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Electrolyte decomposition and solid electrolyte interphase revealed by mass spectrometry

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ABSTRACT

Non-aqueous electrolyte liquids such as carbonate solvents have been widely employed in the commercial lithium-ion batteries and in the development of next-generation rechargeable batteries. The decomposition products of the organic electrolyte and additive molecules contribute to the formation of solid electrolyte interphases (SEIs) on the electrode surface, which have key impacts on battery's electrochemical performance. The rational engineering of electrolyte systems demands precise understanding of the electrochemical reaction pathways as well as the decomposition products of the electrolytes. Mass spectrometry (MS) is a well-established molecular analytical approach that can provide critical information for unambiguous structure assignment based on its mass-resolving power. In recent years, the application of MS for battery research has been expanding rapidly, providing valuable insights about the chemical species generated during battery operation and electrolyte evolution. This review aims to summarize the recent advances of MS technique-based analysis of electrolyte decomposition products as well as SEIs, and thus to demonstrate the high utility of MS methods for characterization of battery systems.

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1. Introduction

The demand for advanced rechargeable batteries grows rapidly in recent years because of the daily need of powering up digital devices, and more importantly, due to the fast-growing market of large-scale electricity storage for electric vehicles, renewable energies, etc. [1–3]. Therefore, the development of next-generation lithium-ion batteries (LIBs) with novel battery materials attracts tremendous research interest due to the high energy density potential of LIBs and their high compatibility with existing industry. For example, silicon (Si) is widely recognized as a promising anode material for LIBs because it theoretically has a high gravimetric capacity of 4200 mAh g^{-1} and is also readily available at large scale thanks to the well-established semiconductor industry [1, 4,5]. The prevailing electrolytes and additives used for LIBs are based on small organic molecules, such as ethylene carbonate (EC)/ethyl methyl carbonate (EMC) electrolytes and fluoroethylene carbonate (FEC) additive [1,6–8]. Such organic-based electrolyte systems are also commonly employed for other types of advanced batteries like lithium-sulfur battery [9–12], lithium-air battery [13,14], lithium metal battery [15–20], dual-ion battery [21], etc.

The rational engineering of the electrolyte systems is essential for the advanced batteries to fully achieve their theoretical capacities. The electrolyte not only serves as Li$^+$ transportation medium during battery operation but also actively participates in and influences the battery electrochemistry. The electrolyte molecules, including additives, could decompose at the electrode surface, which contributes to the formation of solid electrolyte interphases (SEIs) that have key impacts on battery performance [6,22]. Such SEI formation could serve to passivate the electrode surface to prohibit extended electrolyte decomposition as well as lithium inventory consumption, and ideally, the properties of SEIs should include good Li$^+$ conductivity and electronic insulation [23]. The term of SEI is often associated with anodes, and the same phenomena and principles also apply to cathodes, where the term cathode electrolyte interphase (CEI) is used [24,25]. On the other hand, the precise composition, structures and functionalities of SEIs and CEIs still often remain unclear [23,25]. Therefore, it is critical to retrieve the chemical information of the electrolyte/additive decomposition products to illustrate their precise electrochemical reaction pathways, which could help the optimization of electrolyte systems for LIBs [26,27]. Many chemical analytical techniques have been employed for characterizing the battery systems, including Fourier-transform infrared spectroscopy (FTIR) [28,29], nuclear magnetic resonance (NMR) [30,31], X-ray Photoelectron Spectroscopy (XPS) [32], X-ray Absorption Spectroscopy (XAS) [33], etc. Nevertheless,

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these techniques focus on chemical bonding and chemical composition and often cannot provide molecular weight information to deduce precise structures of the analytes. For example, it is difficult for these techniques to distinguish structurally similar species such as polyethylene oxides (PEOs) at various molecular masses, which are the common decomposition products of EC-based electrolytes [34–36].

Mass spectrometry (MS) is a widely employed mass-focused analytical tool for identification of both small organic molecules and polymers based on their masses [37,38]. Generally speaking, the operation of MS analysis includes sample extraction, separation, ionization and detection. Although MS commonly has high sensitivity that is capable of analyzing complex mixtures, carefully planned extraction and separation strategies could minimize the presence of non-interested species as well as the interference between various substances. Many MS instruments nowadays are broad-scope in application, but to maximize experiment effectiveness, it is still vital to evaluate the appropriateness and compatibility of the protocols in MS measurement. In particular, there are various ionization and detection methods available, and therefore, an MS operator should understand the scope of analytes that are suitable for the selected MS method. MS could also be utilized to carry out online and *in situ* investigations with customized sample extraction/separation set-ups to fit an under-operation battery system. The important technical details of different MS methods covered in this review will be provided in later sections.

MS approaches have been commonly applied in battery research for characterization of the organic electrolyte liquids since 1990s [39–41]. The organic electrolytes are not entirely stable in the potential window of LIB charging and discharging, and lithium salts could also induce chemical decomposition of the electrolytes [8,36]. Consequently, MS has been classically employed to reveal the chemical evolution of the organic electrolyte systems. In recent years, the compositions of SEIs have attracted wide research interest, but the exact makeup of the organic portions of SEIs remains challenging to reveal [26]. MS techniques have the advantage of mass-resolving capability that helps to precisely demonstrate the structures of the analytes, and thus have been applied in SEI investigations in the past few years to identify the organic SEI components [42,43].

Despite the expanding applications of MS in electrolyte studies, the battery research community has not been very familiarized with the various utilities of MS techniques, and there have been comparatively limited number of literature reports. The aim of this review is to summarize the recent progresses in characterization of battery electrolyte systems enabled by MS techniques, including the identification of electrolyte/additive decomposition products and the investigation of SEI composition and structures.

2. Decomposition of carbonate electrolytes

The decomposition of carbonate electrolytes has attracted broad research attentions due to their wide application and their important effects on cell performance such as cycle life, gassing, etc. These electrolyte molecules are small organic molecules, and therefore, their decomposition products often also have small to medium molecular weights. Consequently, gas chromatography mass spectrometry (GCMS) and liquid chromatography mass spectrometry (LCMS) are the most frequently employed techniques to investigate the electrolyte systems. The combination of chromatography and MS allows effective separation and identification of each analyte from the battery samples, which commonly have complex compositions. The MS approaches can be applied jointly with other spectroscopy methods such as FTIR to distinguish mass-identical molecules [44].

The thermal stability of carbonate electrolytes can be conveniently evaluated with GCMS by monitoring the generation of gaseous and volatile products [45]. For example, the thermal treatment of EC/EMC electrolyte was found to induce acid-catalyzed transesterification of the EMC molecules to yield dimethyl carbonate (DMC) and diethyl carbonate (DEC) [46]. The transesterification between EC and EMC could lead to formation of diethyl-, dimethyl- and ethylmethyl-2,5-dioxahexane carbonates. More extensive decomposition of LiPF$_6$-based carbonate electrolytes at elevated temperature has also been revealed by GCMS, where the products include CO_2, fluoroethane, ethers, and fluorophosphates [39,47]. The fluorophosphate compounds could further react with electrolyte components to produce organophosphorus molecules, which could be readily tracked with GCMS and could thus potentially serve as marker for determination of electrolyte health condition [48]. It is worth briefly noting here that MS coupled with ion chromatography (IC) could allow detection of organophosphates in their ionic form [49,50], and MS coupled with low-temperature plasma (LTP) desorption/ionization technique can bypass regular sample preparation to allow *in situ* analysis of the electrolyte system (such as monitoring the phosphate species) [51].

LCMS, similar to GCMS, is also useful in battery characterization, but with the advantage of analyzing high-mass and thermally sensitive substances [52,53]. For example, the thermal decomposition products of LiPF$_6$-based electrolyte has been investigated by LCMS [54]. A variety of organophosphorous and organofluorophosphorous compounds were revealed, such as organophosphates with long side chains and eight-member ring structure. The acidic and nonacidic phosphorus-based aging products were identified with hydrophilic interaction liquid chromatography (HILIC) and reversed-phase chromatography, respectively. These discoveries could help better evaluate the safety issues of the batteries as the organo(fluoro)phosphate species potentially have high hazards.

The electrochemical decompositions of EC-based electrolyte has been found by GCMS to yield alkyl dicarbonate species on graphite electrode at potentials lower than 1.5 V vs. Li/Li$^+$ [55]. It was proposed that lithium alkoxides were the active intermediates, which could enable a two-step nucleophilic reaction with the carbonate solvent to yield alkyl dicarbonate products, possibly catalyzed by trace amount of PF$_5$ in the electrolyte system. In another work, quantitative GCMS measurement was applied to track the formation of ethylene bis-carbonate molecules, which could serve as a marker to evaluate the electrolyte health and the roles of different additives in SEI formation [56]. Using this strategy, the dissolved SEI components at the discharge stage helped to illustrate that carbonate-based SEI-reinforcing agents, namely vinylene carbonate (VC) and FEC, led to more favored passivation properties of SEI than 1,3-propane sultone (PS). A study focusing on the impact of VC was carried out jointly with LCMS and Direct Analysis in Real Time mass spectrometry (DART-MS) for a graphite/LiFePO$_4$ cell at elevated temperature [57]. It was found that the generation of phosphate esters and carbonate oligomers was suppressed with VC additive (correspondingly reduced electrolyte decomposition) whereas VC promotes formation of oligomeric phosphate esters on the graphite surface that are thermally resistant.

The LiPF$_6$ salt in LIB electrolyte and its decomposition products (e.g. HF) are reactive, and thus it is imperative to consider chemical compatibility of the chromatograph systems of GC/LCMS [58,59]. A straightforward strategy to avoid damages induced by the battery samples is to remove the lithium salt prior to measurement. Recently, a simple liquid-liquid extraction method was reported to remove the lithium salt from the retrieved electrolyte of a pouch cell cycled with 1 M LiPF$_6$ EC:EMC, which helped effective evaluation of additive consumption [58]. This work discovered that vinyl ethylene carbonate (VEC) additive was quickly consumed at the early stage of formation cycle while the consumption of VC addi-
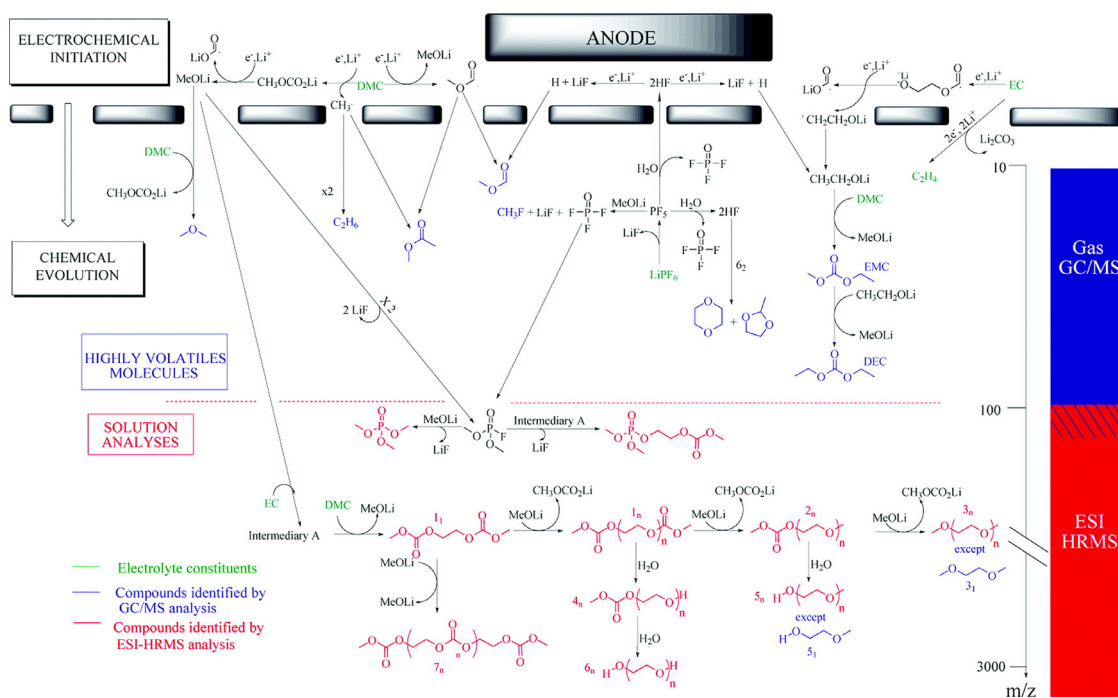
Fig. 1. Proposed LiPF$_6$:EC/DMC electrolyte decomposition pathways at low-potential. Reprinted with permission from Ref. [65]. Copyright 2010 American Chemical Society.

tive continued to later stage of the formation cycle. Solid phase microextraction (SPME) with headspace set-up is another technique for excluding LiPF$_6$ salt in GCMS measurement [60,61]. With SPME, it was found that various additional hydrocarbon species were detected in the electrolyte from a specific commercial 18650 cell, which could not be detected with conventional MS set-up [60]. This result highlights the utility of advanced MS techniques for identifying unexpected components in the electrolyte of commercial LIBs. Tunability of extraction of carbonate solvent and LiPF$_6$ salt has been realized with supercritical carbon dioxide extraction [62,63]. GCMS measurements of retrieved electrolytes from commercial 18650-type cells were carried out to demonstrate the aging mechanisms of the cells [63]. A series of newly discovered propylene carbonate (PC)-based decomposition products were identified, which were similar to those derived from EC but with propylene moieties instead of ethylene units.

The GCMS and LCMS studies together have provided useful insights of the decomposition pathways of EC-based electrolyte at low-potential to form small-molecule and polymeric decomposition products [34,64–67]. The PEO molecules have been identified as the main decomposition products, along with a series of small-molecule ether, organocarbonate, and organophosphate species. There could be a range of different terminal groups of PEOs such as alkoxyl, carbonate, phosphate, and hydroxyl, and therefore, the PEOs were found with different mass patterns. A summary of possible decomposition products and pathways of EC/DMC electrolytes with LiPF$_6$ is shown in Fig. 1. The key reaction route for PEO formation involves the decomposition of DMC and EC solvents that leads to formation of 2,5-dioxahexane dicarboxylate ($\mathbf{1_1}$) intermediate, which is the starting point for generation of various PEO species. As for the reactions of lithium salt, PF$_5$ and POF$_3$ could be generated upon decomposition of LiPF$_6$ and could then lead to formation of the organo(fluoro)phosphate products. In addition, various carbonate molecules, ethers, and gases can be produced, resulting in this complicated reaction scheme. These electrolyte decomposition pathways agree with many other studies [35,52,63,68–70]. It is worth noting here that mass spectrometry has the key advantage of mass-resolving power for identifying the precise structures of analytes, which could help reveal the reaction mechanisms. This makes mass spectrometry an important tool in future mechanistic studies of electrolyte reactions and thus in rational engineering of electrolyte systems. It should also be pointed out that more work is still demanded to construct a complete understanding of the electrolyte decomposition mechanisms in various electrolyte systems.

Isotope labeling is a facile strategy employed in MS analysis to distinguish the same species originated from different sources. For example, lithium nickel cobalt manganese oxide (NCM) electrode bearing ^{13}C-labeled Li$_2$CO$_3$ layer has been used to investigate the CO$_2$ generation route in battery operation [71]. The CO$_2$ products containing different carbon isotopes (*i.e.*, ^{12}CO$_2$ and ^{13}CO$_2$) during cell cycling between 3.0 and 4.8 V vs. Li/Li$^+$ demonstrated the different sources of CO$_2$ production. In particular, Li$_2$CO$_3$ degradation at high potentials was partially responsible for CO$_2$ evolution while electrolyte decomposition was the persistent source of CO$_2$ over long-term cycling. Similarly, outgassing of lithium transition-metal oxide (TMO) electrode has been investigated with discriminate ^{18}O-labeling of surface Li$_2$CO$_3$ and TMO [72]. This method allows distinguishment of the gases generated from surface Li$_2$CO$_3$ and electrolyte. It was found that CO/CO$_2$ evolution was associated with residual Li$_2$CO$_3$, rather than electrolyte decomposition up to 4.8 V vs. Li/Li$^+$. ^{13}C-labeling could also be applied to the EC electrolyte to track the CO/CO$_2$ evolution from conductive carbon agent and electrolyte at high potentials (> 4.5 V vs. Li/Li$^+$) [73]. As the conductive carbon agent is non-labeled while the electrolyte is labeled with ^{13}C isotope, their decomposition products of CO/CO$_2$ in the anodic oxidation processes could be individually distinguished by the different masses of the gas molecules. It was found that the oxidation of both conductive carbon and electrolyte was enhanced by presence of 4000 ppm water, while the electrolyte oxidation showed more significantly increase under high temperature condition. It is also worth briefly noting here that isotope labeling of EC electrolyte could serve to identify the polymerization products of the solvent [35,74].

Electrochemical mass spectrometry including on-line electrochemical mass spectrometry (OEMS) and differential electrochem-

ical mass spectrometry (DEMS) is another useful tool for tracking the electrochemical reactions of LIBs. OEMS can provide quantitative description of gas production during battery operation, which helps to illustrate the governing processes of gas evolution [75]. OEMS has been utilized to compare the stability of carbonate electrolyte over NMC and lithium nickel manganese oxide (LNMO) electrodes in half cells with 1 M LiPF$_6$/EC:EMC electrolyte cycled at 0.05 C of theoretical capacities [75]. It was found that the CO/CO$_2$ evolution (indicator of electrolyte decomposition) occurred at approximately same potential for LNMO and Super C45 (conductive carbon) electrodes, while gas generation potential was much lower for NMC electrodes. The similar potential dependence of LNMO and Super C45 electrodes in gas generation demonstrates that electrochemistry was the source of electrolyte degradation, and that the electrolyte was intrinsically stable toward electro-oxidation at room temperature beyond 5.0 V vs. Li/Li$^+$. As for NMC, the lattice oxygen of NMC participated in chemical oxidation of electrolyte to induce instability of electrolyte before reaching 5.0 V vs. Li/Li$^+$. In another work, OEMS was used to investigate the LiPF$_6$/EC electrolyte reactions with presence of manganese(II) and nickel(II) ions on graphite electrode surface in a half-cell processed by cyclic voltammetry at a rate of 0.2 mV/s between 0.1 and 3 V vs. Li/Li$^+$ [76]. Using ethylene as marker for EC decomposition, it was found that nickel's effect of inducing EC reduction could be readily suppressed with SEI formation, while SEI-enhancing additives such as VC was required to realize suppression of manganese's similar effect. These results demonstrate that it is helpful to reduce manganese content and to employ SEI-reinforcing additive in LIBs. OEMS could also be used to track hydrogen formation, which was found to originate from the trace water in the carbonate electrolyte [77]. DEMS is an on-line MS technique like OEMS for characterization of gaseous and volatile analytes from electrochemical cells, and is capable of correlating the electrode current and the mass ion current to assist precise investigation of electrochemical reactions [78]. For example, DEMS has been used to comparatively study the oxidative stability of EC/DEC, EC/DMC, and PC electrolyte (with LiPF$_6$ salt) over LiCoO$_2$, LiMn$_2$O$_4$, and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathodes [79]. It was found that EC/DMC electrolyte was most stable with LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode up to 5.0 V vs. Li/Li$^+$, while EC/DEC electrolyte was least stable with LiCoO$_2$ at potentials above 4.4 V vs. Li/Li$^+$, as indicated by outstanding gas generation of CO$_2$ and O$_2$.

3. Spatially resolved characterization of electrode/electrolyte interface

It is well known that the composition of SEI has depth dependence (e.g. inner inorganic layer versus outer organic layer in anode SEI), although the mechanism behind this phenomenon is still not fully understood [80]. Secondary ion mass spectrometry (SIMS) [81,82] is a capable MS technique for analyzing surface samples and revealing their composition with spatially resolved profile [83]. SIMS is a destructive approach, where a primary ion beam bombards the surface to produce ionized analytes or fragments of analytes for subsequent MS detection, commonly with a TOF analyzer (thus often referred to as TOF-SIMS). SIMS can apply extensive primary ion beam to continuously sputter and etch the surface, which allows the establishment of chemical depth profile of the surface sample. It should be noted that the working mechanism of SIMS gives this technique the advantage of spatially resolved characterization as well as the ability of analyzing both the electrode surface and the electrolyte phase [27,84]. SIMS also allows *in situ* characterization of the electrode/electrolyte interface inside batteries, which is critical for battery interface analysis under real battery operating condition [26] and thus is a key feature of the SIMS technique.

The SEIs on HOPG (highly oriented pyrolytic graphite) generated with 1 M LiPF$_6$ EC:DEC (1:1) electrolyte were investigated by SIMS, which revealed the non-homogeneity of the SEIs [85]. The SEIs were formed by discharging versus Li counter electrode at 1 mA/cm^2–10 mV vs. Li/Li$^+$ (holding at 10 mV for 2 h), followed by charging at 0.05 mA/cm^2–2 V vs. Li/Li$^+$ (holding at 2 V for 10 h). The SEIs on the cross-sections of HOPG were mainly composed of Li and F elements, although distributed unevenly with many micron-sized Li/F-absent regions; the SEIs on the basal plane were mainly made of organic species (evidenced by fragments of C$_x$H$_y$ and C$_x$H$_y$O$_z$), while the Li/F contents were accumulated in segregated regions of about 100 μm size. SIMS has also been applied to characterize the depth profiles of SEIs. Recently, the SEIs on Li$_4$Ti$_5$O$_{12}$ (LTO) electrodes generated with EC/EMC:LiPF$_6$ electrolyte have been found to present organic and phosphate compounds at the upper section and LiF in the deeper layer, where high temperatures could increase the SEI thickness and partially expand the LiF section to the surface of SEI [43]. These findings are consistent with existing literature [80] and indicate that SIMS is a convenient tool for studying the depth profile of SEIs.

The isotope labeling strategy could be utilized in SIMS measurement to investigate the dynamics of the electrochemical system. For example, the SEI on Cu electrode derived from LiClO$_4$-EC/DEC electrolyte in half cell was examined by TOF-SIMS with ^{6}Li isotope labeling method (tracking Li migration in SEIs), which revealed the heterogeneous structure of the SEI [86]. The SEI film was formed by discharging the cell galvanostatically at 25 μA to 0.4 V vs. Li/Li$^+$, followed by holding at this potential till current dropped below 1 μA. In the porous outer section of about 5 nm thickness, the electrolyte could diffuse at ease; in the lower SEI section densely composed of inorganic species like Li$_2$O and Li$_2$CO$_3$, the electrolyte transport was limited while Li$^+$ migration could take place via interstitials or vacancies. In a follow-up study of this system, a two-layer/two-mechanism model was proposed for Li$^+$ transport in the SEI, where pore diffusion mechanism would occur in the outer layer (fast Li$^+$ diffusion) while knock-off diffusion would take place in the inner inorganic layer (about 20 nm thick) of primarily crystalline Li$_2$CO$_3$ (slow Li$^+$ transport) [87]. The two-layer SEI structure of organic outer layer and inorganic inner layer agrees with literature [88]. Another work focusing on electrochemical oxidation of lithium peroxide in lithium-oxygen (Li-O$_2$) batteries constructed a micro-sized Li$_2$O$_2$ particle with the electrolyte-side labeled with^{18}O isotope (electrode-side was regular ^{16}O isotope) to track down the precise location of O$_2$ production in oxidation process of Li$_2$O$_2$ [89]. With a combined study of SIMS and OEMS, it was discovered that the oxygen loss was initiated at the Li$_2$O$_2$/electrolyte interface rather than at the Li$_2$O$_2$/electrode interface (^{18}O-labeled oxygen gas observed first), providing insights into the precise mechanism of the oxygen evolution reaction in Li-O$_2$ batteries.

SIMS has also been applied to characterize the liquid phases to track the reactions in electrochemical systems [90–93]. For example, *in situ* SIMS technique has been reported for characterization of electrode/electrolyte interface during battery charge/discharge processes [84]. It is worth briefly describing the SIMS set-up here because it adopts an uncommon back-side invasion approach. In this study, a silicon chip with a 100 nm "transparent" Si$_3$N$_4$ membrane window was developed to allow direct characterization of the SEIs on the electrode fabricated on the Si$_3$N$_4$ membrane (Fig. 2d) [84]. The Si$_3$N$_4$ window could be sputtered through (making a small orifice) to enable the ion beam to reach the Cu layer and the bulk electrolyte phase. The Cu|LiCoO$_2$ cell was cycled between 0.5 and 3.6 V vs. Li/Li$^+$. The lithium deposition on Cu working electrode was studied at different cycling stages, and the depth profile as well as the 3D concentration mapping of selected species under different states of charge are shown in Fig. 2a–c. It was found that Li$^+$ and PF$_6^-$ ions migrated to the electrodes
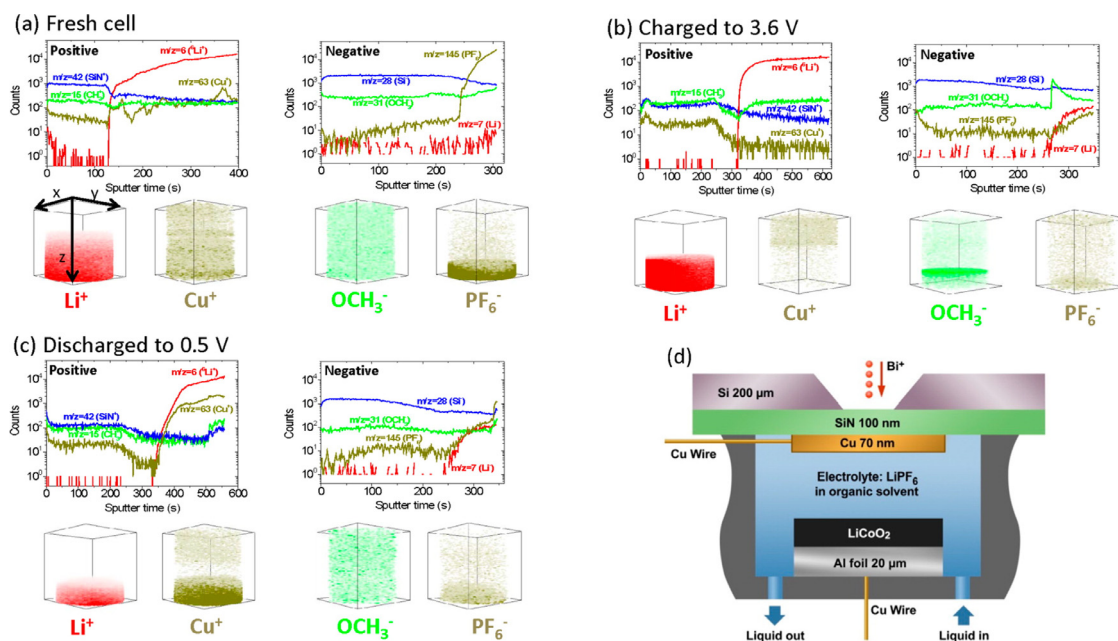
Fig. 2. SIMS depth profiling of representative species near the anode surface (a) before charging, (b) after charging and (c) after subsequent discharging. (d) Schematic demonstration of cell design employed for SIMS analysis, by which the primary ion beam can penetrate the Si_3N_4 window to characterize the Cu film and the electrolyte. Adapted with permission from Ref. [84]. Copyright 2015 American Chemical Society.
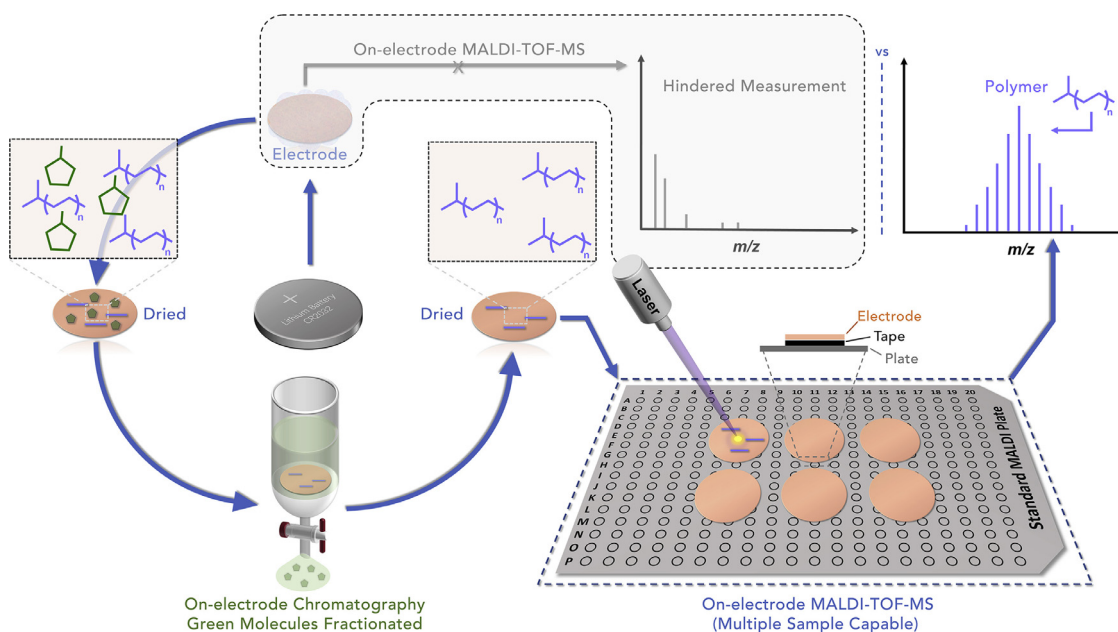

Fig. 3. Schematic depiction of MALDI measurement of electrode surfaces upon treatment of electrodes by on-electrode chromatography. MALDI characterization can be readily hindered by the various non-interested chemical species on the electrode surfaces (top dashed circle), such as ethylene carbonate (green molecule), which can be separated through proper solvent elution (left) to allow effective MALDI detection (right) of the large-molecule electrolyte decomposition products (blue molecules). Reprinted with permission from Ref. [42]. Copyright 2021 Elsevier.

charged oppositely during the process, and it was also found that dead lithium species formed in the channels of the porous Cu electrode after discharge.

The movement of ions upon initial charge could theoretically result in the formation of an electric double layer at the anode/electrolyte interface because the Li^+ ions would migrate toward the negatively charged anode while the counter-anions would be repelled. This double layer configuration could have significant impact on the evolution of the electrode/electrolyte interphase, the formation of SEIs and ultimately the performance of the battery [94]. This matter has been investigated

by monitoring the SEI formation on the Cu working electrode in a lithium bis(fluorosulfonyl)imide (LiFSI)/1,2-dimethoxyethane (DME) electrolyte system with a $LiCoO_2$ cathode using *operando* SIMS technique [94]. A constant-current mode was employed at 1.5×10^{-6} A. Upon charging to 1 V vs. Li/Li^+, the concentration of Li^+ increased at the Cu electrode while the concentration of FSI^- decreased, which was consistent with the proposed double layer structure. The double layer formation was further enhanced upon charging to 2 V vs. Li/Li^+ and the SEI layer was gradually formed with further charging. It was also found that the SEI was structured, with a loose organic-rich outer layer and a compact in-
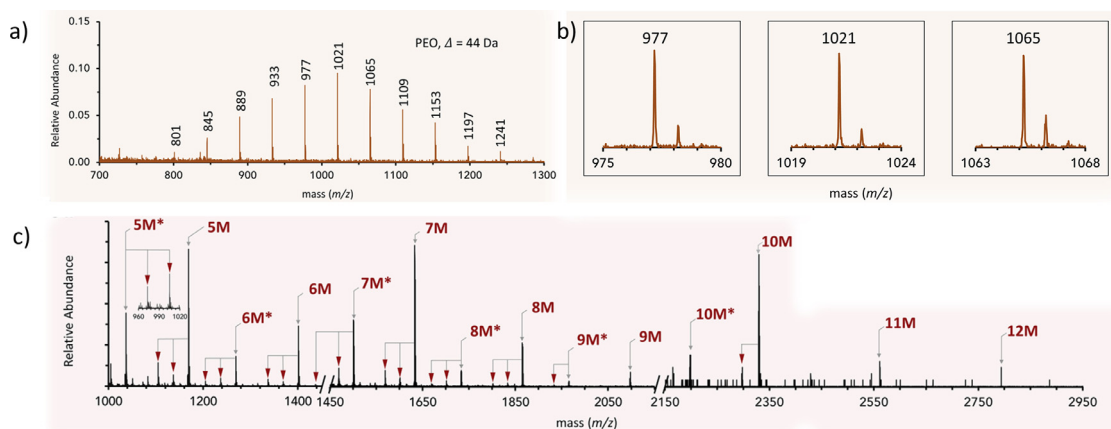
Fig. 4. (a) MALDI detection of PEO species produced with VC-containing LiPF$_6$:EC/EMC electrolyte and (b) isotope features of a few main PEO species. C) MALDI detection of poly(TEGMA) species in the 1000–3000 m/z range produced with TEGMA additive in LiPF$_6$:EC/EMC electrolyte (5M through 12M indicate pentamer through dodecamer, while asterisks and vertical arrows indicates −132 Da and -32 Da fragment peaks, respectively). (a), (b) and (c) reprinted with permission from Ref. [42]. Copyright 2021 Elsevier.

organic Li$_2$O-based inner layer of 15–20 nm thickness. These results demonstrate the key advantage of *in situ* SIMS for revealing the precise electrochemical processes at the electrode/electrolyte interface under real battery working conditions.

Similar to the case of SEI, the CEIs have been characterized by SIMS as well, which provided useful fragment-specific information regarding CEIs [95,96]. In a study of model system with nickel-rich layered lithium transition-metal oxide cathode (half-cell treated with galvanostatic cycling between 3.0 and 4.5 V vs. Li/Li$^+$), it was found that conductive carbon agents have important impacts on CEI, where the carbon could react with the LiPF$_6$/EC-based electrolyte to initiate passivation of the cathode [97]. It was stressed that carbon agents should be carefully examined in cathode interphase studies, and that electrode surface passivation with carbon agent could be a promising approach to prevent undesired reactions of cathode. Composite cathode in all-solid-state batteries has also been examined with SIMS, which visualized the CEI formation on the LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$(NMC622)/Li$_6$PS$_5$Cl electrode [98]. SIMS was found to provide sensitivity below the detection limit of XPS with decent lateral resolution, and demonstrated that the CEI consisted of sulfate- and phosphate-type species but neglectable transition-metal compounds.

4. Polymerization of electrolyte and additive molecules

It has been widely recognized that polymerization reaction could happen due to electrochemical reactions of electrolyte molecules [46,64,99]. The polymer species in SEIs could influence the electrochemical and mechanic properties of SEI layers. Therefore, it is essential to precisely understand the molecular identities of the large-molecule and polymeric species in SEIs. Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS) is a well-established MS technique which can conveniently analyze both small molecules and large polymers [100,101]. In MALDI measurements, the matrix helps to gently transmit the laser energy to analytes for desorption and ionization of the analytes (prerequisites for MS detection), which is particularly suitable for analysis of high-mass molecules. In a conventional MALDI measurement, analytes need to be applied onto the surface of a sample plate. Thus not surprisingly, MALDI has been demonstrated compatible with direct measurement of surface samples as well [102], and MALDI is sufficiently sensitive to reveal trace chemical transformation such as reactions of single-layer molecules [103,104]. These working principles enable MALDI

to effectively detect large-molecule species on the electrode surfaces.

MALDI can be employed for analysis of low-mass molecules in battery systems as well. For example, a Li−O$_2$ battery with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)/triglyme electrolyte was investigated with MALDI to demonstrate the reaction products of the polyether [105]. Triglyme (Li$^+$ adduct at 185 m/z) and a series of its fragments such as [CH$_3$(OCH$_2$CH$_2$)$_2$OLi+Li]$^+$ (133 m/z) and [CH$_3$OCH$_2$CH$_2$OLi+Li]$^+$ (89 m/z) were identified. The discovery of fragments of the electrolyte molecule demonstrates that the electrolyte underwent degradation in battery operation. Therefore, to employ polyether solvents in Li−O$_2$ batteries, it would be necessary to engineer polyether electrolytes to enhance their stability during battery operation.

The main application of MALDI in battery research is to identify the high-mass species in battery systems. The polymerization reaction of carbonate electrolytes has been examined by a series of MALDI studies. A MALDI study of Au electrodes cycled with PC and EC:DMC electrolytes against lithium counter electrode between 0.1 and 2.0 V vs. Li/Li$^+$ revealed repeating mass patterns of approximately 166 and 176 m/z, respectively, which were proposed as polymeric decomposition products of carbonate electrolyte [106,107]. ("Repeating mass patterns" refer to a series of mass signals separated by a given mass interval such as 166 m/z in the above case, and they are commonly associated with polymers.) In comparison, approximately 140 m/z repeating mass patterns were found on Sn electrode surface cycled with EC:DMC electrolyte while no outstanding repeating mass patterns were identified in the case of PC electrolyte, indicating possible dependance of electrolyte decomposition on metal surface type. Similar repeating mass patterns were also found for graphite anodes cycled in carbonate electrolyte at a rate of C/50 between 100 mV and 3.5 V vs. Li/Li$^+$ [108].

Additives could also engage in polymerization reaction and participate in SEI formation, which could help to improve battery performance. For example, 3-hexylthiophene, a thiophene derivative additive with low oxidation potential, was applied to LiPF$_6$ EC:EMC electrolyte and successfully extend the cycling life of the cell [109]. MALDI characterization of the Li$_{1.2}$Ni$_{0.15}$Co$_{0.1}$Mn$_{0.55}$O$_2$ electrode cycled in half cell against lithium counter electrode at a rate of C/3 between 3.0 and 4.9 V vs. Li/Li$^+$ observed a series of signals that were consistent with poly(3-hexylthiophene) species, which confirmed the polymerization of the thiophene additive as well as the formation of a conductive passivation layer on the cathode. In another work, the alpha-lipoic acid additive was found to polymerize

Table 1
Comparison of different MS techniques.

	Application	Advantage	Disadvantage
GCMS	Electrolyte characterization	Analysis of gaseous and volatile species	Unsuitable for analyzing fragile and non-volatile species; Necessary to consider chemical compatibility issues
LCMS	Electrolyte characterization	Analysis of non-volatile and thermally unstable species	Necessary to consider sample extraction and chemical compatibility issues
SIMS	SEI and near-SEI characterization	Analysis of both organic and inorganic species; Capable of *in situ* characterization and depth profiling	Challenging to analyze large molecules
MALDI	SEI composition characterization	Analysis of high-mass molecules and polymers	Challenging to carry out *operando* analysis

on the cathode in a lithium sulfur battery, which formed a protective layer to reject the polysulfide species and helped to improve the performance of the battery (MALDI investigation carried out with a Li/stainless steel model cell processed with galvanostatic cathodic current of 0.1 mA cm^{-2} for 7 h from open-circuit voltage to 1.5 V vs. Li/Li$^+$) [110]. MALDI played critical role in these studies to verify the polymerization of the additive molecules, thus providing valuable information for evaluation and engineering of the electrolyte systems.

It should be noted that the existing literature of MALDI characterization of large-molecule species in battery systems often suffer from limited spectrum resolution [106–108]. As fragmentation and structure rearrangement of the analytes could often occur in MALDI measurements, high quality spectra are crucial for unambiguous identification of the observed signals (e.g. molecular ion versus protonated ion) as well as determination of their structures (by fragmentation pattern, isotope pattern etc.) [103,104,109].

On-electrode chromatography technique has been recently developed, aiming at fractionating different organic and polymeric species on electrode surface to facilitate their individual identification [42,111,112]. This concept was realized by the gradient polarity solvent wash (gradient wash) technique, which involves sequential elution treatments of electrode samples with gradually increased solvent polarities [111]. Such a strategy helped to verify the polymerization of a methacrylate additive, triethylene glycol methyl ether methacrylate (TEGMA), on Cu working electrode (discharging versus lithium counter electrode), and also identified 3:7 ethyl acetate:hexane (EA:Hex) to be a proper elution condition for only removing the residual EC electrolyte to enable effective FTIR measurements of TEGMA polymers.

The on-electrode chromatography method has been combined with MALDI to reveal the electrolyte and additive decomposition products in LIBs (see **Fig. 3**) [42]. In this work, on-electrode chromatography helped to separate the residual electrolyte from the SEI layers (formed by discharging the Cu|Li cell from open-circuit voltage to 50 mV vs. Li/Li$^+$ at 1 mV/s rate, followed by 2 h holding at 50 mV), which was proven critical for detecting high-mass decomposition products. The EC-based electrolyte was found to produce high-mass PEO molecules above 1000 m/z on Cu working electrodes, which seems promoted by VC additive (see **Fig. 4a**). This provides additional insights for the commonly recognized positive effects of VC additive [31,99]. The PEO species presented good signal intensities, with easily recognizable isotope patterns (**Fig. 4b**) that could be used to assist their precise structural assignment [42]. The PEO species identified in this work are consistent with those identified with GC/LCMS reports [34,35,70]. This work also agrees with a CEI investigation by desorption electrosprayionization mass spectrometry (DESI-MS), which identified PEOs from decomposition of carbonate electrolytes although did not detect high-mass PEOs above 1000 mass units [113]. The ability of MALDI to identify the change of polymerization products by

adding additives could help to screen proper additives for desired electrode/electrolyte interface properties.

In addition to PEO formation, the polymerization of TEGMA additive was also examined with MALDI [42]. On-electrode chromatography helped to reveal the high-mass poly(TEGMA) up to about 2800 m/z (dodecamer, see **Fig. 4c**) on Cu working electrode. In comparison, only hexamers were detected without on-electrode chromatography treatment. It should be highlighted that well-defined fragmentation pathways of the poly(TEGMA) species were observed unambiguously. The major fragmentation pattern results from the loss of triethyl glycol chain of TEGMA units (-132 m/z, fragments marked by asterisks in **Fig. 4c**). A minor fragmentation pathway involves loss of one or two terminal methoxy group of the triethyl glycol chaisn (-32 or -64 m/z, marked by red arrows in **Fig. 4c**). Such fragmentation information helped to endorse the assignment of poly(TEGMA) species. To verify the universality of on-electrode chromatography and MALDI approach, polymerization reaction of TEGMA additive was also explored with SiO$_x$ and graphite composite electrodes. It was found that up to TEGMA hexamer was formed in both cases with on-electrode chromatography while only TEGMA trimers were observed without on-electrode chromatography. These results further demonstrated that MALDI characterization of SEIs assisted by on-electrode chromatography is a promising technique for measurement of large molecules on the electrode surfaces. MALDI is a helpful tool in revealing the reaction products of additives in SEIs, based on which MALDI could assist rational design of SEIs, especially the organic SEI sections containing polymeric species.

5. Conclusion

The wide application of organic electrolytes and additives in batteries desire analytical methods specialized for characterization of their decomposition products during battery storage and operation. MS is a highly sensitive technique with the advantage of identifying the accurate molecular weights of the analytes, which helps to precisely deduce their molecular structures and thus reaction pathways. Therefore, MS has been an attractive tool for characterizing the electrolytes and SEIs. A brief summary of the application scenes, advantages and disadvantages of the common MS methods are provided in Table 1. GCMS and LCMS can be conveniently applied to track the small molecules in battery electrolyte, where GCMS is more suitable for gaseous and volatile species while LCMS can readily detect substances with high boiling points and thermally unstable structures. On the other hand, GCMS and LCMS measurements could be complicated by sample extraction and chemical compatibility issues. MALDI technique combined with on-electrode chromatography is suitable for measuring high-mass polymers directly on the electrode surface, bypassing sample extraction. But the involvement of matrix in MALDI measurements would make it challenging to develop *operando* MALDI methodol-

ogy. SIMS approach can simultaneously analyze both the organic and inorganic species *in situ* with depth-resolving power, thus realizing structural analysis of both SEIs and near-SEI layers. The working principles of SIMS limits its capability of capturing relatively large molecules in their intact form.

In summary, MS can serve as a useful analytical tool for investigation of battery electrolytes and electrode/electrolyte interfaces. It is worth noting here that the MS methods in characterization of battery systems are still under constant development. Future works should expand the utilization of various MS techniques in different battery systems like lithium-sulfur batteries and lithium-air batteries. In addition, it is equally important to carefully investigate the technical parameters of the MS techniques such as resolution and detection limit.

Declaration of Competing Interest

The authors have no conflicts of interest to declare.

Acknowledgments

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