using different electrolytes, we more closely observe the role of the SEI layer in extending the cycle life of Li-metal batteries. To carefully examine the atomic structures of the inorganic layer in the SEI, we performed atomic-resolution cryo-TEM imaging of the SEI in the blank EC/DEC electrolyte (Figure 3). Fast Fourier transform (FFT) pattern analysis (matching the component’s crystal plane spacing to known crystals) reveals that the crystalline parts of SEI contain mainly lithium carbonate and Li$_2$O (Figure 3a). Cryo-HRTEM imaging (Figure 3b) further shows that the top layer of the SEI comprised crystalline Li$_2$CO$_3$ (blue-dotted region) and the bottom layer comprised crystalline Li$_2$O (red-dotted region), mingling

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Figure 2. a) Performance of LiMetal|LiMetal symmetric cells at a current density of 1 mA cm$^{-2}$ using different electrolytes. b) Voltage profile of symmetric Li–Li cells with DTD/PS/BLANK electrolyte at 20–26 h. c) Voltage profile of symmetric Li–Li cells with DTD/PS electrolyte at 200–206 h.
with amorphous regions Polymer_{Amor} + Inorg_{Amor} highlighted in white. The region indicated by the blue-dashes (Figure 3c) is lithium carbonate with identifiable (110) \( \text{Li}_2\text{CO}_3 \) and (002) \( \text{Li}_2\text{CO}_3 \) crystal planes in the corresponding FFT pattern (Figure 3d). The red-dash region (Figure 3e) comprised \( \text{Li}_2\text{O} \) with identifiable (111) \( \text{Li}_2\text{O} \) crystal planes (Figure 3g).

In order to more accurately observe the gradient distribution of \( \text{Li}_{\text{Metal}} \), crystalline \( \text{Li}_2\text{CO}_3 \), \( \text{Li}_2\text{O} \), and the spatially percolating Polymer_{Amor} + Inorg_{Amor}, we performed cryo-EELS. From Figure 3g and Figure S2, Supporting Information, we observe that carbon is distributed with higher concentration in the outside layer of the SEI, while oxygen is distributed in all parts of the SEI. Figure S2 (Supporting Information) shows the fine structures of the Li and O K-edge acquired from the center of the dendrite to SEI surface, respectively. The Li K-edge spectrum of the lithium has a major peak starting at 60 eV and a minor peak starting at 65 eV. The outer surface of the SEI has significant O K-edge intensity. Meanwhile, the Li K-edge...
The spectrum of the surface is weak compared to the Li\textsubscript{Metal} region. The C K-edge spectrum (Figure 3h) has a major broad peak at 290 eV, implying that the carbon is likely Li\textsubscript{2}CO\textsubscript{3}. The EELS are consistent with our cryo-TEM imaging and diffraction results, confirming that lithium carbonate is located in the outer part and lithium oxide likely resides at the bottom of the SEI when no additives are added in the electrolyte. Judging from the EELS mapping, the spatially percolating amorphous zones contain Li, O, and possible C elements. The over-lithiated Li\textsubscript{2}CO\textsubscript{3} products (Li\textsubscript{2}O plus LiC\textsubscript{x}) possibly make up the amorphous Inorg\textsubscript{Amor} in the SEI in direct contact with Li\textsubscript{Metal}, as highlighted in white in Figure 3a.

The distributions of Li\textsubscript{2}O and Li\textsubscript{2}CO\textsubscript{3} crystals in SEI vary significantly with additives. The SEI formed in EC/DEC with DTD additive is carefully probed by cryo-TEM and EELS, as shown in Figure 4. The lattice-resolution TEM and corresponding FFT
analysis proved that the SEI contains Li$_2$CO$_3$, Li$_2$SO$_4$, and Li$_2$O crystals. The cryo-TEM image of SEI depicts that the top layer is mostly Li$_2$O (red region); the middle layer is predominantly Li$_2$SO$_4$ (yellow region) on top of Li$_2$CO$_3$ (blue region). Magnified images of the blue region (Figure 4d) show clearly crystalline grains that are identified to be lithium carbonate with its (110)$_{Li_2CO_3}$ crystal planes observed in FFT (Figure 4e). HRTEM images of the yellow region (Figure 4b) are large pieces of Li$_2$SO$_4$ crystal with observed (220)$_{Li_2SO_4}$ and (111)$_{Li_2SO_4}$ diffraction spots (Figure 4c). The (111) crystal planes of Li$_2$O are identified (Figure 4f,g) as well. Beneath the Li$_2$CO$_3$, there is another layer of Li$_2$O and inorganic amorphous Inorg$_{Amor}$ in contact with the Li$_{Metal}$, which helps stabilize the whole SEI and provide barrier against electron tunnelling. The Inorg$_{Amor}$ zone likely contains the over-lithiated Li$_2$CO$_3$ (right-hand side of reaction (I)) and over-lithiated Li$_2$SO$_4$ (right-hand side of reaction (2)) products, Li$_2$O, Li$_x$S, and LiC$_x$ in amorphous atomic structure, judging from the content identified by EELS. In order to probe the distribution of lithium sulfate, carbonate, and oxide at larger scale, we used EELS mapping by tracking the K edges of Li, O, C, and L edge of S at the lithium dendrite with nanoscale resolution in Figure 4h–j. Figure 4j and S3 (Supporting Information) exhibits the fine structures of the Li, C, S, and O-K edge acquired from Li$_{Metal}$ to SEI surface, respectively. Similarly, the Li K-edge spectrum in SEI shows oxidized feature, which is consistent with the pronounced O-K edge intensity. The C K-edge spectrum (Figure 4i) exhibits the Li$_2$CO$_3$ signature fine structures. From the C and S peak intensity at different spots, the Li$_2$SO$_4$ seems to be distributed more in the top part of the SEI than Li$_2$CO$_3$, which is consistent with HRTEM results. The DTD reacts in the electrolyte and generates Li$_2$SO$_4$, which can cover up some Li$_2$CO$_3$ crystalline phases. The Li$_2$SO$_4$ layer and Li$_2$O appear to inhibit the further reaction between lithium carbonate and the electrolyte, resulting in a stable SEI and better cycling stability. Based on statistical HRTEM analysis of a number of locations, we did not locate crystalline Li$_x$S lattices. However, we detected S L edge from the Inorg$_{Amor}$ phase region in the SEI as shown in Figure S5 (Supporting Information), therefore, we speculate that amorphous Li$_x$S probably exists in the percolating amorphous regions.

In the PS-containing electrolyte, the SEI layer is a mosaic-patterned structure as observed in the cryo-HRTEM image in Figure 5a. Using FFT analysis in Figure 5b–g, the SEI contains crystalline Li$_2$CO$_3$, Li$_2$SO$_4$, Li$_2$O, and inorganic amorphous zones. The distribution of lithium oxide and carbonate is less ordered compared to that in the DTD-containing electrolyte. Cryo-HRTEM shows that the top layer contains Li$_2$CO$_3$ (blue region) and Li$_2$O (red region), while the Li$_2$SO$_4$ (yellow region) crystals do not completely shield the Li$_2$CO$_3$ crystals. There is still a portion of lithium carbonate crystals formed in the outer layer of SEI, inducing gas formation and constantly destabilizing the SEI mechanically. The Li metal region also features a coexistence of both crystalline Li$_{BCC}$ phase and Li$_2$O phase as circled in red. The EELS mapping displays the distribution of lithium, oxygen, sulfur, and carbon in Figure 5h. The fine structures of the Li, C, S, and O K-edge acquired at the SEI are exhibited in Figure S5 and Figure S4 (Supporting Information), which also indicates the formation of Li$_2$O, Li$_2$CO$_3$, and Li$_2$SO$_4$. Comparing the S and C signals in Figure 5j, Li$_2$SO$_4$ randomly mixes with the Li$_2$CO$_3$, which is consistent with the cryo-TEM results. The major drawback of PS-containing electrolyte is the existence of a significant portion of naked Li$_2$CO$_3$ located in the outer SEI layer, resulting in a worse battery cycling stability than the DTD-containing electrolyte. The highlighted amorphous zones in Figure 5a containing significant Li, O, and C EELS signals likely result from the decomposition of overlithiated Li$_2$CO$_3$ and electrolyte.

The SEI in the blank electrolyte is dynamically changing, which constantly consumes the cyclable lithium and electrolyte inventories (Figure 6a–c). Calculations predict that the electrolyte molecules decompose to form lithium ethylene dicarbonate Li$_2$C$_4$H$_4$O$_6$ (LEDC), CO$_2$, Li$_2$CO$_3$, and Li$_2$O in the presence of excess Li atoms from Li$_{Metal}$ during the initial stages of SEI formation.[18] The CO$_2$ gas increases the porosity of the as-formed SEI on Li$_{Metal}$ and reduces its passivation power. The Li$_2$CO$_3$ contacting Li$_{Metal}$ produced the overlithiated phases, Li$_2$O and LiC$_x$, on the surface of Li$_{Metal}$. These reactions allow SEI layer to continuously increase in thickness, which reduces the cycle life of the battery.

In comparison, with sulfur-containing additives (PS and DTD), the resulting SEI became more stable and the consumption of electrolyte decreased (Figure 6d–f). The addition of DTD produces Li$_2$SO$_4$ in addition to LEDC, Li$_2$O, and Li$_2$CO$_3$. The Li$_2$SO$_4$ and Li$_2$O can shield lithium carbonate and inhibit further decomposition of lithium carbonate on the top surface. While the Li$_2$SO$_4$ contacting Li$_{Metal}$ produced the overlithiated products of crystalline Li$_2$O and amorphous Li$_x$S as a bottom buffer layer. As a result, the well-covered lithium carbonate in the middle of the SEI remains intact. The resulting SEI is thin and uniform due to the protective effect of Li$_2$SO$_4$. In comparison, the amount of Li$_2$SO$_4$ produced by PS is less than DTD, as a result, its protective effect on lithium carbonate is not as strong. The SEI with PS and blank electrolyte has only partial coverage of Li$_2$CO$_3$ on the surface.

The first stage of the SEI formation reactions is the formation of the polyanion inorganic compounds as intermediates; while the second stage is the further decomposition of these polyanion compounds that are directly exposed to Li$_{Metal}$ or electrolyte as shown by Figure 6. Overlithiated Li$_2$CO$_3$ and Li$_2$SO$_4$ leads to the formation of Li$_2$O, LiC$_x$, and Li$_x$S when contacting with the Li metal. (This may also cause C, O, H, S impurities diffusion into the Li metal and thus the observed amorphous Li metal phase). LiC$_x$ is electrically conductive, which diminishes the stability of the SEI due to electron channeling. In comparison, overlithiated Li$_2$SO$_4$ forms Li$_x$S and Li$_2$O, which are electronic insulators and prevent electron channeling, stabilizing the sandwiched Li$_2$CO$_3$ in the middle. Li$_2$SO$_4$ is a stable blanket on top of Li$_2$CO$_3$ as well to stop its reaction with electrolyte. Therefore, we believe the Li$_2$SO$_4$ is a more desirable component than Li$_2$CO$_3$ in the SEI. The Li$_2$CO$_3$ is very "fragile" as found by our experiment and has to be wrapped by other phases for protection. Thus, desirable electrolyte additive should contain higher amount of sulfur. The SEI formed with DTD (C$_3$H$_6$O$_2$S) additive is better than PS (C$_3$H$_6$O$_3$S) additive due to more Li$_2$SO$_4$ and less Li$_2$CO$_3$ production, attributable to its higher sulfur content (the atomic percentage of sulfur in the DTD(C$_3$H$_6$O$_2$S) and PS (C$_3$H$_6$O$_3$S) is 9% and 7.7%, respectively).
Yet, the PS additive is still better than the blank EC–DEC electrolyte due to some content of sulfur that offers protection for the fragile Li$_2$CO$_3$, which we have observed also but has dubious barrier properties. In addition, our experimental observation of Li$_2$CO$_3$ in the middle or outer layer of the SEI (but not directly contacting Li$_{\text{Metal}}$) suggests that Li$_2$CO$_3$ further
away from Li\textsubscript{Metal} does not react with Li\textsubscript{Metal}, likely due to slow electron transfer kinetics.

There are amorphous organic and amorphous inorganic components in the SEI. The amorphous organic polymeric phases are mechanically resilient upon Li metal stripping and plating\cite{34}. The amorphous inorganic components consist of both ceramic-like Inorg\textsubscript{Amor}, and metallic Li\textsubscript{Amor}. Similar percolating composite SEIs including inorganic phases of Li\textsubscript{2}O/LiF randomly distributing inside a polymer matrix are also observed in 1,3-dioxolane/1,2-dimethoxyethane based electrolyte, which ensures the stable cycling of Li-metal batteries. The optimal SEI should have Li\textsubscript{2}O, LiF, and overlithiated Li\textsubscript{2}SO\textsubscript{4} to separate the Li\textsubscript{2}CO\textsubscript{3} components from directly touching Li metal. The ionic conductivity of Li\textsuperscript{+} in the nanocrystalline Li\textsubscript{2}O, Li\textsubscript{2}SO\textsubscript{4}, Li\textsubscript{2}CO\textsubscript{3}, and percolating amorphous phases that make up the SEI\cite{35}, plus interfacial diffusion along the grain boundaries and phase boundaries, should be further investigated. Reports showed that the space charge effect along the interfaces of these nanocrystalline inorganic phases can sometime generate a higher ionic carrier concentration and improves the ionic conductivity\cite{35,36}. The success of the DTD additive is attributed to the formation of stable SEI with a gradient distribution of the organic and inorganic components that have high mechanical and chemical stability. In particular, a gradient amorphous matrix (polymeric $\rightarrow$ inorganic $\rightarrow$ metallic) with nanocrystalline embedded phases of Li\textsubscript{2}SO\textsubscript{4}, Li\textsubscript{2}CO\textsubscript{3}, Li\textsubscript{2}O appear to be a quite general structural model.

3. Conclusions

To understand both the electronic insulation and percolating Li$^+$ transport across the SEI components, we first need to accurately determine the nanoscale phase distribution in the SEI for different electrolyte formulations. Using aberration-corrected cryo-TEM, we captured atomic-scale pictures showing the composition and exact distribution of SEI components on the Li-metal anode. HRTEM reveals that the Li\textsubscript{2}O or the overlithiated amorphous phase (LiO\textsubscript{x}, LiC\textsubscript{x}, Li\textsubscript{x}S) always buffer the Li\textsubscript{2}CO\textsubscript{3}, and Li\textsubscript{2}SO\textsubscript{4} from directly contacting the Li\textsubscript{Metal}. The content of sulfur in the additive and resulting Li\textsubscript{2}SO\textsubscript{4} crystals are desirable for a stable SEI on Li\textsubscript{Metal}, which dictates the cyclability of the battery. Without additives, the naked Li\textsubscript{2}CO\textsubscript{3} in the outer SEI layer continuously react with the electrolyte, resulting in bad cycling performance. However, the addition of sulfur-containing DTD additive produces large amounts of Li\textsubscript{2}SO\textsubscript{4} It and its overlithiated products (Li\textsubscript{2}O and amorphous Li\textsubscript{x}S and Li\textsubscript{x}O) can securely sandwich Li\textsubscript{2}CO\textsubscript{3} in the middle. Our study reveals

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**Figure 6.** a–c) Schematic of SEI formation on the Li\textsubscript{Metal} electrode with blank electrolyte, due to the continuous decomposition of LEDC and Li\textsubscript{2}CO\textsubscript{3}, lots of lithium oxide remains on the surface of the Li\textsubscript{Metal}. The Li\textsubscript{2}CO\textsubscript{3} decompose once touched Li\textsubscript{Metal} surface. The partial exposure of the Li\textsubscript{Metal} leads to the continuous reaction. d–f) SEI formation using the DTD electrolyte additive greatly expands the stability of SEI. DTD produces Li\textsubscript{2}SO\textsubscript{4}, which cover lithium carbonate and inhibit the decomposition of lithium carbonate and electrolyte.
how sulfur-containing additives work, and we have new directions for better electrolyte design that specifically targets the amorphous and crystalline components architecture in the SEI.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
B.H. and Z.Z. contributed equally to this work. M.G. and J.L. designed and supervised the experiment. B.H., Z.Z., Y.Z. carried out the cryo-TEM and battery testing; M.G., B.H., J. L., Z.Z. analyzed the data; M.G., J.L. wrote the manuscript. All authors discussed and contributed to editing of the paper.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- Li-metal anodes
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- low-dose imaging
- solid electrolyte interphase

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