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Thermal behaviour of the lithiated-graphite/electrolyte interface through GC/MS analysis

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A B S T R A C T
The risk of thermal runaway is, for Li-ion batteries, a critical issue for large-scale applications. This compels manufacturers to find suitable materials or additives, which are able to minimize the heat generation and thereby mitigate safety-related risks. In an attempt to get more insight and understand the exothermic processes that take place at the negative electrode/electrolyte interface, we implemented GC/MS analytical technique to detect volatile compounds. Based on a mechanistic study, we propose a general electrolyte degradation scheme in the 100–250 °C temperature range, involving electrolytically driven carbonates reduction followed by chemical reactions. The mechanisms for decomposition deduced from these analyses shed new light on the processes involved in the formation of the precipitated (SEI layer) and soluble molecules upon cell formation cycles and ageing.

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1. Introduction

Li-ion batteries are now used in a vast array of portable electronics but have a history of erratic fire incidents when damaged or abused. Manufacturers are now having a serious look at the safety of large batteries destined to electric transportation; this is needed to ensure safe operation, but also during storage, transport and recycling. Underscoring the aforementioned challenges, there is a worldwide effort by research institutions to design new chemistry of materials that withstand abuse conditions. In this context, a worldwide research effort is devoted to minimize the runaway risk induced by electrical factors (long-term cycling, high rate, overdischarge or overcharge), temperature and mechanical damage (external or internal shorts after a crash, water ingress) [1,2]. Most large conventional Li-ion cells use a carbon-based negative electrode, a spinel-type structure LiMn2O4 (LMO) or mixed with a layered LiNi1/3Mn1/3Co1/3O2 (NMC), LiNi0.8Co0.15Al0.05O2 (NCA) oxide for the positive; LiFePO4 (LFP) is another alternative positive; the liquid electrolyte is invariably LiPF6 dissolved in carbonates solvents, though volatile and flammable. As the 4V cell working voltage extends beyond the electrochemical stability window, a beneficial layer of degradation/reduction products (solid electrolyte interphase) is formed at the surface of the negative electrode material allowing cell operation.

The Li-ion thermal runaway phenomenon, usually studied by means of differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC) [3–8], can result in gas release [9], overpressurization and rupture of the battery casing. This phenomenon has been studied over the last twenty years giving rise to a valuable comprehensive survey of materials, morphology and role of electrolyte additives (vinylene carbonate, vinyl ethylene carbonate, fluoro ethylene carbonate, 1,3-propane-sultone as solvents, oxalatotetrafluorophosphate as salt, etc.) [10–15] that modify the exotherm onset temperature. Authors usually describe a heat-releasing multi-stage process starting at the negative electrode around 110 °C. The SEI layer cracks or decomposes, giving direct electrolyte/LiC6 contact. Later, around 300 °C, the negative electrode binder, if PVDF, will be reduced by residual lithium if still present in carbon. At the positive electrode, starting at ≈230 °C, oxygen is released from the delithiated positive electrode material and is consumed through carbonate solvents oxidation to form water and CO2; the release temperature and the amount of oxygen depend highly on the material type (LMO < NMC < NCA, no O2 release for LiFePO4) [16–22]. Finally, the full decomposition of materials occurs beyond 300 °C that adds to the exothermic events. From all of these reactions, SEI decomposition is the first exothermic phenomenon. Recently, K. Amine’s group [23] studied its kinetics through activation energy calculation and found that

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it varied, according to the graphitized carbons type, from 50 to 100 kJ mol⁻¹; the assumption was put forward that the local morphology at the edge of graphite or the functional surface groups may play a key role in determining the kinetics of SEI decomposition.

In this article, as a fundamental work, we chose to start focusing on the chemical reactions involved at the LiC₆/electrolyte interface without binder, in the 100–250 °C temperature range. The thermal activity was followed by DSC and volatile compounds evolved from the LiC₆/electrolyte reaction were analysed by means of GC/MS. Further, with a mechanistic study, we propose an overall electrolyte degradation scheme, involving electrochemically driven carbonates reduction followed by chemical reactions.

2. Experimental

2.1. Cells assembling and cycling

The studied negative active material is composed of 90 wt% of SFG6 graphite (particle size of 6.5 μm (d₅₀) and BET surface area of 17 m²/g) and 10 wt% Super P carbon black. The electrolyte composition was 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (50/50, w/w) from commercial sources known as LP30® (Merck). The Swagelok-type half-cells were assembled in an argon-filled glove-box using 10–15 mg composite powder as working electrode, an electrolyte-impregnated Whatman GF/D borosilicate glass fibre separator and a lithium metal foil. Once assembled, the cells were subjected to a C/20 galvanostatic discharge (forming LiC₆) or a discharge/charge (delithiation forming LiₓC₆) at 20 °C. The cells were cut off at 0.01 V (lower) or 1.5 V (upper) vs. Li⁺/Li⁻, respectively.

EC–DMC/LiPF₆ electrolyte (LP30) and DMC solvent SelectiLyte® were purchased from Merck. The lithium alkyl carbonates were synthesized using a described procedure [24].

2.2. DSC conditions

DSC measurements were performed using a DSC204F1 Netzsch calorimeter, at a heating rate and constant argon flow of 10 °C/min and 200 mL/min respectively. Immediately after the charge (delithiation) or discharge (lithiation), the cells were disassembled and the powder samples, which were either washed with DMC or not, were placed into an aluminium crucible before sealing inside an argon-filled glove box (O₂ and H₂O < 0.1 ppm). To keep isobaric condition throughout the DSC measurement, the sealed capsules were pierced once they were introduced in the DSC machine, which was flushed with argon to avoid any interference with trapped air or moisture. To ensure reproducibility, two DSC measurements were conducted on each sample with similar quantities.

2.3. GC/MS conditions

2.3.1. GC conditions

The loaded DSC crucible was pierced inside the glove box before being immediately placed into a laboratory-designed stainless steel cell. This cell was introduced in a furnace heated from room temperature to final experimental temperature (80, 140 or 200 °C) at 10 °C/min then maintained at this temperature for 3 h. Then, the evolved gases were transferred to a heated six-port, 2 positions valve (Valco®) equipped with an injection loop [32]. The filling time of this loop was adjusted to reach a constant sample volume of 0.5 mL which was then transferred into the split/splitless injector maintained at 200 °C (with a split ratio of 10:1). Note that the separation of the highly volatile constituents required the use of a large film stationary phase column (20 μm) and of a post-capillary column to preserve the source from the well-known bleeding of this first column as well as from corrosive HF.

2.3.2. MS conditions

The GC was connected to an ITQ 1100 mass spectrometer. The transfer line was maintained at 250 °C. Calibrating of the mass spectrometer was done using perfluorotributylamine ionization fragments. The mass spectrometer was operated with a filament current of 250 μA and electron energy of 70 eV in the electron ionization (EI) mode. The ion source was set at 200 °C. The mass range was 10–300 u and data acquisition and processing were performed with Xcalibur 2.0.7 software. Compounds identification and corresponding structural formulae were assigned using the National Institutes of Standards and Technology (NIST) library.

3. Results and discussion

3.1. Thermal study of lithiated graphite in presence of electrolyte using DSC and GC/MS

3.1.1. DSC experiments

The DSC curve of the lithiated graphite LiC₆ in presence of its electrolyte (Fig. 1b) displays a broad multi-step exothermic signal spanning from 120 to 270 °C whose energy was calculated to be around 700 J/g of sample mass (the electrolyte representing roughly half the mass, as calculated from the difference of the crucible weight before and after heating experiments). This general behaviour is assigned in the literature to the reduction of electrolyte with the lithium stored in graphite after SEI cracking. This clearly explains why no phenomenon is observed on washed sample (Fig. 1d). The DSC curve (Fig. 1c) of the electrochemically delithiated graphite LiₓC₆ in presence of its electrolyte presents a weakly exothermic peak around 145 °C followed by a broad endothermic peak due to electrolyte behaviour as shown in Fig. 1a. Assuming the complete delithiation of the graphite, this
exothermic peak could be linked to the SEI decomposition as suggested by Du Pasquier et al. [5]. This hypothesis will be discussed in a forthcoming paper.

3.1.2. GC/MS experiments at 200 °C

To get deeper insight into the multi-step exothermic reactions, we undertook the analysis of the reduction products formed over the entire temperature range where exothermic peaks occur. The usual approach is to characterize the Li salts (Li₂CO₃, ROCO₂Li, LiF, etc.), oligomers or phosphorous derivatives precipitated at the electrode/electrolyte interface by means of powerful techniques such as XPS and valence band analysis, TOF-SIMS and IR. While the expediency of these techniques is indisputable [25–31], the need to develop complementary analytical techniques aiming at understanding the formation pathway and gases release phenomena [32,33] is also of great importance. Mindful of these concerns, we analysed the gases released upon heating the lithiated samples by using GC/MS, an in situ technique qualified to assess, post-mortem, the volatile degradation compounds desorbed from an electrolyte soaked separator [34].

Fig. 2 features the four GC/MS chromatograms corresponding to the samples analysed by DSC in Fig. 1, namely: the pristine electrolyte soaked in graphite composite; LiC₆ + the electrolyte used to effect the lithiation, the delithiated graphite Li₀C₆ + the electrolyte used for lithium removal; finally DMC-washed LiC₆ sample. Each chromatogram was obtained after heating the sample at 200 °C for 3 h and was found to be line with the thermal phenomena displayed in Fig. 1; the number of peaks in GC/MS spectra is proportional to the exothermic event in DSC measurement. Fig. 2a shows a predominant peak corresponding to the evaporation of DMC with a CO₂ trace, indicating a slight decarboxylation of alkylcarboxates at such temperature. It is worth recalling here that the EC solvent, the phosphates compounds and most of the fluorinated gases cannot be detected in these conditions because of their too low volatility.

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**Fig. 2.** GC/MS chromatograms of (a) electrolyte (LP30) soaked in graphite composite, (b) LiC₆ + the electrolyte used to effect the lithiation, (c) delithiated graphite Li₀C₆ + electrolyte used for lithium removal and (d) DMC-washed LiC₆, heated at 200 °C for 3 h.
or the presence of the post column trapping fluorine containing species reacting with siloxanes.

As expected from the highly energetic exothermic reaction, LiC₆ heated with the electrolyte generates numerous species (Fig. 2b). The absence of volatiles release (Fig. 2d) and of thermal event for DMC-washed LiC₆ prove that the SEI layer formed during the first electrochemical lithiation process does not decompose or the thermal event is too weak to be detected. On the other hand, Li₃C₆ in presence of electrolyte (Fig. 2c) reveals few peaks that could be linked to the small 140 °C exotherm claimed as pertaining to the SEI thermal decomposition and/or to soluble species formed during cycle. The identification of these peaks as well as their reaction mechanisms will be itemized in a following section.

3.1.3. GC/MS experiments on LiC₆ + electrolyte at different temperatures

As aforementioned, numerous volatile products arise from the exothermic reaction between LiC₆ and electrolyte. In an attempt to determine the successive reactions responsible for the broadening of the DSC peak signals, we performed two additional “gas” GC/MS analyses at 80 °C before the onset temperature and at 140 °C during the first predominant peak so as to be compared to the reported 200 °C tests (Fig. 3). The chromatogram obtained at 80 °C (Fig. 3a) reveals several peaks in addition to that of DMC; the three main ones correspond to the esters HCO₂CH₃ (methyl formate), CH₃CO₂CH₃ (methyl acetate) and C₂H₅O₂CO₂CH₃ (ethyl methyl carbonate – EMC). Therefore, these three products are formed during the first electrochemical lithiation and thus they are still found later in the LiC₆/electrolyte chromatogram (Fig. 2c). As far as the latter is concerned, the CO₂, methanol and dimethyl ether peaks are of higher intensity indicating they could stem from other reactions as the SEI decomposition or DMC decarboxylation occurring at high temperature. At 140 °C (Fig. 3b), aside from the compounds observed at 80 °C, other esters, ether and carbonate are identified as well as hydrocarbons; the highest peaks of this chromatogram corresponds to CO₂, ethylene oxide, methyl and ethyl formates, methyl acetate, DMC, EMC and DEC. The intensity of these peaks increases at 200 °C (Fig. 3c) and, notably, two peaks attributed to methanol and ethanol.

The gas GC/MS chromatograms together with the DSC curves bear evidence of thermally driven redox reactions between LiC₆ and electrolyte, giving rise to a reproducible series of volatile molecules, the reaction mechanisms of which we propose to elucidate hereafter.

3.2. Study of thermally driven reaction mechanisms between lithiated graphite and electrolyte

3.2.1. Mechanistic study for the formation of the degradation products

Scrutinizing the overall volatile molecules identified through GC/MS experiments, we were able to sort them out in five families, i.e. esters (methyl or ethyl formate, methyl formate or
acetate), hydrocarbons (C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4}), ethers (dimethyl ether, ethylene oxide, 1,4-dioxane, monoglyme, 2-methyl-1,3-dioxolane), carbonates (EMC, DEC), and alcohols (methanol, ethanol). As we were attempting to determine their formation pathway, we discovered they were ensuing from only two types of reaction: (i) a reduction process of linear or cyclic carbonate and (ii) a reaction involving nucleophilic attack, as schematized below.

**Reduction processes**

\[ \text{ROCO}_2\text{Li} + e^- \rightarrow \text{RO}^- + \text{Li}^+ + \text{ROCO}_2\text{Li} \]  

**Nucleophilic attacks**

\[ \text{ROCO}_2\text{Li} + \text{RO}^- \rightarrow \text{ROCO}_2\text{Li}^- + \text{RO}^- \]

The injection of one electron in the molecule leads to the formation of radical and anionic molecules. For instance, the reduction of DMC leads to CH\textsubscript{2}OCO\textsuperscript{•} or CH\textsubscript{3}\textsuperscript{•} radicals (Eqs. (1) and (2)) respectively which form, by recombination, esters or the alkane C\textsubscript{2}H\textsubscript{6} as well as lithium alkoxide ROLi and lithium alkyl carbonate RO\textsubscript{2}CO\textsubscript{Li} (Fig. 4) ionic compounds. The anionic carbonate-based molecules contribute to a SEI layer formation while the most electrolyte-soluble products, the alkoxides, can hydrolyse to form alcohols or trigger nucleophilic attacks. The attack by alkoxide of DMC gives rise to other carbonates (EMC, DEC) according to a transesterification reaction (Eq. (3)) or to the dimethyl ether along with RO\textsubscript{2}CO\textsubscript{Li} (Eq. (4)) salt formation.

Similar reduction processes starts with a single electron injection on EC, entailing the formation of radical anion molecules whose dimerization eventually leads to the dianionic salt (CH\textsubscript{2}OCO\textsubscript{2}Li)\textsubscript{2} with C\textsubscript{2}H\textsubscript{4} release (Eq. (7)). These radical anion molecules can undergo a second subsequent one electron reduction or an intra nucleophilic attack to yield ethylene oxide as well as lithium oxalate (Li\textsubscript{2}C\textsubscript{2}O\textsubscript{4}), lithium carboxylates (RO\textsubscript{2}CO\textsubscript{Li}) and lithium ethoxide salts after radicals recombination (Eq. (5) and (6)). The presence of H\textsuperscript{•} radicals coming from HF or H\textsubscript{2}O reduction allows the formation of lithium ethoxide molecules then EMC and DEC through transesterification. Finally, the sequential injection of two electrons on EC or DMC leads to Li\textsubscript{2}CO\textsubscript{3} and C\textsubscript{2}H\textsubscript{4} or C\textsubscript{2}H\textsubscript{6} respectively.

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**Fig. 4.** Global scheme of solvents degradation processes.
As we reported earlier [35,36], EC can also be subjected to a nucleophilic attack by RO− to form the “Intermediary A” (see Eq. (8)). There are three possible fates for this anion: (i) it attacks DMC (“a” attack) giving rise to the first compound [37] (DMDOHC called 11) of the PEO-based oligomers series (1n−6n) (n < 10) having carbonate, methoxy, or hydroxyl end-groups. The heaviest compounds have been clearly identified by means of ESI-HRMS [36] whereas the most volatile molecules, like the monoglyme, are only detected thanks to this gas GC/MS technique; (ii) according to Eq. (8), “Intermediary A” can attack its homologue (“b” attack) to form a lengthened anion which undergoes an intra-nucleophilic attack to yield 1,4-dioxane and RO2CO2Li. It must be stressed here that another pathway [34] was also suggested by us for the 1,4-dioxane and the 2-methyl-1,3-dioxolane molecules; The 62 compound (diethylene glycol) could undergo a high temperature-driven cyclo-dehydration in presence of H+ (from HF) to form both these molecules; (iii) the “Intermediary A” undergoes an intra-nucleophilic attack to yield RO2CO2Li and ethylene oxide.

In summary, a straightforward sequence of reaction mechanisms (Fig. 4) accounts for almost all the volatile molecules detected by gas GC/MS, namely the hydrocarbons, esters, ethers, alcohols and carbonates formed gradually upon heating LiC6 with electrolyte from ≈120 to 250 °C. It must be emphasized that two types of reaction, i.e. reduction followed by a chemical reaction account for the formation of volatiles as well as organic/inorganic salts. RCO2Li and Li2C2O4 require the recombination of LiCO2•

Nucleophilic attack b

Reduction: attack 1

Reduction: attack 2

Nucleophilic attack
radicals resulting from a reduction followed by another reduction or alternatively an internal nucleophilic reaction. Similarly ROCO₂Li and ROH formation can be the direct result of reduction, or of reduction followed by an internal nucleophilic attack. As for Li₂CO₃, it is the product of a two-step reduction process. It is quite conceivable that these salts are precipitating at the graphite surface upon heating, acting as an extra SEI layer (referred to as 2nd SEI layer in literature [5,38–42]), which could impede the redox processes then cracks and re-forms during the entire exothermic event. The appearance of the high concentration of MeOH and EtOH between 140 °C and 200 °C is likely originating from the decarboxylation of ROCO₂Li. The resulting lithium alkoxides can undergo hydrolysis to form these alcohols as well as initiate ether formation through nucleophilic attacks.

Around 200 °C we note, on the DSC curve (Fig. 1b), a noticeable heat generation and this phenomenon is likely due to exfoliation of LiC₆ providing fresh contact of electrolyte to lithiated carbon [43]. It must be stressed here that the global scheme (Fig. 4) deduced from the products detected during the LiC₆/electrolyte heating could also be applied to the electrochemical reduction processes taking place upon cycling. Hence, we compared these GC/MS chromatograms with those obtained from LP30 electrolyte soaked in separator recovered from a long-term cycled [44] negative electrode (Cr₂O₃ conversion reaction material)/Li half-cell at 55 °C, i.e. from electrochemically induced electrolyte reduction processes [34]. Fig. 5 regroups both the GC/MS traces for the same heating conditions, at 200 °C for 3 h.

3.3. Comparison between thermally and electrochemically induced reduction processes

Overall, despite a few missing species and different peak intensities, similar reaction mechanisms based on reduction and nucleophilic attacks can be invoked. Esters are present in both cases; though, the cycled cell electrolyte shows only the methyl derivatives HCO₂CH₃ and CH₃CO₂CH₃ that stem from DMC reduction (Eqs. (1) and (2)). Along with these species, CH₃CO₂Li and MeO Li salts are also formed. This latter is responsible for the ethers and MeF formation. The large dimethyl ether peak (Fig. 5a) can also be the result of DMC decarboxylation catalysed by PF₅, as this sample contains a large quantity of electrolyte.

Note that very few compounds as ETF and EMC contain the ethyl group originating from the two-step EC reduction. Their presence entails the formation of RCO₂Li (R = H or CH₃) and/or Li₂C₂O₄ [45,46] in the SEI layer. The relative high ethylene peak intensity would lead to the conclusion that, as often suggested in the literature, EC is mainly reduced through a two-electron reduction leaving Li₂CO₂ salt [47] and/or Li₂[O₂COC₂H₄OCO₂]. This very volatile gas is evolved in large quantity during the first cell cycles and contributes, together with C₂H₆, CH₄ and H₂ [48], to the swelling of the cell when cycled in abused conditions.

Finally, it is worth comparing also this long-term cycled cell electrolyte chromatogram with earlier chromatograms of the electrolyte with LiC₆ at 80 °C (Fig. 3a) and LiO Li at 200 °C (Fig. 2c). The three chromatograms display EMC and the esters HCO₂CH₃ and CH₃CO₂CH₂, which are formed during the electrochemical process, forming the SEI then solubilized in electrolyte. At 200 °C with LiO Li, the additional formation of methanol stems from CH₃CO₂Li decarboxylation.

However, we do not observe any ether formation induced by RO⁻ nucleophilic attacks in the lithiated (80 °C) and delithiated (200 °C) graphite samples. This could be explained by the quantity of ROH which is not enough to trigger such chemical reaction unlike the long-term cycling.

4. Conclusions

Complementing the DSC with a GC/MS technique has proven to be powerful in assessing the thermal behaviour of lithiated graphite in contact with classical carbonates-based electrolyte. This newly adopted analytical strategy consists in analysing the in situ gas release, providing insightful information on the reaction mechanisms. From two reaction types (reduction and nucleophilic, see Fig. 4) we can explain the formation of the majority of carbonates degradation products. Linear and cyclic solvent reduction leads to esters, hydrocarbons and alcohols that are miscible in the electrolyte, while lithium salts precipitate to build-up the secondary SEI, namely lithium carbonate, alkyl carbonates, oxalate and/or carboxylates and alkoxides. The latter yield ethers and carbonates through nucleophilic reaction.

The mechanisms for decomposition deduced from these analyses (Fig. 4) shed new light on the processes involved in the formation of the precipitated (SEI layer) and soluble molecules upon cell formation (first cycles) and ageing as well.

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