Glyoxylate acetals as electrolytes for Si/Graphite anodes in lithium-ion batteries

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ABSTRACT

Using silicon-containing anodes in lithium-ion batteries is mainly impeded by undesired side reactions at the electrode/electrolyte interface leading to the gradual loss of active lithium. Therefore, electrolyte formulations are needed, which form a solid electrolyte interphase (SEI) that can accommodate to the volume changes of the silicon particles. In this work, we analyze the influence of two glyoxylate acetals on the cycling stability of silicon-containing graphite anodes, namely TMG (1 M LiTFSI in 1,1,2,2-tetramethoxyethane) and TEG (1 M LiTFSI in 1,1,2,2-tetraethoxyethane). The choice of these two electrolyte formulations was motivated by their positive impact on the thermal stability of LIBs. We investigate solid electrolyte decomposition products employing x-ray photoelectron spectroscopy (XPS). The cycling stability of Si/Gr anodes in each electrolyte is correlated to changes in SEI thickness, composition, and morphology upon formation and aging. This evaluation is completed by comparing the performance of TMG and TEG to two carbonate-based reference electrolytes (1 M LiPF 6 in 1:1 ethylene carbonate: dimethyl carbonate and 1 M LiPF 6 in the same solvent mixture). Cells cycled in TMG display inferior electrochemical performance to the two reference electrolytes. By contrast, cells cycled in TEG exhibit the best capacity retention with overall higher capacities. We can correlate this to better film-forming properties of the TEG solvent as it forms a smoother and more interconnected SEI, which can better adapt to the volume changes of the silicon. Therefore, TEG appears to be a promising electrolyte solvent for silicon-containing anodes.

1. Introduction

To fulfill increasing market demands, Li-ion batteries are required to deliver higher energy and power densities and be safer during operation compared to state-of-the-art batteries. Higher energy densities can be obtained by increasing the specific charge of the anode material. This is achieved by blending graphite with a low amount of a material with high theoretical specific capacity such as silicon ($Q_{th} = 3579 \text{ mAh g}^{-1}$) [1–8]. However, silicon exhibits high volume changes during (de)lithiation processes amounting up to 280% [1,9,10]. As the silicon volume is continuously changing upon cycling, the electrode material is gradually pulverized and parts of the active material become isolated [1, 9–12]. Furthermore, the large volume expansions and contractions expose the SEI to high mechanical strain [11,13–16]. The SEI is a result of electrolyte instability in the applied voltage range (~below 1 V vs. Li/Li$^+$) and consists of insoluble electrolyte decomposition products [17]. While this layer allows lithium-transport, it is electrically insulating and thereby decreases further electrolyte decomposition. Thus, the electrode surface is passivated, and long-term cycling becomes possible. A well-functioning SEI is therefore essential for the long-term stability of a battery. This is especially the case with Si/Gr anodes, where the SEI oftentimes cannot accommodate the electrode volume changes. Consequently, cracks are formed, which causes a re-exposure of Si-/Gr electrode material to the electrolyte, leading to new SEI formation. Every electrolyte decomposition reduces the lithium reservoir and ultimately leads to the failure of the cell. Hence, electrolyte formulations are needed which can accommodate to these volume changes.

State-of-the-art electrolytes consist of a lithium salt (e.g., lithium-hexafluorophosphate - LiPF 6 ) dissolved in a mixture of a cyclic carbonate of high dielectric constant (e.g., ethylene carbonate - EC) with a linear carbonate of low viscosity (e.g., dimethyl carbonate - DMC). These solvent combinations result in low viscosities and high ionic conductivities [18,19]. Drawbacks are mainly safety issues and thermal instabilities of both, electrolyte salt and solvent [20,21]. When cycled with carbonate-based electrolytes such as LP30 (1 M LiPF 6 in 1:1 EC: DMC), Si/Gr anodes show poor capacity retention. Besides silicon and...
electrode degradation effects, the SEI formed by the LP30 electrolyte is one reason for the insufficient capacity retention, which is linked presumably to unfavourable SEI properties, such as insufficient flexibility upon volume expansion. To improve the cycling stability of Si/Gr electrodes, sacrificial electrolyte additives such as fluoroethylene carbonate (FEC) are used [11,16,22-24]. Upon decomposition, FEC is suggested to form elastomeric poly(VC)-type species thereby increasing the SEI flexibility upon electrode volume changes [25]. However, as FEC is consumed with each cycle, the capacity stabilizing effect disappears the moment the additive is exhausted [13,26].

Investigations of alternatives to carbonate-containing electrolytes such as LP30 focus on overcoming safety issues and thermal instability, as well as better SEI forming properties. Several alternative electrolytes have been studied in the last years. Among them, those based on glyoxal acetals with other solvents such as propylene carbonate [28,29]. Also, the SEI formed by glyoxal-based electrolytes has yet to be investigated.

Therefore, we focus in this work on the SEI properties derived from glyoxal-based electrolytes. We report for the first time about the effect of glyoxal-based electrolytes 1 M LiTFSI in TMG and 1 M LiTFSI in TEG (Fig. 1) on the cycling stability of Si/Gr anodes. To simplify the system, we omit using organic carbonates as ionic conductivity boosters and the SEI formed via ultrasonic dispersion with an ultrasonic homogenizer (Kinhematica, Polytron PT 2500). The obtained slurry was coated on a copper foil with a doctor blade (wet thickness was set to 150 µm) and later dried at room temperature overnight. Individual electrodes were cut into discs with 12 mm in diameter and dried under vacuum at 120 °C for 12 h. The resulting electrodes had a silicon-graphite mass loading of around 2.5 mg/cm².

2. Experimental

2.1. Electrolyte preparation

Battery-grade LP30 (i.e., 1 M LiPF₆ in 1:1 ethylene carbonate: dimethyl carbonate) electrolyte (Merck) was used as received (water content <10 ppm as measured by Karl-Fischer titration). The solvents DMC and EC as well as the LiTFSI salt were purchased from Merck and dried over a molecular sieve before usage (water content <15 ppm as measured by Karl-Fischer titration). The solvents TMG and TEG were obtained from Weylchem and dried with an over-pressure Schlenk filtration through vacuum-pre-dried aluminum oxide. The water content for both solvents was reduced to under 20 ppm, as measured by Karl-Fischer titration.

2.2. Electrode preparation

Electrodes were prepared using a slurry of 81 wt% graphite (SFG6L, TIMCAL), 9 wt% silicon nanopowder (Nanostructured & Amorphous Materials Inc., 50-100 nm, purity >99%), 5 wt% carbon nanofibers (Showa Denko), and 5 wt% lithium-polyacrylic acid binder solution. The binder solution was obtained by diluting a ready-made 45 wt% polyacrylic acid in water solution (Sigma Aldrich) and subsequently adding lithium-hydroxide (LiOH, Sigma Aldrich) until a pH of 5 was reached. In the following, the lithium polyacrylate binder is referred to as LiPAA. The slurries were prepared in a two-step process. The premixing was done with a planetary mixer (Thinky ARV-310P). Firstly, silicon nanopowder (9 wt%) was mixed with carbon nanofibers (5 wt%) and graphite (81 wt%) in water: ethanol mixture of 1:1.2. Subsequently, the mixture was dried and gradually transferred into a glass vial containing the LiPAA solution. To break particle agglomeration, mixing was performed via ultrasonic dispersion with an ultrasonic homogenizer (Kinhematica, Polytron PT 2500). The obtained slurry was coated on a copper foil with a doctor blade (wet thickness was set to 150 µm) and later dried at room temperature overnight. Individual electrodes were cut into discs with 12 mm in diameter and dried under vacuum at 120 °C for 12 h. The resulting electrodes had a silicon-graphite mass loading of around 2.5 mg/cm².

2.3. Half-cell assembly and cycling

The electrodes were assembled in an Ar-filled glovebox in a CR2025-type coin cell half-cell setup. All cells consisted of the Si/Gr working electrode, a microporous polypropylene separator (Celgard 3235), a glass fiber separator (VWR), and Li foil (thickness: 0.25mm, purity: 99.9%, PI-KEM) as counter electrode. The Celgard 3235 separator was applied directly on the electrode surface to protect it from possible glass fiber contaminations. 150 µL of the respective electrolyte solution was applied between 1.5 V - 0.01 V. After every lithiation step, a constant-current constant-voltage (CCCV) was applied at C/5 for 30 minutes.

![Fig. 1. Molecular structures of 1,1,2,2-tetramethoxyethane (TMG), 1,1,2,2-tetraethoxyethane (TEG), and lithium bis(trifluoromethansulfonyl)imide (LiTFSI).](image-url)
2.4. Post-mortem analysis (XPS & SEM)

All samples were washed by a 1-minute submersion in the following solvents: For LP30 and L-ED, dimethyl carbonate (DMC) was used. For the glyoxal electrolytes, the respective solvent (i.e., 1,1,2,2-tetramethoxyethane or 1,1,2,2-tetramethylethylene) was applied. After washing, all electrodes were dried and mounted on a sample holder using conductive copper tape. The sample preparation was carried out in an argon-filled glove box (H<sub>2</sub>O, CO<sub>2</sub> < 1 ppm). After the photoelectron spectrometer or the SEM was done via a transfer module under inert gas conditions. To ensure SEI stability in lithiated and delithiated states, the lithiation and delithiation endpoint potentials were held for 1 hour after the electrochemical cycling.

X-Ray photoelectron spectroscopy (XPS). XPS measurements were carried out with a K-alpha spectrometer from Thermo-Fisher Scientific applying a micro-focused, monochromated Al-K<sub>α</sub> X-Ray source with 400 μm spot size. A pass energy of 50 eV was used. Data acquisition and handling were done via the Thermo Advantage software by K.L. Parry et al. [32]. Spectra were fitted with one or more Voigt profiles and Scofield sensitivity factors were applied for quantification. All spectra are referenced in binding energy to the hydrocarbon C 1s peak at 285 eV. For clarity of presentation, all spectra are normalized in intensity to the maximum intensity.

Scanning electron microscopy (SEM). Scanning electron microscopy (SEM) measurements were conducted using a thermal field emission scanning electron microscope (FESEM, Carl Zeiss SMT AG) equipped with energy-dispersive spectroscopy (EDS, Quantax 400 SDD, Bruker) at an acceleration voltage of 7 kV.

3. Results & discussion

3.1. Electrochemistry

Galvanostatic cycling of Si/Gr half-cells cycled in the respective electrolytes TMG (blue), TEG (black), L-E/D (green), and LP30 (pink) are shown in Fig. 2a. Corresponding coulombic efficiencies are displayed in Fig. 2b. As shown during the 1<sup>st</sup> cycle, the electrodes exhibit higher specific lithiation capacities than the theoretical values in all 4 investigated electrolytes. This is due to extensive SEI formation during this first cycle. The cell cycled in the L-E/D electrolyte displays the highest lithiation capacity with 964 mAh g<sup>-1</sup>. Also, the largest irreversibility appears for L-E/D as can be seen in the coulombic efficiency of only 71%. Cells cycled in TMG, TEG, and LP30 display lower initial lithiation capacities of around 780 mAh g<sup>-1</sup> and higher coulombic efficiencies of around 80%.

Upon cycling, the cell with the TMG electrolyte displays the fastest capacity drop out of all electrolytes. Already after 10 cycles, a decline of around 100 mAh g<sup>-1</sup> can be observed. This decrease is reflected by a decline in coulombic efficiencies of 1.5%, indicating a possible loss of active material and solid electrolyte interphase evolution. After 100 cycles, only 38% of capacity can be retained from the 647 mAh g<sup>-1</sup> observed in the 2nd cycle. In comparison, cells cycled in TEG show the smallest capacity decrease out of all electrolytes. After 100 cycles, 488 mAh g<sup>-1</sup> are retained (i.e., 72%). Coulombic efficiencies remain at around 98.9% throughout the cycling experiment. When using the two reference electrolytes LP30 and L-E/D better performances are achieved compared to the TMG case. However, the capacity retention is much worse than in presence of TEG. A significant capacity drop can be seen after 15 cycles for both carbonate-based electrolytes, leading to a retention of 53% and 56% after 100 cycles, respectively.

Fig. 3 compares the evolution of the differential capacity (dQ/dE) of the Si/Gr electrodes for selected cycles over the first 100 cycles. Regardless of the used electrolyte, the Si/Gr electrodes generally display the same electrochemical processes, but with different rates of intensity decay for the characteristic intercalation/alloying peaks. In all systems, the first cycle shows the most intense dQ/dE signals during both lithiation and delithiation. The following graphite lithiation intercalation reactions are observed: 0.2 V (stage IV), 0.13 V (stage III, LiC<sub>6</sub>), 0.1 V (stage II, LiC<sub>12</sub>), and 0.07 V (stage I, LiC<sub>6</sub>) [33,34]. Lithiation of crystalline silicon occurs via a two-phase mechanism in which crystalline silicon is transformed to lithiated amorphous silicon (Li<sub>x</sub>Si) [35–38]. The alloying reactions extend over the whole lithiation profile and are difficult to distinguish from the graphite intercalation signals. At the end of the first lithiation, the amorphous Li<sub>x</sub>Si phase reacts to crystalline Li<sub>15</sub>Si<sub>4</sub> corresponding to the minima at 0.04 V in the dQ/dE plot [39–41]. Upon delithiation, the crystalline Li<sub>15</sub>Si<sub>4</sub> transforms back to amorphous silicon in which state it remains during the whole delithiation. In the dQ/dE profile of the 10<sup>th</sup> cycle, a new signal can be observed at 0.3 V for all electrolytes corresponding to the lithiation of the amorphous silicon.

Cells cycled in the TMG electrolyte show the most pronounced intensity decrease upon cycling. Already after 10 cycles, a large amount of graphite and silicon activity is lost, reflecting the dramatic capacity drop observed in Fig. 2. Both reference electrolytes L-E/D and LP30 show higher electrochemical activity than TMG, which results in the higher capacity retentions observed in Fig. 2. Especially graphite intercalation reactions are better retained upon cycling. However, both silicon and graphite show losses in activity, mirroring the capacity drop in Fig. 2. By contrast, when using TEG, only small losses in silicon activity are observed as can be seen in the signal at 0.3 V and 0.04 V from the 10<sup>th</sup> to the 100<sup>th</sup> cycle. Moreover, the electrochemical activity of graphite is completely retained throughout the GCPL experiment. This better retention in the activity of both silicon and graphite explains the improved electrochemical performance displayed in Fig. 2.

At this stage, neither electrolyte viscosity nor ionic conductivity appear to play a role. For TMG and TEG, both parameters are very similar, however, their electrochemical performances are very different. Compared to L-E/D and LP30, TEG has much higher viscosities and lower ionic conductivities. However, much higher capacity retention is achieved during cycling with TEG. Different film-forming abilities might be one reason for the observed differences in electrochemical activity, as will be discussed in the following part of this manuscript.

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**Table 1**

Overview of the used electrolyte compositions.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LP30</td>
<td>1 M LiPF&lt;sub&gt;6&lt;/sub&gt; in 1:1 ethylene carbonate:dimethyl carbonate (Merck, battery grade)</td>
</tr>
<tr>
<td>L-E/D</td>
<td>1 M LiTFSI (Merck) in 1:1 ethylene carbonate (Merck): dimethyl carbonate (Merck)</td>
</tr>
<tr>
<td>TEG</td>
<td>1 M LiTFSI (Merck) in 1,1,2,2-tetramethoxyethane (Weylchem)</td>
</tr>
<tr>
<td>TMG</td>
<td>1 M LiTFSI (Merck) in 1,1,2,2-tetramethoxyethane (Weylchem)</td>
</tr>
</tbody>
</table>

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![Fig. 2](image-url). (a) Cycling stabilities and (b) coulombic efficiencies of Si/Gr electrodes cycled in TMG (blue), TEG (black), L-E/D (green), and LP30 (pink) electrolytes.
3.2. SEI analysis

Glyoxalic acetal decomposition products. To analyze the properties of TMG and TEG film formation, solid decomposition products of these electrolytes are characterized by XPS and used as the basis for all XPS analyses to follow. Fig. 4 shows the C1s spectra of Si/Gr electrodes in their pristine state, as well as after the first lithiation with TMG and TEG electrolytes. The spectrum of the pristine electrode demonstrates peaks corresponding to the electrode material, namely graphite (284.6 eV) and -CO\_2\_Li-groups of the LiPAA binder (288.4 eV). Hydrocarbons associated with both adventitious carbon and LiPAA emerge at 285 eV. After lithiation in the respective glyoxal electrolytes, four peaks are observed: -CH (285 eV), -C-O (286.5 eV), -CO\_2 (i.e., carboxylic -C(=O)O environment at 289 eV), and -CO\_3 (i.e., carbonate -O(C=O)O environment at 290.4 eV). While the formation of carbonates upon reduction of glyoxalates might seem unusual, electrochemical reactions of e.g., CO\_2 and lithium are possible. Carbonate species are known to form by reaction of CO\_2 with lithium [42]. Furthermore, the binding energy of 290.4 eV is typical for carbonate environments. Another indicator is a relation close to 1 between the atomic percentages of -C=O species detected in the C1s and the O1s spectrum (see Table S1 for more information).

SEI thickness. The SEI thickness was determined by an approximation in which the graphite C1s intensity of a pristine electrode is divided by the graphite C1s intensity after cycling, see Fig S1. Thereby, an attenuation value is obtained which indicates how much the intensity of the graphite signal is weakened by the SEI layer. The thus obtained SEI thickness approximations or attenuation values at different potentials during the first lithiation (i.e., at 2.5 V, 1.3 V, 0.9 V, 0.5 V, and 0.01 V) as well as after the 1\textsuperscript{st}, the 10\textsuperscript{th}, and 100\textsuperscript{th} cycle (all in the delithiated state at 1.5 V) are displayed in Fig. 5. The formation potentials are motivated by specific minima in the differential capacity plots of Fig. S2.

During the first lithiation at 2.5 V and 1.3 V, less graphite is detected for cells containing LiTFSI-salt i.e., TMG, TEG, and L-E/D. In presence of LiPF\_6 (i.e., LP30 electrolyte) the detected graphite intensity is higher. However, only small changes are observed in the attenuation between these two potentials, which indicates similar surface layer thicknesses. At 0.9 V, the observed attenuation values decrease in all four cases from around 0.9 - 0.6 to 0.5 - 0.3 indicating an increase in layer thickness. This increase coincides with the electrochemically observed onset of electrolyte decomposition (i.e., 1.5-1.0 V vs. Li/Li\textsuperscript{+}) seen in Fig. S3. The attenuation values continue to drop at 0.5 V to below 0.2 for TMG and TEG. In comparison, both carbonate-containing electrolytes, L-E/D and LP30 display higher attenuation values and therefore a thinner SEI layer. At 0.01 V, no graphite is observed for any electrolyte. Thus, the SEI is thicker than 5-10 nm, which corresponds to the probing depth of the x-ray photoelectron spectrometer. After the 1\textsuperscript{st} delithiation, graphite reappears in the case of TMG, TEG, L-E/D, and LP30. Such SEI layer thickness increase during lithiation and decrease during delithiation is already known in literature. Especially in presence of silicon, the SEI layer is known for such a “breathing behavior” [43-45]. It can be explained by a mechanical instability of the SEI during the silicon volume decrease from the lithiated to the delithiated state. Thereby, graphite is re-exposed and can be detected via XPS due to emerging cracks in the SEI or parts of it detaching or dissolving into the electrolyte. After 10 cycles, no graphite is observed for TMG and TEG while it is still being detected for L-E/D and LP30. There can be two reasons for this observation: 1) glyoxal-based electrolytes decompose to a stronger degree, which would lead to a faster SEI coverage of the electrode, or 2) glyoxal-based electrolyte accommodate to the electrode volume changes to a higher degree. After 100 cycles, graphite disappears in all cases suggesting a considerable SEI layer is build-up during longer cycling. Overall, the electrolyte solvent seems to play a more important role.
in SEI thickness than the electrolyte salt. We detect higher similarities between the same group of electrolyte solvents than we do for the same electrolyte salt. The SEI thicknesses of electrolytes containing carbonate solvents (i.e., LP30 and L-E/D) are more comparable to each other, as are the thicknesses between electrolytes containing glyoxal solvents (i.e., TMG and TEG). In contrast, the thicknesses of LiTFSI-containing TMG, TEG, and L-E/D are much less comparable. Also, TMG and TEG show similar absolute values and trends in attenuation, which would suggest similar SEI thicknesses during the first ten cycles. Possible changes in SEI thickness upon longer cycling, especially when the achievable capacities and thus the amount of active material being (de) lithiated differ significantly from each other, cannot be detected because of the limited probing depth of XPS (i.e., 5-10 nm).

**Evolution of SEI composition during formation.** To understand the SEI formation in the investigated electrolytes, electrodes were cycled up to 2.5 V, 1.3 V, 0.9 V, 0.05 V, and 0.01 V in the first cycle, and subsequently analyzed via XPS. C 1s spectra are displayed in Fig. 6 and the atomic percentages derived from these data are summarized in Fig. 7. The corresponding F1s spectra and the atomic percentage evaluation are presented in Figs. 8 and 9, respectively. N1s, O1s, P2p, and S2p spectra can be found in the supporting information, Figs. S4-6. An overview of all detected species can be found in Tables S2-5. Assignment of different surface species follows previous reports in literature [46, 47].

**Solvent decomposition.** The C1s spectra of Fig. 6 show electrodes cycled in TMG and TEG electrolyte to display very similar C 1s spectra at 2.5 V and 1.3 V. Six peaks are observed in each spectrum: graphite (284.8 eV) with its corresponding $\pi \rightarrow \pi^*$ shake-up (290.8 eV), hydrocarbons (285 eV) caused by LiPAA, adventitious carbon and in case of TEG also by -CH groups, H$_2$C-O- or H$_3$C-O-groups (286.5 eV) resulting from the TMG and TEG solvent respectively, -CO$_2$ groups (carboxylic environment at 289 eV) of the LiPAA binder, and -CF$_2$ groups (293.4 eV) caused by the LiTFSI salt. The -O-C-O-groups of both the TEG and TMG molecules cannot be seen in the C1s spectra due to the low amount of TEG and TMG present on the surface. At these voltages, the measured electrolyte components (i.e., TEG or TMG solvent and LiTFSI salt) most probably correspond to solvent and electrolyte salt residues and not to electrolyte decomposition products. Electrolyte solvent residues might derive from the electrode washing process. TEG and TMG are used as washing solvents after cycling. As they have high vapor pressures, the respective solvent might not completely evaporate, and a small residue remains on the surface.

At 0.9 V, a distinct difference in surface composition is observed. A new peak emerges corresponding to -CO$_3$ (290.4 eV). Hydrocarbons, -C-O, and -CO$_2$-containing compounds are increasing in intensity, while the graphite intensity is decreasing. These observations indicate the decomposition of the glyoxal solvents. When lowering the potential further down to 0.5 V and 0.01 V, the SEI components continue to increase, while graphite decreases in intensity. In the fully lithiated state, the SEI is so thick that no more graphite is detected. Here, the C1s spectra are dominated by hydrocarbons (~22 at.%), see Fig. 7. Overall, TEG and TMG display very similar C1s spectra as well as atomic percentages of the different carbon surface species.

C1s spectra of electrodes cycled in the two reference electrolytes LP30 and LiTFSI-EC/DMC show four peaks at 2.5 V, corresponding to graphite (284.4 eV) with the corresponding $\pi \rightarrow \pi^*$ shake-up (290.8 eV), adventitious carbon and -CC/CH groups at 285 eV, and -CO$_2$-groups of the LiPAA binder (288 eV). L-E/D shows an additional peak corresponding to -CF$_2$ groups of the LiTFSI salt (293.3 eV). Substantial changes in the C1s spectra can be observed for both reference electrolytes when the cell potential is lowered to 0.9 V. At this stage, a decrease in graphite intensity is detected, while the intensities for hydrocarbons and -CO$_2$-groups are increasing. The -CO$_2$-groups now correspond to EC/DMC decomposition products, rather than to the LiPAA binder. Furthermore, two new peaks are observed corresponding to -C-O (286.5 eV) and -CO$_2$-groups (290.3 eV) of EC/DMC decomposition products. The -C-O-component at 286.5 eV could also be attributed to carbon neighboring a carbonate group (i.e. -CO$_3$-), as is the case for alkyl-carbonates [48]. Alkyl-carbonates such as lithium ethylene glycolates...
dicarbonate are typical degradation products of carbonate-containing electrolytes \[42, 49\]. At 0.5 V and 0.01 V, all SEI components continue to increase in intensity, indicating ongoing electrolyte solvent decomposition. The amount of detected graphite further decreases and disappears completely in the fully lithiated state. A previous XPS study on graphite electrodes showed comparable SEI evolution over cycling for both L-E/D and LP30 electrolytes, respectively \[50\].

Both glyoxal- and carbonate-based solvents show initial SEI formation between 1.5 V and 0.9 V, which is also supported by the dQ/dE plots in Fig. S2. In the fully lithiated state, they display similar amounts of hydrocarbons, while -C-O compounds are more abundant for L-E/D and LP30. The -CO\(_2\) species are similar for TMG, TEG, and LP30, while -C-O compounds are more abundant for L-E/D. Carbonate-containing compounds are more abundant for the LiTFSI containing electrolytes, i.e., TMG, TEG, and L-E/D but less present for the LiPF\(_6\) containing LP30.

Salt components and decomposition. LiTFSI is suggested to be reduced via the intermediate product LiSO\(_2\)CF\(_3\) to a combination of LiF, Li\(_2\)S, Li\(_2\)S\(_2\)O\(_4\), Li\(_2\)SO\(_3\), and Li\(_2\)SO. It was further proposed for LiTFSI to form C\(_2\)F\(_x\)Li\(_y\)-like compounds \[53\]. In Fig. 8, F1s spectra of cells cycled in TMG and TEG display two peaks corresponding to -CF\(_3\) (689.1 eV) and LiF (685.1 eV). At higher potentials such as 2.5 V and 1.3 V, the -CF\(_3\) peaks most probably correspond to residual LiTFSI electrolyte salt. At lower voltages, the LiTFSI-CF\(_3\) peak overlaps with possible -CF\(_3\) containing decomposition products. However, we cannot differentiate between -CF\(_3\) groups which correspond to either salt or salt decomposition products. As can be seen in Tables S2-4, the ratio of -CF\(_3\), -N-SO\(_2\), and -SO\(_2\) match the ratios observed in LiTFSI. This increases the possibility for -CF\(_3\) to belong to the LiTFSI salt. Because the intensity is normalized to a scale of 0 to 1, changes in the detected -CF\(_3\) species cannot be readily analyzed from the shown graphs. Therefore, the absolute atomic percentages displayed in Fig. 9 are examined. At higher potentials (i.e., from 2.5 V to 0.5 V), both LiTFSI-containing TMG and TEG electrolytes demonstrate only small changes in atomic percentages of the -CF\(_3\) species. In the fully lithiated state at 0.01 V, both display a decline in the detected -CF\(_3\) amount of 10 at.%. This suggests a stronger reduction of LiTFSI to LiF. Indeed, the relative intensity of the LiF peak increases from 2.5 V to 0.01 V for both TMG and TEG electrolytes, while only small changes are observed in atomic percentages. Compared to TEG, TMG displays higher LiF amounts at each investigated potential, indicating higher LiTFSI-salt decomposition with this electrolyte. No C\(_2\)F\(_x\)Li\(_y\)-like compounds are observed. S2p spectra in Fig. S6 of electrodes cycled in TMG and TEG display an intensive doublet at 169.3 eV which corresponds to the -SO\(_2\) group in the LiTFSI-salt. The second doublet at 167 eV is ascribed to oxidized sulfur species such as -SO\(_x\). Some works also assigned this species to Li\(_2\)SO\(_3\) components \[53\]. During formation no additional sulfur decomposition products such as Li\(_2\)S, Li\(_2\)S\(_2\)O\(_4\), Li\(_2\)SO\(_3\), or Li\(_2\)SO are detected. N1s spectra in Fig. S5 display a peak at 399.8 eV corresponding to N-SO\(_2\) groups. At 0.01 V, cells cycled TEG show an additional peak at 397.5 eV corresponding to Li\(_3\)N. With TMG, no such component is observed.

Cells cycled in the L-E/D reference electrolyte display two peaks corresponding to -CF\(_3\) (689 eV) and LiF (685.1 eV) in Fig. 8. At 0.01 V, an additional peak emerges, which can be ascribed to groups in C\(_2\)F\(_x\)Li\(_y\)-like compounds \[53\]. Compared to the -CF\(_3\) peak at 689.1 eV, these -CF\(_3\) components emerge at much lower binding energies of 687 eV. We explain this by the absence of neighboring -NSO\(_2\) groups. Interestingly,
both glyoxal-based electrolytes do not display this species. Similar to TMG and TEG, L-E/D shows an increase in the relative intensity of LiF from 2.5 V to 0.01 V. Also, S2p spectra exhibit two doublets at 169.5 eV corresponding to -SO\textsubscript{2} from 2.5 V to 0.01 V. The error bars indicate the standard deviation between two measurements on one electrode.

Fig. 7. Atomic percentages of detected SEI species -CH, -C-O, -CO\textsubscript{2} and -CO\textsubscript{3} of electrodes cycled in TMG, TEG, L-E/D, and LP30 electrolyte at 2.5 V, 1.3 V, 0.9 V, 0.5 V, and 0.01 V. The following species are found at the electrode surface for all four electrolytes, see Fig. 10: hydrocarbons (285 eV), -C-O groups (286.5 eV), -CO\textsubscript{2} groups (288.9 eV), and -CO\textsubscript{3} groups (290.4 eV). Electrodos cycled in TMG, TEG, and L-E/D show an additional peak at 293.2 eV corresponding to -CF\textsubscript{3} groups resulting from the remaining LiTFSI salt as previously discussed in the formation analysis part of this manuscript. Upon cycling, TMG and TEG display very similar trends in atomic percentages. While -C-O components remain at around 4 at.% throughout all 100 cycles, hydrocarbons, -CO\textsubscript{2}, and -CO\textsubscript{3} groups increase in abundance. This suggests TMG and TEG solvents to be decomposing to -CH, -CO\textsubscript{2} and -CO\textsubscript{3} containing products upon prolonged cycling. After 100 cycles, a higher abundance in -CO\textsubscript{3} species is observed for TMG than for TEG. Similarly, -CO\textsubscript{3} components are increasing when cycling in L-E/D. However, -C-O components also increase while a decrease is observed for -CO\textsubscript{2}. For L-E/D, a much stronger increase in -C-O and -CO\textsubscript{3} species is observed. Cells cycled in LP30 exhibit an increase in hydrocarbons and -CO\textsubscript{3} compounds upon cycling. The amount of detected -C-O and -CO\textsubscript{3} however stays very similar between the 1\textsuperscript{st} and the 100\textsuperscript{th} cycle. However, the SEI formed by LP30 exhibits the highest abundance in -CO\textsubscript{3} out of all electrolytes.

In a similar way to the observation made for SEI formation, the composition of the organic part of SEI is affected by the electrolyte solvent during aging. SEIs formed in glyoxal-based electrolytes TMG and TEG display very similar compositions that are more abundant in hydrocarbons. By contrast, both SEI layers derived from carbonate-based electrolytes show higher contents of -C-O and -CO\textsubscript{3} species, which is expected for carbonate-based electrolytes [42].

Salt decomposition. The decomposition products of the different electrolyte salts LiTFSI and LiPF\textsubscript{6} can be followed in the F1s spectra displayed in Fig. 12. As seen during the SEI formation, two peaks are detected when cycling in TMG or TEG, namely LiF and -CF\textsubscript{3}. While -CF\textsubscript{3} decreases upon cycling, the amount of detected LiF increases for both electrolytes from the 1\textsuperscript{st} to the 10\textsuperscript{th} cycle (i.e., 18 at.% for TMG and 10 at.% for TEG, see Fig. 13). After 100 cycles, LiF decreases by 14 at.% for TMG and 9 at.% for TEG. In all cases, TMG displays higher LiF abundance than TEG, indicating higher salt decomposition for the TMG electrolyte. In addition to fluoride-containing decomposition species, TMG and TEG show emerging LiF\textsubscript{3} (397.4 eV), -SO\textsubscript{2} or LiSO\textsubscript{2} (167.3 eV), and additional sulfur decomposition products (~163.9 eV and 161.8 eV), see Figs. S8 and S9. These additional sulfur decomposition products are already present after the 1\textsuperscript{st} cycle with TMG, while they only emerge after 100 cycles with TEG. This observation might be explained by TEG forming a more stable SEI and suppressing LiTFSI salt decomposition to a stronger extent.

The F1s spectra of cells cycled in the L-E/D reference electrolyte display three peaks as already seen after 0.01 V, corresponding to -CF\textsubscript{3}, C\textsubscript{2}F\textsubscript{5}Li\textsubscript{3}, and LiF species. Upon cycling, the amount of detected LiF increases by 11 at.% from the 1\textsuperscript{st} to the 10\textsuperscript{th} cycle. Unlike TMG and TEG, the amount of LiF does not drop upon continued cycling but stays at around 12 at.%.

Evolution of SEI composition during aging: To investigate SEI aging in the different electrolyte systems, XPS was conducted after 1, 10, and 100 cycles on electrodes in the delithiated state (i.e., at 1.5 V). Fig. 10 shows the C 1s spectra of electrodes cycled in TMG, TEG, L-E/D, and LP30 electrolyte, respectively. Derived atomic percentages from these data are summarized in Fig. 11. F1s spectra are displayed in Fig. 12 with corresponding atomic percentages in Fig. 13. Spectra of the remaining elements O1s, N1s, P2p, and S2p can be found in the supplementary information Fig. S7-9. An overview of all detected species can be found in Tables S2-5.

Salt decomposition. The following species are found at the electrode surface for all four electrolytes, see Fig. 10: hydrocarbons (285 eV), -C-O groups (286.5 eV), -CO\textsubscript{2} groups (288.9 eV), and -CO\textsubscript{3} groups (290.4 eV). Electrodos cycled in TMG, TEG, and L-E/D show an additional peak at 293.2 eV corresponding to -CF\textsubscript{3} groups resulting from the remaining LiTFSI salt as previously discussed in the formation analysis part of this manuscript. Upon cycling, TMG and TEG display very similar trends in atomic percentages. While -C-O components remain at around 4 at.% throughout all 100 cycles, hydrocarbons, -CO\textsubscript{2}, and -CO\textsubscript{3} groups increase in abundance. This suggests TMG and TEG solvents to be decomposing to -CH, -CO\textsubscript{2} and -CO\textsubscript{3} containing products upon prolonged cycling. After 100 cycles, a higher abundance in -CO\textsubscript{3} species is observed for TMG than for TEG. Similarly, -CO\textsubscript{3} components are increasing when cycling in L-E/D. However, -C-O components also increase while a decrease is observed for -CO\textsubscript{2}. For L-E/D, a much stronger increase in -C-O and -CO\textsubscript{3} species is observed. Cells cycled in LP30 exhibit an increase in hydrocarbons and -CO\textsubscript{3} compounds upon cycling. The amount of detected -C-O and -CO\textsubscript{3} however stays very similar between the 1\textsuperscript{st} and the 100\textsuperscript{th} cycle. However, the SEI formed by LP30 exhibits the highest abundance in -CO\textsubscript{3} out of all electrolytes.

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10 nm of the SEI can be probed with the here used laboratory x-ray aluminum source, differences in composition of deeper layers cannot be identified. Nevertheless, the here observed increase of organic species in the outer SEI layer is known in the literature. It has been repeatedly observed for the outer SEI layer to consist of more organic layer, whereas the inner layer is more inorganic in nature [42, 58].

**SEI and electrode morphology.** SEM images of a pristine Si/Gr electrode and electrode surfaces after 100 cycles are presented in Fig. 14. The uncycled electrode of Fig. 14(a) displays graphite as large rectangular-shaped particles, silicon as small and round shapes spread into different agglomerations, and carbon nanofibers as long tubes. After 100 cycles, all surfaces display pronounced changes in electrode morphology. In the case of TMG, L-E/D, and LP30 graphite particles are covered with electrolyte decomposition products. The previously sharp graphite edges are covered by bright and small particles, that are either closely sticking together or forming intricate networks. Corresponding magnifications show a strong SEI coverage of graphite, carbon nanofibers and silicon particles. However, it is difficult to differentiate between silicon particles and electrolyte decomposition products such as LiF. For all three cases, the surface morphology is very rough, suggesting continuous breaking and reformation of the SEI layer.

By contrast, the surface of the electrode cycled in TEG is covered by a smooth SEI film, which makes it difficult to distinguish between separate graphite particles. This difference in electrode surface morphology is also observed in the magnification, suggesting an extensive coverage of the electrode material. Furthermore, the SEI film does not exhibit obvious cracks, suggesting that TEG forms an SEI with an increased ability to accommodate to the volume changes of the Si/Gr electrode.

**Correlating film-forming properties to electrochemical performance.** In this study, we kept all experimental parameters the same except for the electrolytes. Therefore, the differences in cycling stability and SEI properties between Si/Gr electrodes can be related to the electrolyte formulations. The reference carbonate-based electrolytes showed similar capacity profiles with a pronounced capacity decrease after 20 cycles. Also, very similar retentions could be achieved after 100 cycles, indicating a loss in both silicon and graphite electrochemical activity. As can be expected of an SEI formed by the same carbonate-solvents (i.e., EC and DMC), the organic part of the SEI is very similar. The same species are detected, namely -CH, -C-O, -CO₂, and -CO₃. Furthermore, LiF is the main electrolyte salt decomposition product for both
electrolytes. The observed changes in the abundance of the SEI species are not always identical, however, the following trend is observed: Upon cycling, the amount of detected LiF decreases, while an increase is seen for -C-O, and -CO$_2$ containing species. Also, changes in SEI thickness are comparable. After 10 cycles, the electrode material is still observed in the delithiated state. This suggests L-E/D and LP30 to be forming an SEI that is less stable upon the electrode volume changes as it breaks apart and reveals new electrode material. SEM pictures of electrode surfaces after 100 cycles show a very rough SEI film, indicating high mechanical strain as well as pulverization of the electrode material.

The investigated glyoxal-based electrolytes TMG and TEG only differ by a methyl group in the solvent molecule. Still, very different cycling profiles are observed. Cells cycled in TMG exhibit worse electrochemical performance than TEG and the two carbonate-bases electrolytes. A dramatic decrease of both silicon and graphite activity is already observed in the first 10 cycles. By contrast, TEG outperforms L-E/D, and LP30. While small losses are observed in silicon activity, graphite can completely retain its electrochemical activity. While small losses are observed in silicon activity, graphite can completely retain its electrochemical activity. Contrary to their obvious differences in electrochemical performance, TEG and TMG display similar trends in SEI composition and initial thickness, as seen with XPS. The SEI thickness evolution during long term cycling cannot be accurately estimated with XPS for these systems as in both cases, no bulk signal can be observed after the first cycle anymore, indicating an SEI thickness larger than the XPS probing depth. Concerning the SEI composition, the same functional groups are observed within the probed volume, namely -CH, -C-O, -CO$_2$, -CO$_3$, LiF, and -SO$_x$/Li$_2$SO$_3$. Throughout the first formation cycle, the abundance of these compounds changes in a very similar way, suggesting the generation of comparable initial SEI films. While the amount of detected -CH, -C-O, and -CO$_2$ remains very similar for TEG and TMG, the following differences are observed when cycling in TMG-based electrolyte: 1) earlier LiTFSI salt decomposition, as seen in additional sulfur decomposition products from the 1$^{st}$ cycle on. These are not observed for the SEI formed by the TEG electrolyte, 2) higher LiF amounts are detected after 10 and 100 cycles, and 3) more carbonate species are detected after 100 cycles. The earlier and stronger salt decomposition with TMG as electrolyte solvent may indicate poor SEI stability. It should also be noted that the XPS probing depth is limited and possible divergences in deeper SEI layers cannot be detected. To analyze deeper layers, experiments such as sputtering or synchrotron...
measurements can be conducted, which are beyond the scope of this work. While XPS showed a more similar trend in SEI composition and initial thickness for TMG and TEG, SEM displays evident differences in the SEI morphology. With TMG a more fractured and rough surface morphology is observed, indicating repeated breaking of the SEI layer upon cycling. This further indicates a poor film forming ability of TMG on the Si/Gr anode. By contrast, TEG forms an SEI layer with a very interconnected coverage, suggesting a higher ability to adjust to the volume changes of the Si/Gr electrode. Alongside SEI formation on the Si/Gr anode, it is important to scrutinize the film-forming abilities of TEG and TMG on the lithium metal counter electrode. We observe that TMG shows higher reactivity against the lithium metal counter electrode than TEG. Fig. S10(1a) of the supporting information shows that after 100 cycles in TMG, the lithium counter electrode is completely black, very brittle, and contains almost no metallic lithium. This most likely results from poor lithium metal passivation by the TMG solvent. By contrast, the lithium electrode cycled in TEG, still displays a high amount of metallic and thereby electrochemically active lithium. The bigger size of the ethoxy groups in TEG could reduce reactions between the electrode and electrolyte due to steric hindrance. Such steric effects have been observed with other methoxy and ethoxy containing solvents [59,60].

In summary, TMG shows poor film-forming abilities on both lithium-metal electrodes and Si/Gr electrodes, explaining its poor electrochemical performance. When using TEG, a more stable interphase is formed on both electrodes. Our results further indicate that the good electrochemical performance of Si/Gr electrodes in TEG electrolytes might be related to the formation of an SEI that accommodates the silicon volume changes more easily.

4. Conclusion

In this work, we investigated the first use of glyoxal-based electrolytes (i.e., 1 M LiTFSI in TMG and 1 M LiTFSI in TEG) in combination with silicon-containing anodes. Two reference electrolytes LiTFSI-EC/DMC (L-E/D) and LiPF6-EC/DMC (LP30) were analyzed in comparison. We showed that while the cell cycled in TMG performed worse than cells cycled in the reference electrolytes L-E/D and LP30, the cell cycled in TEG exhibited a much more stable capacity profile with overall higher capacities. The poor performance of TMG was related to a dramatic drop in both graphite and silicon activity after already 10 cycles. XPS did not supply a conclusive indication (in terms of SEI compositions and thicknesses) as to why TEG outperformed TMG so significantly, besides a more pronounced LiTFSI salt decomposition when using TMG as the solvent. Thus, future work will address the reactivity of TMG and TEG versus lithium metal and study glyoxal-based electrolytes in full cells. Analysis of the electrode morphology revealed TEG to form a smoother and continuously connected SEI. This surface layer most probably has higher ability to accommodate the silicon volume changes upon cycling, rendering TEG a very promising electrolyte candidate for realizing silicon-containing anodes with high capacity and high stability. Even without SEI stabilizing electrolyte additive or ionic conductivity enhancing co-solvent, TEG showed enhanced electrochemical performance with Si/Gr anodes compared to the standard LP30. Future studies will concentrate on further improving electrolytes based on TEG to become true alternatives to current commercial electrolytes with improved safety, environmental friendliness, and reduced toxicity.
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L.G. and J.M oversaw the project; L.G. carried out the experiments and discussed the results with J.M., F.J. and A.B.; C.L. and A.B. provided the resources (TMG & TEG electrolytes); K.P. conducted SEM measurements, L.G. wrote the preliminary draft, all authors contributed to interpreting the results and reviews and revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials


References


Fig. 14. SEM pictures of a pristine Si/Gr electrode (a) and after 100 cycles in TMG (b), TEG (c), L-E/D (d), and LP30 (e) electrolyte.


