



Unraveling battery interface chemistry and architecture with TOF-SIMS: Recent advances, unique advantages and future trends

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Received: 3 March 2026 / Revised: 17 April 2026 / Accepted: 20 April 2026 / Published date: 10 June 2026

ABSTRACT

Battery interface behavior is a critical factor determining battery performance, but the complex chemical composition and nanoscale dynamic evolution impose extremely high demands on the precision of characterization techniques. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has emerged as a core technique in battery interface research, with its unique advantages such as ultra-high sensitivity, nanoscale spatial resolution, and three-dimensional chemical imaging capabilities. This review systematically introduces the technical principles and development process and functional characteristics of TOF-SIMS, focusing on summarizing its advances and strengths in studying electrode interface evolution, electrolyte decomposition, and ion migration. Using representative interface components as examples, it provides an in-depth discussion on the analytical strategies and principles for accurate identification through cluster ions, providing crucial support for enhancing the reliability of data interpretation. Furthermore, this review explores emerging trends, including the development of *in-situ* TOF-SIMS and its integration with multi-modal characterization techniques. Finally, proposing development directions including standard database construction, machine learning-assisted data analysis, and wide-temperature-range *in-situ* characterization to advance TOF-SIMS as a standardized and synergistic technology for battery interface research.

KEYWORDS

battery interfaces, TOF-SIMS, nanoscale chemical imaging, depth profiling analysis, 3D reconstruction, interface evolution

1 Introduction

Under the background of global environmental degradation and fossil energy depletion, the transition from a highly polluting and energy-intensive production model to a green and sustainable development model is necessary [1, 2]. As the core carrier of energy storage and conversion, secondary batteries (e.g., lithium-ion batteries [2–5], sodium-ion batteries [6–9], metal-air battery [10, 11], zinc battery [12, 13], solid-state batteries [14–17], flow batteries [18, 19], etc.) have become the key hub connecting clean energy production and end-use applications. However, the performance and lifetime of batteries are not only dependent on the electrochemical properties of the materials themselves, but also affected by the complex interface interactions between the

electrodes and the electrolyte. Interface problems have been the hot-spot and core challenge in battery research [20–24], and their complexity directly affects the energy density, cycle life and safety of the battery.

Using advanced characterization techniques to reveal the composition, architecture and dynamic evolution mechanism of the battery interface from different dimensions is an effective method to solve the battery interface problems. Currently, the main methods for characterization of cell interfaces include X-ray photo-electron spectroscopy (XPS) [25–30], cryo-transmission electron microscopy (Cryo-TEM) [31–35], synchrotron radiation techniques [36–43], atomic force microscopy (AFM) [44–48], Raman spectroscopy [49–53], and scanning electrochemical

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microscopy (SECM) [54–58], as shown in Fig. 1. However, these techniques face many limitations in practical applications: XPS can accurately analyze the surface chemical states, but its detection depth is limited to 5–10 nm, and the depth profiling relying on ion sputtering will destroy the sample structure, which cannot realize non-destructive three-dimensional (3D) compositional imaging [59]; Cryo-TEM enables the observation of interfacial morphology at the atomic scale, but its compositional analysis relies on EDS, which is insufficiently sensitive and statistically poor for the lighter elements (Li, H) with insufficient sensitivity and poor statistical properties [60]; synchrotron radiation techniques are good at dynamically tracking elemental oxidation states and phase transitions, but the detection limit for trace elements is high and data processing is complicated [61]; AFM can characterize the morphology and mechanical properties at nanoscale, but it cannot directly provide information on the chemical composition [62]; Raman spectroscopy can identify organic molecules in SEI *in-situ*, but it is sensitive to amorphous substances and fluorescence interference, and it is difficult to analyze the depth distribution of components [63]; SECM can monitor the electrochemical activity of the interface in real time, but it cannot resolve the composition and structure information [64]. To facilitate intuitive comparison among these techniques, a summary of their key analytical capabilities is provided in Table 1.

Under this background, time-of-flight secondary ion mass spectrometry (TOF-SIMS), with its unique 3D depth profiling capability [65] and ultra-high sensitivity [66], has become a core tool to make up for the shortcomings of the above technologies. Comparing with the shallow analysis limitations of XPS and Raman spectroscopy, TOF-SIMS achieves nanoscale depth resolution through layer-by-layer stripping [67, 68], and reveals

the longitudinal gradient distribution of LiF inorganic and organic layers in SEI membranes [69–71]; in response to the lack of sensitivity of synchrotron radiation and neutron diffraction, the detection limit of TOF-SIMS reaches the level of ppb [66, 72], which can accurately capture the trace transition metal deposition at the negative interface [73]; comparing with the lack of compositional information in AFM and SECM, TOF-SIMS can identify organic decomposition products in SEI through fragment ions generation, and visualize the compositional distribution with micron-level spatial resolution by combining with 3D imaging [65]; for amorphous materials or complex multilayer interfaces that are difficult to be resolved by Raman spectroscopy, TOF-SIMS can analyze the spatial distributions of inorganic, organic, and polymer components simultaneously to avoid the problem of missing signals [74–77].

Although the application of TOF-SIMS in battery interface research is increasing [78–87], there is still a lack of systematic summaries of the technology. Most of the existing reviews focus on traditional characterization methods [59, 60, 63], and rarely discuss the unique value and challenges of TOF-SIMS from the dimensions of technical principles, functional adaptability and battery application scenarios. In this work, we comprehensively review the achievements of TOF-SIMS in the research of battery interface from the development history, principle, advantage, recent advances (including cathode, negative anode, electrolyte and diaphragm), as well as its limitations and future prospect. This review can help people understand TOF-SIMS technology in depth and clarify the role of TOF-SIMS in battery interface research, to promote the application of TOF-SIMS in battery research, and ultimately provide scientific, effective, and systematic theoretical guidance for the design of high-stability battery interfaces.

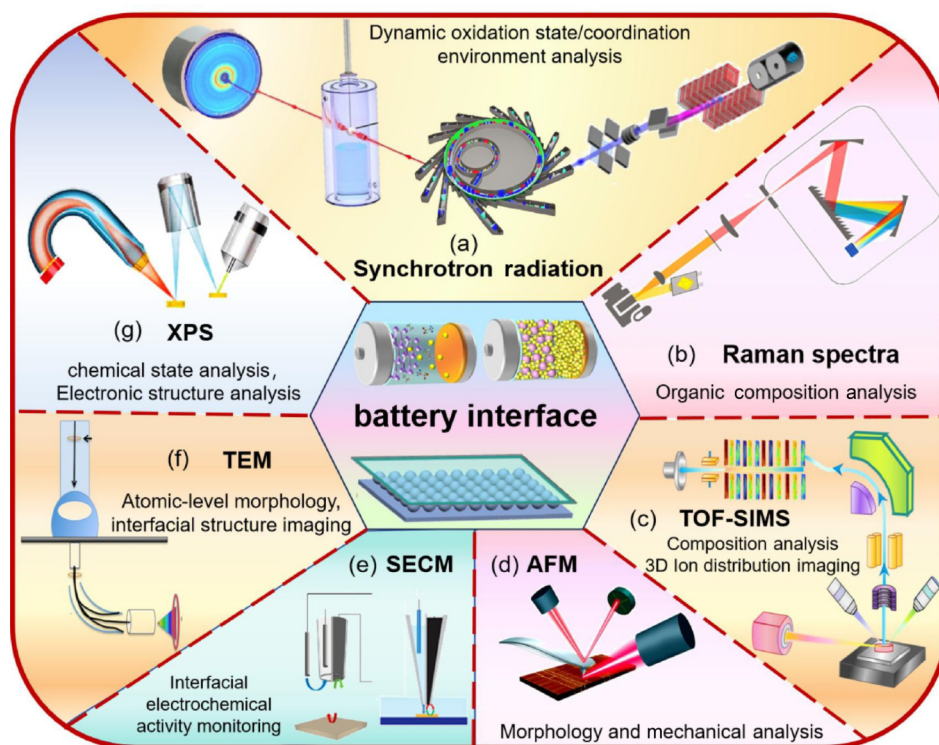


Figure 1 The main characterization techniques in secondary battery studies. (a) Synchrotron radiation. Provided by Institute of high energy, Chinese Academy of Sciences. (b) Raman spectra. Provided by Bruker Corporation. (c) TOF-SIMS. Provided by ULVAC-PHI corporation. (d) AFM. Reproduced with permission from Ref. [57], © 2017 American Chemical Society. (e) SECM, provided by IPS corporation. (f) TEM, Provided by Bruker corporation. (g) XPS, provided by ULVAC-PHI Corporation.

Table 1 Comparison of representative characterization techniques for battery interface analysis

Technique	Spatial resolution	Detection limit	Depth	Strength	Limitation
TOF-SIMS	~50–100 nm (lateral); ~1–5 nm (depth)	ppm–ppb	~1–3 nm (surface), extendable to μm (depth profiling)	Ultra-high sensitivity; simultaneous detection of elements, molecular fragments, and isotopes; 3D chemical imaging	Extreme quantification difficulty due to strong matrix effects; complex spectral interpretation
XPS	~10–50 μm	~0.1 at. %	~5–10 nm	Reliable chemical state analysis of surface elements; semi-quantitative	Poor spatial resolution; insensitive to H and He
Cryo-TEM	0.1–0.2 nm	Not sensitivity driven (structure focused)	Bulk (thin lamella)	Atomic resolution; preserves near- native structure of hydrated and beam-sensitive specimens	Extremely complex sample preparation; severe electron beam damage
Raman	~0.5–1 μm	Moderate (depends on cross section)	Surface to sub- surface ($\sim\mu\text{m}$)	Sensitive to molecular structure, chemical bonding, and crystallinity; <i>in-situ</i> , non-destructive, no vacuum required	Severe fluorescence interference; weak signals often require enhancement that introduces artifacts
AFM	~1–10 nm (lateral), sub-nm (vertical)	Not compositional	Surface only	Sub-nm vertical resolution; high- resolution topography and mechanical properties in various environments	No chemical information provided
SECM	~1–10 μm (depends on probe size)	Electrochemical sensitivity (high for redox species)	Near-surface ($\sim\mu\text{m}$ scale)	Real-time electrochemical activity imaging; non-contact measurement of local reaction rates	Sensitive only to electroactive species; resolution limited by probe size
Synchrotron radiation techniques	~30 nm– μm (technique-dependent)	ppm–ppt (element- dependent)	Bulk to <i>operando</i> depth	Extremely high elemental sensitivity; access to electronic structure, coordination environment, and oxidation state; <i>operando</i> capability	Dependence on large-scale synchrotron facilities; scarce beamtime, high cost, not portable

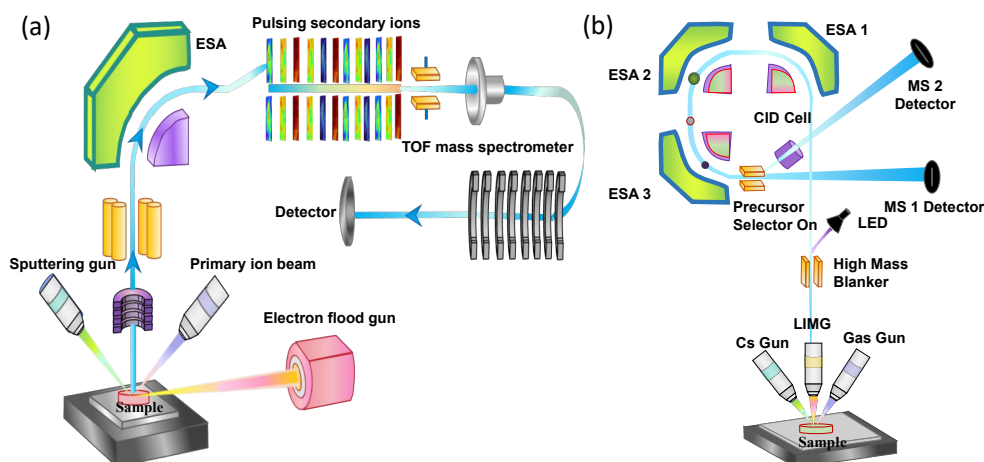
2 Principles and advantages of TOF-SIMS characterization of battery materials

2.1 Principles and functions of TOF-SIMS

TOF-SIMS is one of the most widely used surface analysis techniques. It is a micro-beam micro-area analytical technique [88], which is applicable to the analysis of various solid materials in energy [89–91], biological [92, 93], medical [94, 95], electronic [96–98], geological [99, 100], archeological [101–103], environmental [104, 105], forensic [106, 107] and other fields. TOF-SIMS has high detection sensitivity, high mass resolution and high spatial resolution capabilities. It can be used for mass spectrometry analysis, imaging analysis and depth profiling analysis.

The principle of TOF-SIMS is to bombard the surface of the incident sample with primary ion beams [108] (e.g., Bi_3^+ , Ar^+ , Cs^+ , O_2^+ , C_{60}^+ , etc.) under ultra-high vacuum [109], the energy of primary ion beams is usually between several thousand eV and

several tens of thousands of eV [110], and the diameter of the beam spot is relatively small ($< 50 \text{ nm}$) [111]; the incident ion beams and the surface of the sample (1–2 nm) interact with the surface sputtering effect, resulting in partial ionization of atoms or molecules on the surface of the sample [112]. Upon interaction of the primary ion beam with the sample surface ($\sim 1\text{--}2 \text{ nm}$), sputtering occurs, leading to the emission and partial ionization of surface atoms or molecules and the generation of secondary ions; the generated secondary ions are accelerated and sent to the flight tube; in the flight tube, the secondary ions vary in time due to their different mass/charge ratios (m/z) and initial velocities [113], with lighter ions arriving at the detector earlier due to the higher velocities, and heavier ions later; according to the measurement of the flight time of secondary ions, it is possible to determine the time of flight of the secondary ions. Based on the measurement of the flight time of the secondary ions, the mass/charge ratio can be precisely determined, to obtain the information of the chemical composition and spatial distribution of the most superficial layer, as shown in Figs. 2(a) and 2(b).

**Figure 2** Principle of TOF-SIMS. (a) TOF-SIMS from ION-TOF company. (b) TOF-SIMS from ULVAC-PHI company.

2.2 Development history of TOF-SIMS

The origin of TOF-SIMS can be traced back to the 1940s (Fig. 3). In 1946, W. E. Stephens first proposed the concept of time-of-flight (TOF) mass spectrometry [114], laying the theoretical foundation. In the late 1970s, Alfred Benninghoven's team combined the TOF analyzer with static secondary ion mass spectrometry (S-SIMS) [115], developing the prototype of TOF-SIMS. In the mid-to-late 1980s, the German company IONTOF developed the first commercial TOF-SIMS instrument, bringing the technology into practical use [112, 116]. In the 21st century, TOF-SIMS has been widely applied in both industry and academia. Currently, the main instruments are primarily from German IONTOF Company (such as TOF.SIMS 5, TOF.SIMS M6) and Japanese PHI Company (such as nano TOF II, nanoTOF 3).

2.3 Advantages of TOF-SIMS in characterizing electrode materials

2.3.1 Ultra-high surface sensitivity and trace detection capability

The nanometer-scale surface detection depth (1–3 nm) of TOF-SIMS, combined with its ultra-high secondary ion yield (10^4 – 10^6 cps/nA), enables trace detection at the ppb level [66, 72]. This provides a decisive advantage for the precise analysis of chemical composition and structural evolution at the nanoscale interfaces within batteries. Specifically, TOF-SIMS exhibits extremely high sensitivity to H^+ / H^- ions [81–83], enabling direct detection of any hydrogen-containing ion fragments in electrodes or electrolytes.

This allows precise localization of trace moisture, HF contaminants, and hydrogen-containing organic compounds—capabilities that are unattainable with most other surface analysis techniques.

2.3.2 Low detection limit and wide detection range

The mass resolution of TOF-SIMS is greater than 10,000, enabling it to detect all elements from H to U and their isotopes [84–86]. TOF-SIMS can simultaneously detect elements, isotopes, atomic clusters, molecules, and polymer fragments, thereby providing comprehensive and detailed chemical information. It can also fully identify both organic and inorganic components in battery nano-interfaces. Additionally, the characteristic fragment peaks of key elements such as Li, F, C, and B, which are of interest in battery research, are typically located at the low-mass end and are minimally interfered with by complex organic matrices, making them easy to identify.

2.3.3 Nano-scale chemical imaging

TOF-SIMS uses a focused primary ion beam (such as a liquid metal ion gun) to scan the sample surface at the micron or nanometer scale (typically < 100 nm, with advanced equipment capable of reaching < 50 nm) and simultaneously collects complete mass spectrometry information for each pixel, thereby generating a two-dimensional chemical distribution map of specific elements, isotopes, fragment ions, or complete molecular ions (Fig. 4). This imaging technique can intuitively reveal spatial distribution differences in the chemical composition of battery interfaces [79–83].

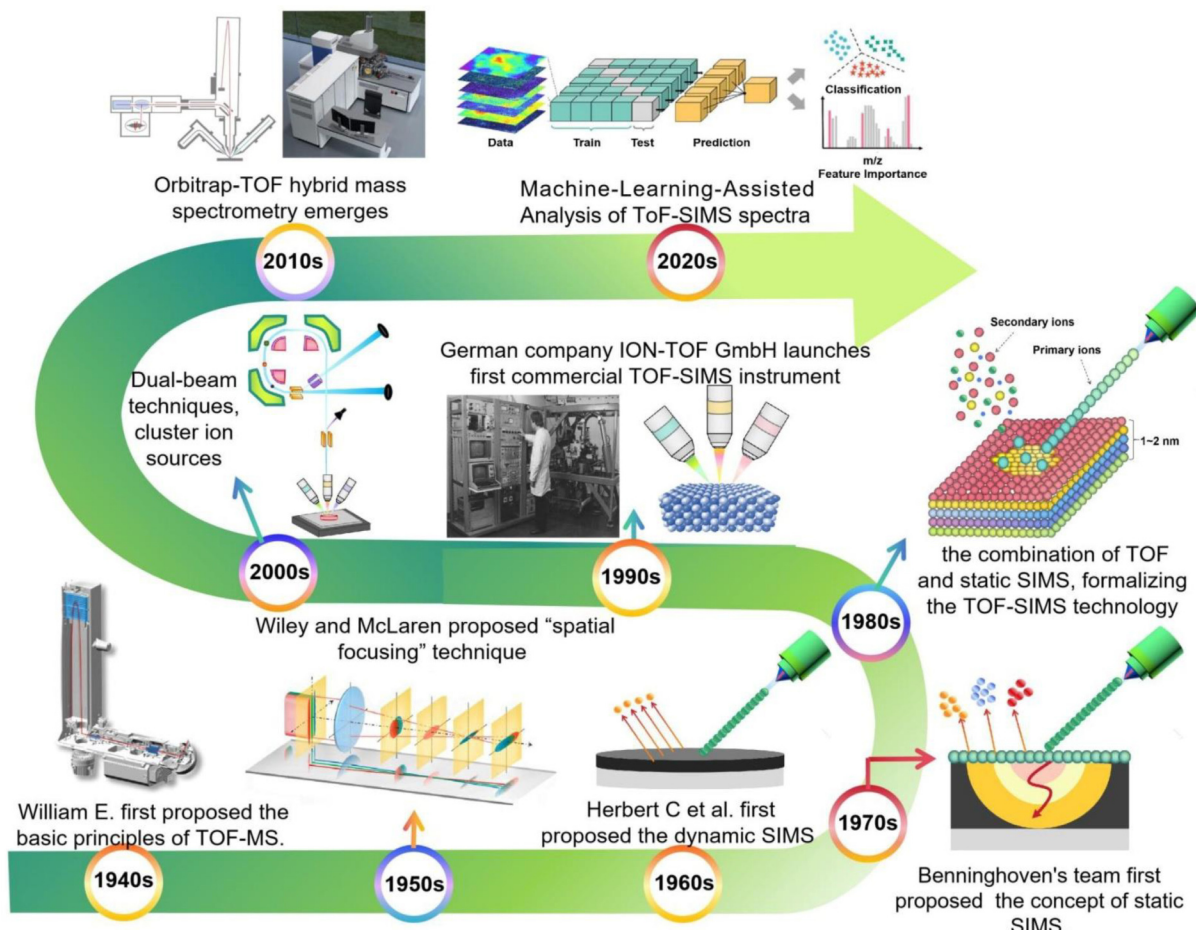


Figure 3 Chronology of TOF-SIMS development.

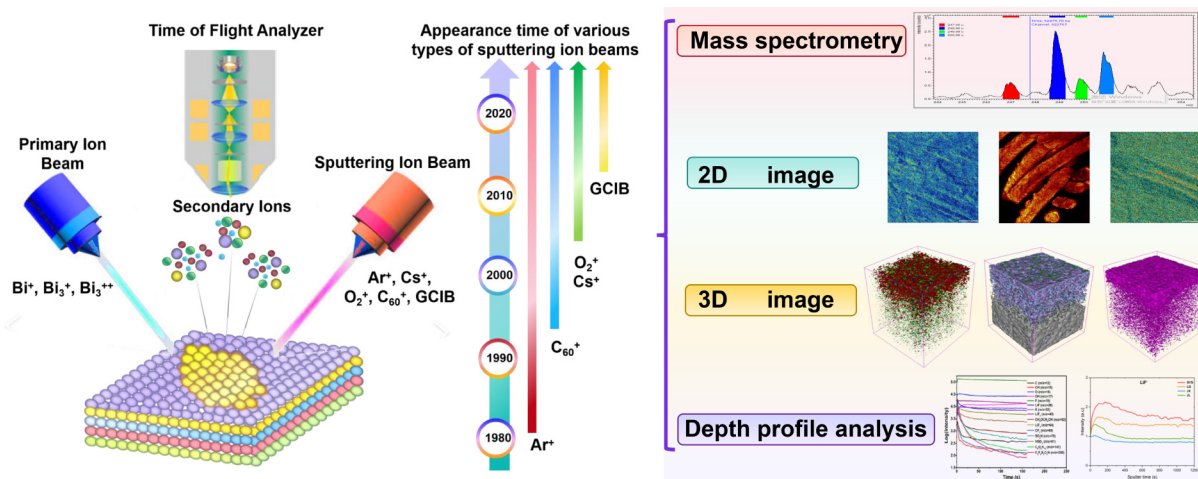


Figure 4 Ion sources and main functions of TOF-SIMS.

2.3.4 Depth profiling analysis and 3D reconstruction

TOF-SIMS has the capability for depth profiling analysis [67–71]. By alternately performing sputtering etching and analysis using sputtering ion sources (such as O_2^+ , Cs^+ , Ar^+ clusters, and gas clusters) in the analysis region, the sample surface can be peeled off layer by layer, and chemical information from the newly exposed surface can be obtained after each sputtering cycle. By recording the signal intensity of each component at different depths, distribution curves of various ions at the electrode interface can be obtained as a function of depth. More importantly, by combining depth profiling with surface scanning imaging, the chemical composition of the sample's internal architecture can be reconstructed in 3D by analyzing and recording the chemical images of each layer or specific depth intervals [74–77]. This is essential for understanding the bulk distribution of ions at the electrode interface.

2.3.5 Isotope resolution and tracing

TOF-SIMS can provide isotope information and clearly distinguish isotope peaks with extremely small mass differences [72, 78, 83], such as $^{12}C^{14}N^-$ (m/z 26.003) and $^{13}C_2^-$ (m/z 26.007), or $^{16}O_2^+$ (m/z 31.9898) and $^{32}S^+$ (m/z 31.9721). This unique advantage enables the use of stable isotopes for tracer studies, allowing the tracking of tracers' diffusion paths, reaction processes, and final distribution at battery interfaces, while also reducing interference from overlapping mass peaks and improving the accuracy of elemental and molecular identification.

2.3.6 Near-non-destructive analysis and simple sample preparation

Samples do not require complex pretreatment. Electrode samples can be tested directly, and powder samples only need to be compacted. Additionally, the sample consumption is minimal. Compared to other analytical techniques (such as Nano-SIMS), TOF-SIMS delivers a lower ion dose to the sample surface during testing, thereby reducing surface damage to less than 1% of a single atomic/molecular layer (virtually no damage to the sample surface) [74–77, 85].

2.3.7 Flexible selection of multiple ion sources and modes

Researchers can flexibly select test modes and ion sources based on the properties of battery materials and the characteristics of target analytes. Commonly used primary ion sources in TOF-SIMS include Bi_n^{m+} (e.g., Bi^+ , Bi_3^+ , Bi_3^{3+}), Ga^+ , and O_2^+ ; commonly used sputtering ion sources include Ar^+ , Cs^+ , O^+ , C_{60}^+ , and gas cluster ion beam (GCIB) [112, 116], as shown in Table 2. Analysis modes include static SIMS, dynamic SIMS, high-mass resolution mode, high-resolution mode, and switching between positive and negative ion modes. This combination of multiple ion sources and modes enables TOF-SIMS to be optimized for different analytical requirements.

3 Advances in TOF-SIMS analysis of CEI/SEI

The solid electrolyte interphase (SEI) and the cathode electrolyte interphase (CEI) are passivation layers formed on the anode and

Table 2 Main types of ion sources for TOF-SIMS and their characteristics

Ion source	Type	Energy	Advantages	Applicable scenarios	Limitations
Bi_n^{m+}	Analysis source	10–30 keV	High organic molecule yield and high spatial resolution	Surface molecular imaging, high-resolution morphology, and chemical correlation analysis	Sputter damage to samples
O_2^+	Analysis/Sputtering source	0.5–20 keV	High sputtering rate, high metal ion yield	Analysis of metal elements and oxides	Surface oxidation, low resolution
Cs^+	Sputtering source	0.5–15 keV	High sputtering rate, high yield of electronegative elements	Trace impurity analysis, metal elements, oxide analysis	Limited spatial resolution
Ar_n^+ (GCIB)	Sputtering source	5–60 keV	Fewer chemical bonds are broken, and the intact molecular signal is retained	Analysis of electrode interfaces, organic coating layers, and polymer electrolytes	Slow sputtering rate
C_{60}^+	Sputtering source	10–40 keV	Low damage, intact organic molecular information, high spatial resolution	Analysis of organic coating layers and polymer electrolytes	Carbon deposition pollution, analysis of ion yield decay

cathode surfaces during the initial charge-discharge cycles of lithium-ion batteries. The chemical composition, microstructure, and dynamic evolution of SEI/CEI directly impact battery performance (Fig. 5(a)). However, the precise characterization of SEI and CEI remains a significant challenge in battery research, primarily due to their nanoscale thickness, complex composition,

environmental sensitivity, and dynamic evolution. TOF-SIMS has emerged as a core technology for analyzing the chemical structure and evolution patterns of CEI/SEI due to its exceptional surface sensitivity, precise mass resolution, nanoscale depth profiling analysis capabilities, and unique 3D chemical imaging [117–137]. This section will focus on how the core functional advantages of

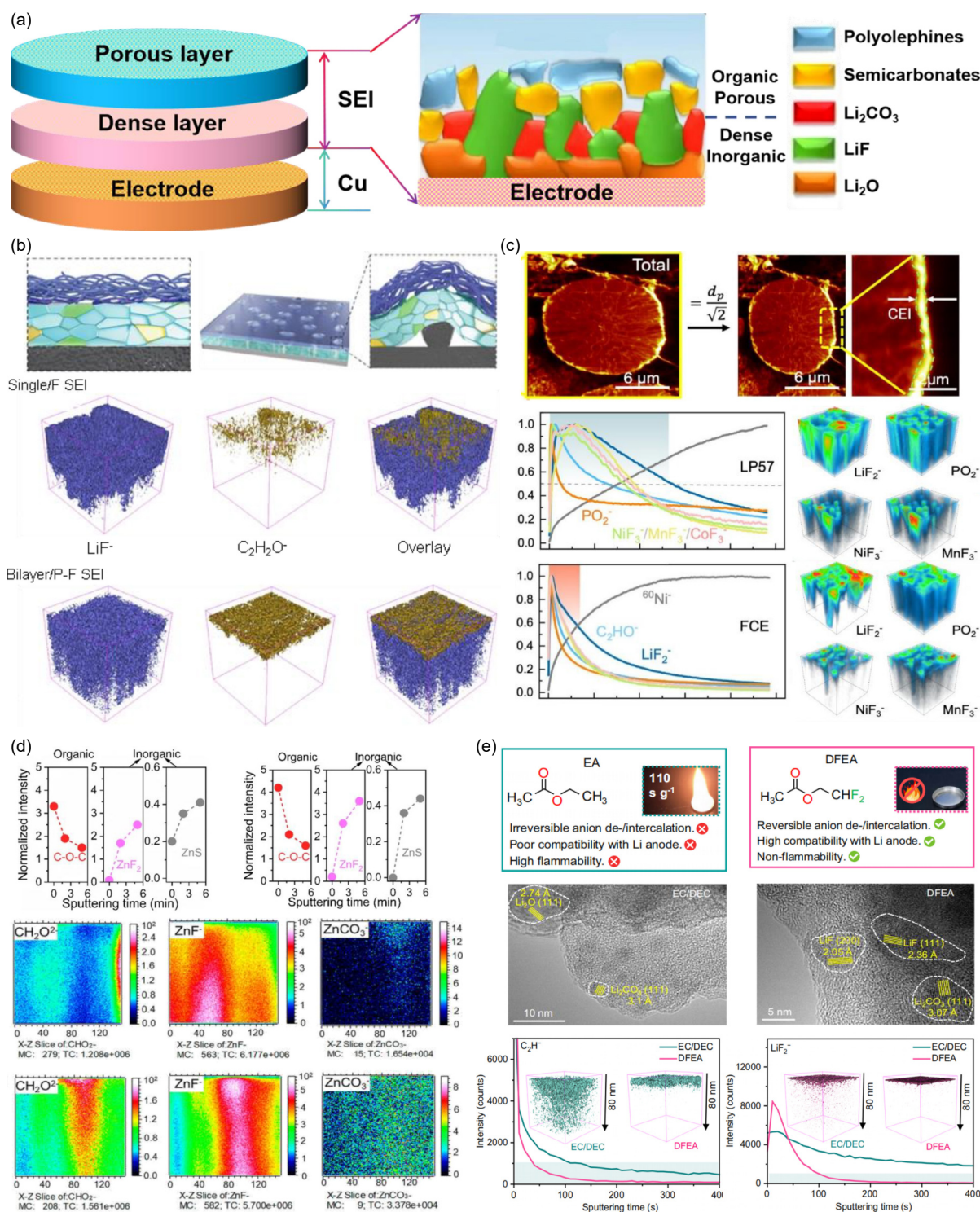


Figure 5 (a) Structure and composition of SEI. (b) Schematic structural evolution of bilayer SEI membranes during lithium plating and 3D nanostructures of TOF-SIMS resolved SEI. Reproduced with permission from Ref. [138], © 2024 Springer Nature. (c) Depth profiling curves and TOF-SIMS imaging of regions of interest (ROI) for SEI under LP57 and FCE electrolyte systems. Reproduced with permission from Ref. [139], © 2025 American Chemical Society. (d) Depth profiling analysis curves and 3D spatial distribution images of the SEI layer under Zn (OTf)₂ and β -CD-Zn (OTf)₂ electrolyte systems. Reproduced with permission from Ref. [142], © 2024 Springer Nature. (e) Depth profiling analysis curves and TEM images of the SEI on the lithium metal surface under EC/DEC and DFEA electrolyte systems. Reproduced with permission from Ref. [143], © 2024 Springer Nature.

TOF-SIMS provide critical insights into addressing key scientific questions in SEI/CEI research.

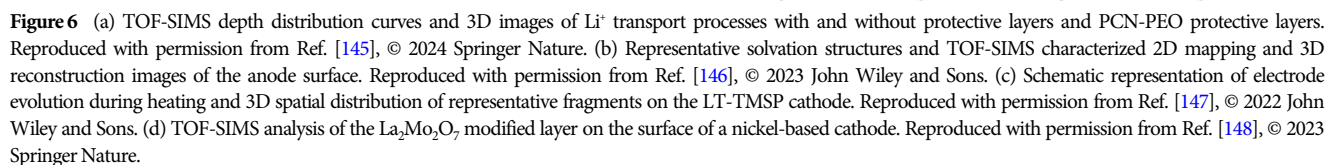
The depth profiling analysis capability of TOF-SIMS enables the layer-by-layer etching of the interphase at the nanoscale while detecting the distribution of all elements, thereby directly revealing the vertical chemical distribution and gradient structure of the SEI/CEI. Zhang et al. [138] utilized TOF-SIMS to reveal the differences between two distinct types of SEI: monolayer/F-type and bilayer/P-F-type. Depth profiling analysis showed that the bilayer/P-F-type SEI was richer in LiF and contained more organic species (Fig. 5(b)). 3D reconstruction imaging further reveals the spatial distribution of LiF and organic components within the bilayer SEI, indicating that the bilayer/P-F SEI possesses superior uniformity and mechanical stability. Similarly, Liu et al. [139] employed TOF-SIMS to reveal differences in the CEI formed in different electrolyte systems. Depth profiling analysis demonstrated that the conventional LP57 electrolyte formed a bilayer CEI structure (Fig. 5(c)), whereas the novel FCE electrolyte formed a thinner (approximately 80 nm), LiF-rich monolayer CEI structure. By combining the focused ion beam (FIB) cross-section imaging with 3D reconstruction, this study found that inorganic components in the FCE system preferentially accumulated at the surface of the active material. Spatial correlation analysis further confirmed its higher chemical homogeneity. This characteristic directly correlates with the excellent fast-charging performance of the FCE system, clearly revealing the structure-property relationship between the interfacial chemical distribution and battery performance. Sun et al. [140] also utilized the depth profiling analysis of TOF-SIMS to reveal the thickness difference between a nanoscale gradient coating (Li@Gr10) and an inverse gradient coating (Li@RGr10) on the lithium metal anode, and demonstrated bulk phase changes of elemental Zn in both coatings, confirming the ability of molecular layer deposition technology to precisely control coating composition. Additionally, Ma et al. [141] revealed the regulatory mechanism of the GHOC network structure on the SEI layer of silicon-based electrodes using TOF-SIMS. Depth profiling analysis showed that the μ Si-MTCNF-PAA electrode formed a thinner and more uniform bilayer SEI structure, characterized by a thinner outer organic phase and a denser distribution of inner LiF, which was significantly superior to the loose, uneven LiF and thicker organic layer in the μ Si-PAA electrode. This suggests that the GHOC network effectively enhances SEI stability by providing reinforced mechanical support. Luo et al. [142] employed TOF-SIMS to demonstrate that a β -CD additive induces the formation of an SEI layer with an organic-inorganic gradient distribution in zinc metal batteries (Fig. 5(d)), comprising an outer organic layer (C-O-C/CF/CF₃) and an inner inorganic layer (ZnF₂/ZnCO₃/ZnSO₃/ZnS). This gradient structure effectively suppressed electron tunneling effects and the reduction reaction of water molecules. Wang et al. [143] characterized the SEI formed on a difluoroester (DFEA)-based electrolyte using TOF-SIMS. Depth profiling analysis showed a significant increase of the LiF⁺ signal with increasing sputtering time, whereas the signal from organic decomposition products (C₂H⁺) was suppressed. The SEI thickness was calculated to be approximately 18 nm (Fig. 5(e)).

Interfacial stability depends not only on the vertical structure but is also related to the chemical uniformity within the 3D space. The 3D reconstruction technique of TOF-SIMS transforms the mass spectrometry dataset acquired from depth profiling analysis into 3D spatial distribution images of chemical components. This visualizes the spatial location and signal intensity of different

chemical species within the bulk phase of the SEI/CEI, thereby transforming the abstract concept of "uniformity" into visual and quantifiable spatial distribution image.

Gu et al. [144] employed TOF-SIMS to analyze the SEI layer formed by *in-situ* electro polymerization (ISEP). 3D reconstruction images revealed that the polymerization products of the AVIM⁺ monomer (signified by C₂H⁺ and CN⁺ signals) and the decomposition products of the FSI⁻ anion (signified by O⁺, S⁺, and F⁺ signals) were highly uniformly distributed within the SEI layer, confirming that this strategy constructs an interfacial structure with stable integration of organic and inorganic components. Chen et al. [145], focusing on the challenge of dendrite suppression in high-energy-density lithium metal anodes, utilized TOF-SIMS to reveal the Li⁺ selective conduction mechanism of a carbon nitride-based (PCN-PEO) protective layer (Fig. 6(a)). Depth profiling analysis showed that the TFSI anion signal attenuated rapidly with increasing sputtering depth, while the Li⁺ signal continuously intensified, confirming that the protective layer effectively blocks electrolyte penetration and guides ordered Li⁺ transport. 3D imaging further demonstrated a high spatial correlation between C₃N⁺ and Li⁺ distributions, indicating that the microporous structure of carbon nitride forms low tortuosity Li⁺ transport channels. Similarly, Xu et al. [146] used TOF-SIMS 3D imaging to reveal the role of a G3-LiNO₃ synergistic additive (GLN) in regulating the uniformity of lithium deposition on graphite anodes (Fig. 6(b)). In contrast to the localized lithium enrichment observed in conventional electrolytes, the SEI layer induced by GLN exhibited a dense and homogeneous distribution of LiF. Tang et al. [147] applied the TOF-SIMS 3D reconstruction capability to demonstrate that a laser-induced strategy achieved a uniform distribution of PO_x-related species across the interface between active material and conductive agent within the CEI (Fig. 6(c)), with a depth exceeding 10 nm, forming a stable interfacial structure with cross-phase synergy. Dai et al. [148] found that the signal intensities of interfacial side reaction products (e.g., PO₂F⁺, C₂HO⁺) were significantly reduced at the La₂Mo₂O₉-modified nickel-based cathode (L-NCM) interface through TOF-SIMS depth profile analysis (Fig. 6(d)). Furthermore, the distribution gradients of fragments related to transition metal dissolution, such as MnF₃⁺, were thinner, confirming the effective suppression of electrolyte decomposition by this modification layer. 3D chemical imaging further revealed the stable distribution characteristics of Li⁺ in the near-surface region, providing direct evidence for the gradient element distribution strategy.

In summary, through surface mass spectrometry analysis, depth profiling analysis and 3D reconstruction imaging, TOF-SIMS has transformed the understanding of SEI/CEI from an abstract concept of a "passivation layer" into a concrete entity with defined chemical composition, vertical gradients, 3D spatial distribution, and dynamic evolution behavior. Thereby, it provides direct evidence linking interfacial structure to performance in interface engineering. Notably, many studies utilizing TOF-SIMS for interface analysis identify chemical constituents within the SEI/CEI through characteristic secondary ion fragments. For inorganic components, [Li_mF_n]⁺ cluster ions such as LiF⁺, LiF₂⁺, and Li₂F₃⁺ serve as key evidence for identifying lithium fluoride, formed through the rupture and specific recombination of Li-F bonds during ion sputtering; Similarly, Li₂O⁺/LiO⁺ indicate lithium oxide; CO₃⁺ and LiCO₃⁺ indicate lithium carbonate; while PO₂⁺/PO₃⁺ and SO₃⁺/S⁺ point to phosphorus- and sulfur-containing inorganic species, respectively. For organic components,



More importantly, in battery interface analysis, different fragment ions are often used to collectively identify the same chemical species. Taking lithium fluoride (LiF)—a critical inorganic component in the SEI—as an example, researchers often

employ LiF , LiF_2^- , or Li_2F_3^- to indicate lithium fluoride, rather than relying solely on the F signal. The underlying principle is that these specific polyatomic clusters are not simply sputtered directly from the crystal lattice. Instead, they form through recombination events in a transient excited environment created by primary ion bombardment, where atoms reassemble based on their inherent bonding patterns and local atomic arrangements as present in the original material. Therefore, the detection of clusters reflecting the stoichiometric ratio of LiF (e.g., LiF_2^- , Li_2F_3^-) indicates the presence of a LiF -rich phase region at the nanoscale.

Furthermore, using multiple correlated cluster ions for identification not only significantly enhances the reliability of chemical component identification and excludes interference from other fluorine-containing species, but also provides robust internal cross-validation for the qualitative and semi-quantitative analysis of interfacial chemical composition through the correlated intensity variations among these secondary ions.

4 Advances in TOF-SIMS analysis of ion transport processes and interface evolution

4.1 Ion migration and diffusion kinetic analysis

The migration and diffusion kinetics of lithium ions in electrode materials is a key factor in determining the cycle stability, rate performance and lifetime of secondary batteries. From the perspective of interface stability, ion diffusion behavior is not only a kinetic parameter but also a key factor influencing the long-term structural integrity of interphases. Non-uniform ion transport can lead to localized accumulation or depletion, thereby accelerating interfacial degradation. Accurately analyzing the ion transport behavior at the electrode body and interface not only helps to reveal the failure mechanism of the material, but also provides a theoretical basis for optimizing the design of the electrode structure. TOF-SIMS has also been used to evaluate the ion diffusion in electrode materials in recent years, which can reveal the ion transport mechanism at the electrode/electrolyte interface by obtaining the information of the depth distribution of the ions and isotopes, and then calculate the apparent diffusion coefficients of the ions.

Berthault et al. [149] revealed the lithium isotope exchange kinetics of the SEI layer using TOF-SIMS depth profiling (Fig. 7(a)). By comparing the ${}^6\text{Li}/{}^7\text{Li}$ distribution under free

diffusion and constant-current charging and discharging conditions, they found that the SEI layer can complete rapid lithium exchange within 20 min in the absence of an external field, whereas the charging and discharging process significantly slows down the rate of the exchange, and combined with the modeling of the Weibull equation, they also found that SEI plays a role similar to that of ion-exchange resins in lithium transport, and its structure evolves from an initial homogeneous state to a two-layer heterogeneous state (dense inorganic layer/porous organic layer), and this gradient structure exerts a significant modulation effect on lithium-ion diffusion kinetics. In order to further understand the "dynamic self-regulation" mechanism of SEI, Ho et al. [150] further found that 90% of the ${}^7\text{Li}$ in the pristine SEI was replaced by ${}^6\text{Li}$ after a single cycle of SEI formation, and the content of ${}^6\text{Li}$ was close to that of the ${}^7\text{Li}$ -enriched control group after 25 cycles by TOF-SIMS quantitative analysis (Fig. 7(b)), which suggests that the SEI layer can be used as an organic layer even if it is initially homogeneous.

Based on the knowledge of the dynamic properties of naturally occurring interfaces, researchers have begun to use TOF-SIMS to guide the rational design of artificial protective coatings. Moryson et al. [151] quantitatively compared the oxygen diffusion coefficients of the natural passivation layer with those of the plasma polymerization coating by combining TOF-SIMS and ${}^{18}\text{O}_2$ isotope tracing. The depth profiling shows that the plasma polymerized 1,4-biphenyl coating can form a homogeneous and non-porous protective layer with an oxygen diffusion coefficient that is two orders of magnitude lower than that of the natural layer (Fig. 7(c)), which can effectively inhibit the oxidation of lithium metal for more than 30 min, confirming the protective effect of the coating. At the same time, it also shows that TOF-SIMS has changed from a "phenomenon description tool" to a "design verification platform", and that TOF-SIMS can not only capture

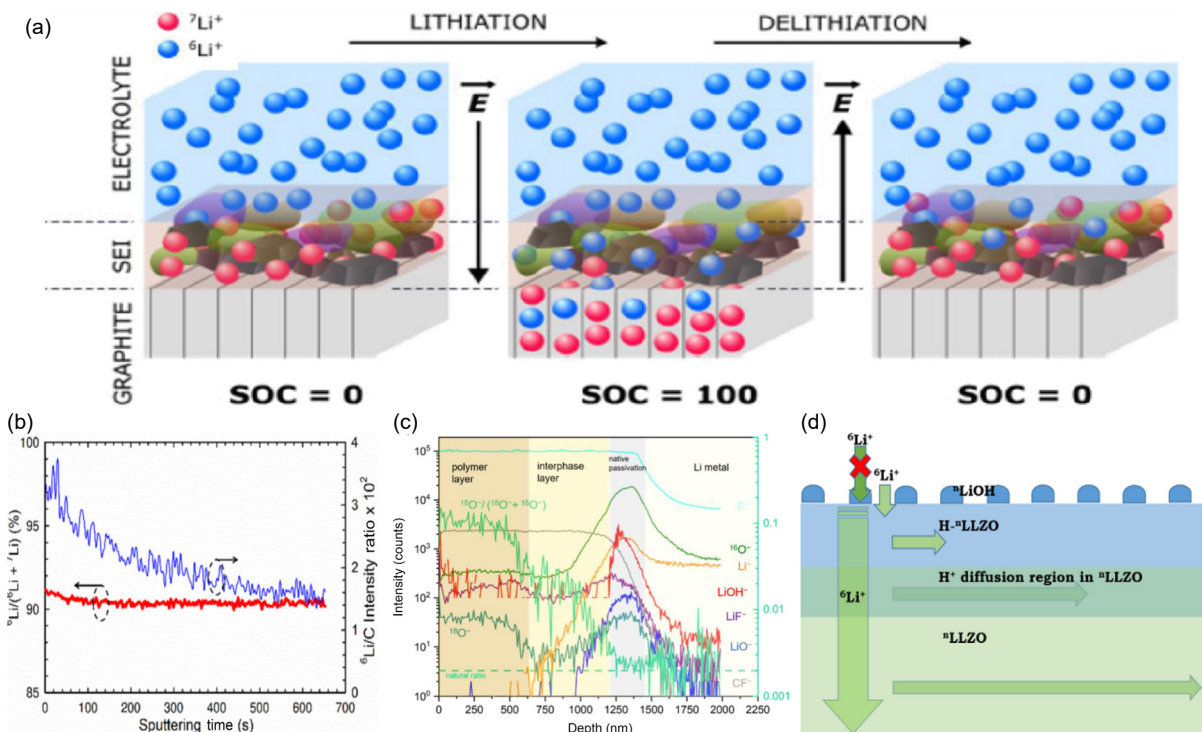


Figure 7 (a) ${}^7\text{Li}^+ / {}^6\text{Li}^+$ isotopic ion exchange occurs during lithiation and delithiation of graphite electrodes Reproduced with permission from Ref. [149], © 2021 American Chemical Society. (b) TOF-SIMS sputtering profiles of ${}^6\text{Li}^+$ substitution for ${}^7\text{Li}^+$ in SEI during one cycle. Reproduced with permission from Ref. [150], © 2021 MDPI. (c) TOF-SIMS depth distribution of polymer coatings. Reproduced with permission from Ref. [151], © 2023 American Chemical Society. (d) Schematic of possible Li diffusion pathways in a LLZO grain which has undergone proton-Li exchange. Reproduced with permission from Ref. [152], © 2021 IOP Publishing.

the natural law of interface evolution, but also quantitatively evaluate the effectiveness of artificial interventions, thus promoting the change from "passive adaptation" to "active regulation" in the study of battery interfaces.

Based on the interfacial dynamics studies in liquid batteries, TOF-SIMS has been further extended to solid-state electrolyte systems, providing a new perspective for solving the bottleneck of ion transport at the solid-solid interface. Brugge et al. [152] analyzed the lithium diffusion coefficients in solid-state lithium-conducting ceramic electrolytes, LLZO, using TOF-SIMS, and realized a direct measurement of lithium diffusion coefficients in solid-state LLZO by tracing the lithium isotopes (^6Li and ^7Li) gradient distributions (Fig. 7(d)), thus revealing the lithium diffusion behavior. Long-range diffusion coefficients were directly measured to reveal the lithium diffusion behavior in LLZO. It is worth noting that the research logic of solid-state systems is complementary to that of liquid-state SEI layers: the former focuses on the homogeneity of bulk-phase diffusion, while the latter is concerned with the dynamic non-equilibrium properties of interface dynamics, and TOF-SIMS realizes the comparative study of the two types of systems through the unified methodology (isotope tracing and depth profiling), which highlights the universality of its technology.

It should be emphasized that diffusion-related information obtained from TOF-SIMS is inherently indirect and relies on depth-resolved isotope or ion distribution profiles rather than absolute quantification. In typical analyses, isotope labeling is combined with depth profiling to track the spatial evolution of ion distributions as a function of sputtering time. By correlating these profiles with diffusion models, apparent diffusion behavior can be inferred. However, due to the strong matrix effect and sputtering-induced redistribution, the extracted diffusion coefficients should be regarded as semi-quantitative or relative indicators rather than absolute values. Despite these limitations, TOF-SIMS provides a unique capability to visualize diffusion pathways and compare relative transport kinetics across different interfacial structures, which is difficult to achieve using conventional electrochemical or spectroscopic methods alone.

4.2 Interfacial chemical characteristics and microstructural evolution of separators

The ultra-high sensitivity TOF-SIMS is able to detect the signals of various elements and compounds in the separator at very low concentrations, which is important for analyzing trace substances in the separator [153–156], such as solvent decomposition products and additive degradation products. In addition, the spatial resolution of TOF-SIMS enables it to analyze the composition of tiny areas on the surface of the separator, providing qualitative data, which is valuable for studying the internal micro-structure of the separator as well as the distribution and reaction of the electrolyte on the separator. However, TOF-SIMS generally exhibits limited quantitative capability due to strong matrix effects, where the secondary ion yield is highly dependent on the local chemical environment. This limitation should be carefully considered when interpreting signal intensities.

TOF-SIMS can accurately analyze the dynamic evolution of the interfacial chemical composition of the separator with electrochemical cycling by means of depth profiling. Kia et al. [157] compared the interfacial properties of TiN separators prepared by atomic layer deposition (ALD) with those prepared by pulsed chemical vapor deposition (pCVD) before and after

cycling, and the TOF-SIMS depth profiles showed that the ALD-TiN separator has significantly lower byproducts content than pCVD-TiN separators after cycling (Fig. 8(a)), indicating higher chemical stability at the interfaces such as TiO_x , TiO_xN_y , and TiCl by-products were significantly lower than that of pCVD-TiN separator, indicating its higher chemical stability. In addition, the interlayer exfoliation phenomenon triggered by fluorination and silicon volume expansion of pCVD-TiN separator was also directly captured by TOF-SIMS, which confirmed the advantages of ALD-TiN separator in inhibiting the diffusion of lithium ions into the silicon substrate. Similarly, Priebe et al. [85] characterized Li-rich NMC811 films using TOF-SIMS, revealing the presence of $\sim 400 \pm 100$ nm of per lithiated grains and 100 ± 30 nm of nanoparticles enriched with $^7\text{Li}^+\text{O}^+$ ions in the fresh samples (Fig. 8(b)), and the decomposition of these structures after 30 days in ambient conditions led to a significant change in the film's chemical structure, and FTIR tests also further confirmed the TOF-SIMS analysis results. These studies highlight the key role of TOF-SIMS in evaluating the interfacial side reactions and structural degradation mechanisms of separators.

The diffusion behavior of elements at the interface between the separator and the electrode/electrolyte is a core factor affecting the performance of batteries. Duan et al. [158] analyzed the chemical distribution at the LiPON/LCO interface in all-solid-state thin-film Li-ion batteries (TFBs) by using TOF-SIMS, and found that the system without the introduction of the LiF intermediate layer showed the damage of the LCO film and the phenomenon of uneven distribution of the elements after the cycling, and that the presence of the LiF layer effectively inhibits the element diffusion and promotes the rapid transport of Li-ions. Similarly, Aribia et al. [159] combined the FIB-TOF-SIMS 3D reconstruction technique to confirm the uniform distribution of transition metal oxides (e.g., Mn and Co) in Li-rich NMC811 films, and also found a good correlation between NiO- , MnO- , and CoO- signals correlate well with each other, indicating that no segregation of transition metal oxides occurs throughout the cathode film, and TOF-SIMS reveals the positive effect of heat treatment on the stability of the cathode interface. These cases show that TOF-SIMS can pinpoint interfacial elemental diffusion paths, providing direct evidence for optimizing the design of the separator-electrode interface.

In addition, the microstructure (e.g., porosity, coating distribution) of the separator is crucial to its ion transport characteristics and mechanical properties. Kim et al. [160] revealed the difference in the penetration depth of Al_2O_3 nanoceramic particles in polyethylene separators with different porosities by using TOF-SIMS 3D imaging, and the depth profiling showed that the penetration depth of Al_2O_3 in the separators with high porosity reached 850 nm, which was significantly higher than that in the separators with low porosity of 625 nm. The 3D imaging further revealed the distribution characteristics of Al_2O_3 inside the separator, indicating that the particles in the high-porosity separator could penetrate deeper into the microporous interior. In addition, Dai et al. [161] confirmed that the solid electrolyte film is a LiCPON/LiNbON/LiCPON three-layer structure by TOF-SIMS 3D mass spectrometry imaging (Fig. 8(c)), and provided the spatial distribution characteristics of Li^+ , Nb^+ , and NbO^+ plasma on the surface of the lithium metal anode, which elucidated the role of the intermediate layer of LiNbON in the reduction of the interfacial impedance and the inhibition of lithium dendrites. These studies demonstrate the irreplaceability of TOF-SIMS in resolving the 3D chemical structure of the separator and the coating-substrate interaction.

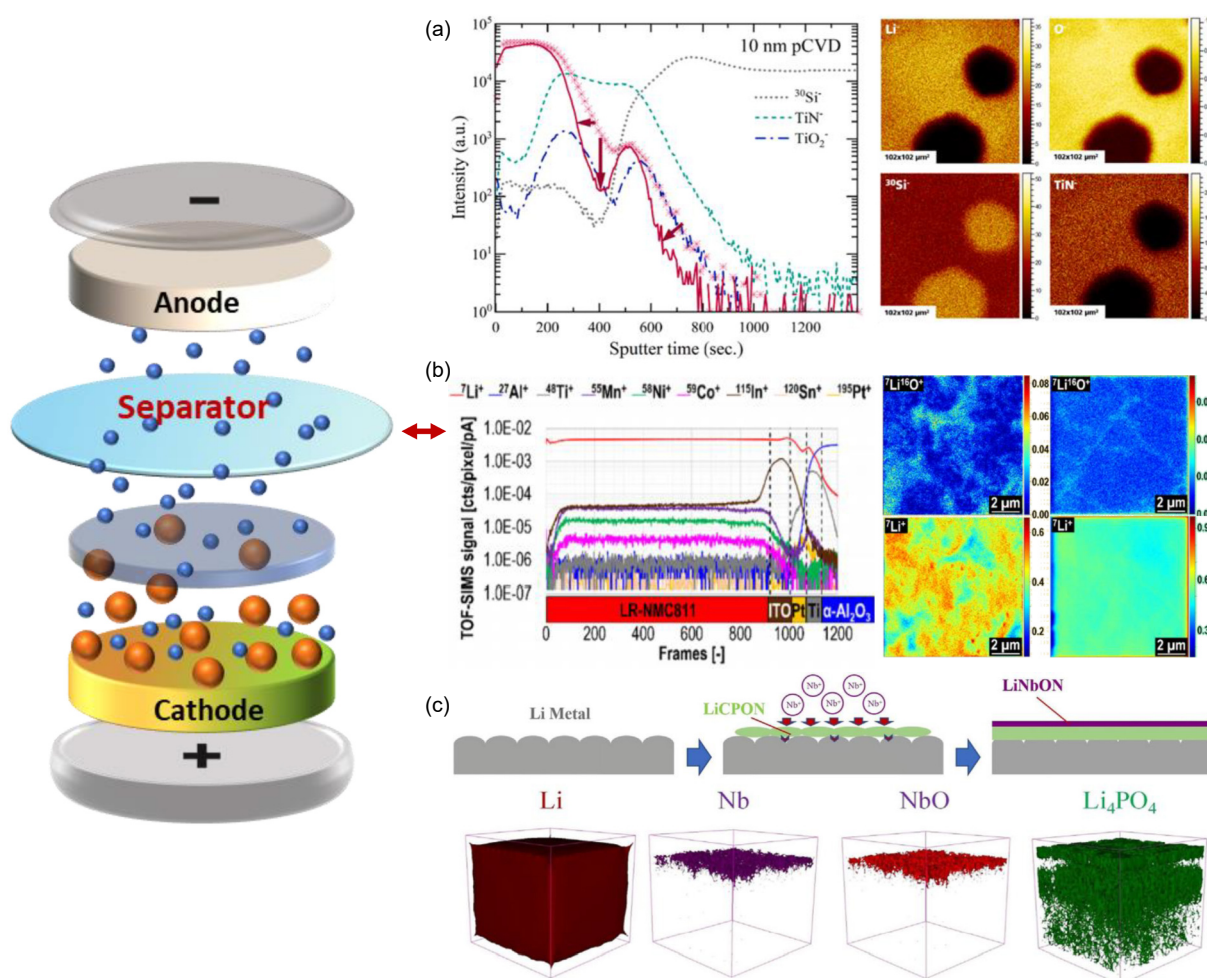


Figure 8 (a) TOF-SIMS sputtering profile and 2D image at the interface between TiN separator and Si. Reproduced with permission from Ref. [158], © 2021 Elsevier. (b) Chemical structure of LR-NMC811/ITO/Pt/Ti/ α - Al_2O_3 measured with TOF-SIMS. Reproduced with permission from Ref. [78], © 2023 American Chemical Society. (c) TOF-SIMS 3D images of the sandwich-structure solid electrolyte separator of LiPON/ LiNbON/ LiPON. Reproduced with permission from Ref. [159], © 2022 AIP Publishing.

TOF-SIMS provides a comprehensive analysis of separator material performance and failure mechanisms through multiple dimensions, including interface chemical characteristics, elemental diffusion behavior, and micro-structural characteristics. This technique provides crucial technical support and research methodology for the design and optimization of high-performance separators. It not only precisely characterizes the dynamic evolution of chemical composition at separator interfaces, but also visualizes elemental diffusion pathways and micro-structural features, thereby providing a unique research perspective for understanding the structure-property relationship of separator materials.

5 Recent trends in electrode interface characterization by TOF-SIMS

5.1 Breakthroughs in *in-situ* characterization techniques

The secondary battery interface undergoes continuous evolution during charging and discharging, encompassing dynamic processes such as lithium dendrite growth, SEI rupture and reconstruction, CEI formation, and the spatial distribution of by-product species. However, traditional TOF-SIMS is constrained by its incompatibility with battery cycling environments (e.g., liquid

electrolyte evaporation, gas byproduct release) and ultra-high vacuum (UHV) conditions. It can only provide "static snapshots" of post-cycling interfaces, failing to track real-time dynamic chemical and morphological changes driven by electrochemical processes. This results in significant loss of critical intermediate-state information and spatiotemporal evolution details. Recent breakthroughs in vacuum-compatible microfluidic electrochemical cells and integrated three-electrode system designs have successfully overcome these limitations, significantly advancing the application of *in-situ* TOF-SIMS characterization for electrochemical interface studies.

In the study of interfacial processes in liquid electrolyte systems, Liu et al. [162] developed a microfluidic electrochemical device capable of operating under high vacuum conditions (Fig. 9(a)), achieving the first successful integration of cyclic voltammetry with TOF-SIMS. By fabricating a micron-scale injection port on a silicon nitride window and integrating Pt counter/reference electrodes with an Au working electrode, the study successfully maintained a stable liquid film and acquired high-quality mass spectrometry data under an ultra-high vacuum of 10^{-7} mbar. The TOF-SIMS spectra obtained at different applied potentials (-0.2 to 0.8 V) clearly revealed a potential-dependent evolution of reaction intermediates and products. A series of potential-dependent intermediates and products, including AuI_2^- , I_2^- , I_3^- , and IO_3^- , were

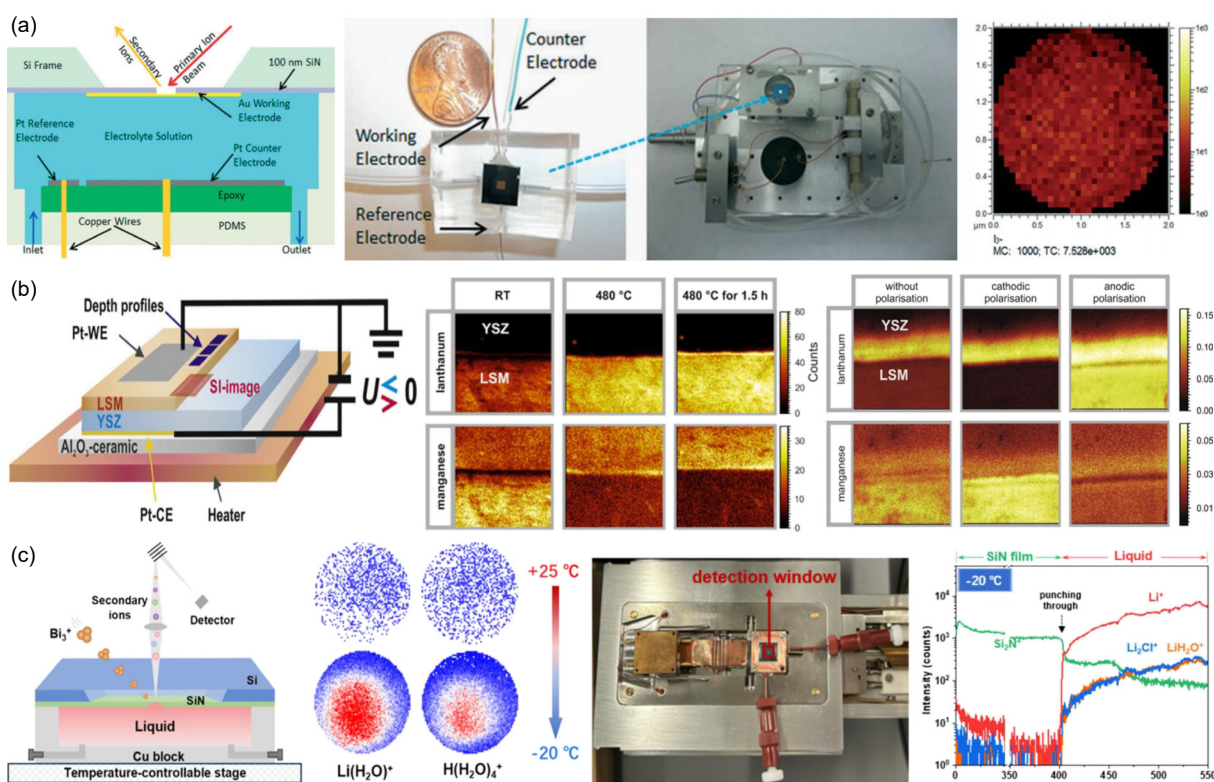


Figure 9 (a) Schematic diagram of the microfluidic electrochemical probe, photograph of the probe mounted on the ToF-SIMS platform, and 2D image of the test sample. Reproduced with permission from Ref. [162], © 2013 The Royal Society of Chemistry. (b) Schematic diagram of the *in-situ* TOF-SIMS measurement apparatus and SI image under high-temperature conditions. Reproduced with permission from Ref. [163], © 2017 Elsevier. (c) Schematic diagram and photograph of an *in-situ* variable-temperature liquid TOF-SIMS apparatus, along with depth-profile analysis curves of LiCl aqueous electrolyte. Reproduced with permission from Ref. [164], © 2025 American Chemical Society.

successfully detected, distinctly illustrating the complete reaction pathway from iodine ion oxidation to iodate ion formation. This groundbreaking work demonstrates for the first time that TOF-SIMS possesses the capability to capture transient chemical processes at solid-liquid interfaces, providing unprecedented *in-situ* molecular-level insights into the mechanisms of electrochemical interfacial reactions.

For high-temperature electrochemical systems, Rohnke et al. [163] achieved *in-situ* characterization of LSM/YSZ model electrodes at 430 °C under controlled oxygen partial pressure (10^{-8} mbar) by custom-integrating a high-temperature sample stage, an electrochemical control unit, and a TOF-SIMS analysis system (Fig. 9(b)). This system employs alternating scanning with a Bi³⁺ analysis beam and an O₂⁺ sputtering beam over a 500 μm × 500 μm area, the technique enabled dynamic elemental mapping with sub-micrometer lateral resolution (~100 nm level). It directly captured real-time processes including Mn diffusion toward the YSZ surface and La/Sr resorption during cathode polarization, as well as Sr/La surface segregation and elevated Mn oxidation states during anode polarization. This work directly revealed the correlation between surface component reorganization and electrode activation/deactivation mechanisms during LSM cathode polarization via *in-situ* ToF-SIMS. It provides a spatiotemporally resolved surface chemistry tracking methodology for studying surface processes in SOFCs and other high-temperature electrochemical devices.

Regarding the study of interfaces in low-temperature electrochemical systems, Liu et al. [164] successfully constructed a thermally conductive copper-based microfluidic device integrated with a temperature-controlled sample stage, enabling for the first

time *in-situ* temperature-dependent TOF-SIMS molecular probing of supercooled brine electrolytes (Fig. 9(c)). This technique employs a focused Bi₃⁺ ion beam to etch micrometer-scale sample introduction holes *in-situ* on a 100 nm thick SiN film. It enables real-time monitoring of the decrease in Si₂N⁺ signals during breakdown alongside the sudden increase in electrolyte signals such as Li⁺ and Li₂Cl⁺. Charge compensation was achieved using a low-energy electron gun, ensuring signal stability under high vacuum (5×10^{-7} mbar). Through acquisition of two-dimensional chemical imaging and mass spectra during temperature variation from 25 to -20 °C, the study captured dynamic structural transitions in real time, including the shift of the dominant lithium hydration structure from Li(H₂O)₃⁺ to Li(H₂O)₄⁺, enhanced hydrogen bonding in Cl(H₂O)₂⁺, and significant formation of LiCl(H₂O)₃ complexes. This work demonstrates that advanced *in-situ* variable-temperature liquid TOF-SIMS possesses unique capabilities for resolving key molecular species within complex micro-environments, providing a powerful technical approach for investigating interfacial processes in low-temperature battery systems.

Overall, the rapid advancement of *in-situ* TOF-SIMS technology has achieved significant breakthroughs: from room temperature to extreme temperatures, from solid to liquid states, and from 2D imaging to 3D reconstruction. These technological advances enable researchers to directly observe the dynamic evolution of battery interface chemistry under realistic operating conditions, capture key intermediate species, and elucidate interfacial reaction mechanisms. Notably, the technique's ability to simultaneously provide chemical composition and spatial distribution information, achieving true four-dimensional

characterization. This offers direct experimental evidence for understanding critical scientific issues such as SEI/CEI formation mechanisms, dendrite growth kinetics, and interfacial side reactions. With continuous refinement of *in-situ* characterization capabilities and further improvements in spatial resolution, TOF-SIMS will play an increasingly pivotal role in the development of next-generation high-performance batteries, providing a solid technical foundation for the precise design and regulation of battery interfaces.

5.2 New paradigm of multi-modal technique integration for interface characterization

Single characterization techniques often struggle to comprehensively analyze the complex chemical and structural information at battery interfaces. In recent years, multi-modal coupling strategies that integrate TOF-SIMS with other analytical techniques have been evolving into a new paradigm. By leveraging complementary information, these multi-modal coupling strategies are proving powerful in revealing the composition, 3D structure, and evolution mechanisms of interfaces.

Regarding the development of multidimensional high-resolution characterization techniques, Niehuis et al. [165] developed a novel integrated instrument combining TOF-SIMS and scanning force microscopy (SFM) within a single ultra-high vacuum analysis chamber. This system employs a piezo-driven XYZRT sample stage that enables rapid switching between TOF-SIMS analysis and SFM detection positions with sub-micrometer precision, ensuring consistency in the analysis area. The TOF-SIMS component utilizes a Bi_3^+ liquid metal cluster primary ion beam with a spot diameter of 20 nm, complemented by O_2^+/Cs^+ beams for sputtering inorganic materials and a gas cluster ion beam (GCIB) for low-damage sputtering of organic materials, achieving outstanding depth resolution of 1 nm (inorganic) and 5 nm (organic). The integrated SFM module enables direct measurement of actual sputter crater depth and morphology, thereby correcting for morphological distortion in TOF-SIMS depth profiling. This methodology has been successfully applied to 3D chemical imaging of both inorganic multilayer films and organic nanostructures, providing powerful technical support for battery interface research, particularly in the accurate resolution of 3D SEI structures.

To address the damage issues of fragile interfaces during conventional sample preparation, Smentkowski et al. [166] developed an *in-situ* FIB-TOF-SIMS analysis method. By integrating FIB profiling with TOF-SIMS chemical imaging under the ultra-high vacuum condition, this method successfully achieved high spatial resolution analysis of lithium-ion battery anode cross-sections at depths of tens of micrometers (Fig. 10(a)). Further processing of massive mass spectrometry data using multivariate curve resolution algorithms clearly revealed the 3D distribution of key components such as sodium fluoride, small-molecule hydrocarbons, and oxygen/chlorine-containing organic compounds. This method effectively overcomes the challenges of damage and light element detection inherent in traditional sample preparation, providing a crucial technical platform for interfacial chemistry research in energy materials and related fields.

To prevent contamination of air-sensitive samples during transfer, Delfino et al. [167] developed a removable sample preparation and multiscale correlation analysis method based on the FIB-SIMS platform (Fig. 10(b)). By employing FIB for precise electrode extraction combined with a sealed transfer system under inert atmosphere, contamination during sample transfer was

eliminated. Utilizing the platform's integrated magnetic sector secondary ion mass spectrometer, this work achieved chemical imaging with spatial resolution as high as 16 nm. It simultaneously obtained complete cross-sectional information from the current collector to the electrolyte interface, realizing pixel-level correlation analysis between electrode morphology and chemical composition at the nanoscale for the first time.

Furthermore, the multi-modal technology integration paradigm is advancing toward the ultimate capabilities of enhancing spatial resolution and achieving automated 3D analysis. To realize high-throughput 3D chemical imaging of complex heterogeneous structures, Jiao et al. [168] developed an automated FIB-TOF-SIMS method for analyzing the 3D distribution of lithium ions in NMC811 cathode materials (Fig. 10(c)). This approach employs Xe^+ plasma FIB for sequential sectioning, integrated with a wobbling milling strategy to improve cross-sectional planarity, enabling simultaneous "global volumetric" imaging and "localized volume" depth profiling. The automated workflow completes stable data acquisition within 23 hours, successfully identifying lithium-enriched regions within micro-structures such as internal cracks in particles, significantly enhancing spatial resolution for analyzing lithium distribution behavior in heterogeneous materials.

To address the challenge of correlating interfacial micro-structure with chemical distribution in 3D space, Dluhoš et al. [169] developed an integrated analysis platform based on FIB-SEM tomography. This method employs sequential sectioning to simultaneously capture SEM morphology, EDS elemental distribution, and high-sensitivity lithium signals from TOF-SIMS (Fig. 10(d)). The method's advantage lies in integrating diverse signals into a unified 3D dataset, effectively correcting quantitative biases caused by uneven milling rates in heterogeneous samples. This enables synergistic analysis of multidimensional information—including pore structure, particle damage, interfacial delamination, and lithium dendrite growth—within battery components, providing a comprehensive perspective from micro-structure to chemical composition for understanding battery degradation mechanisms.

To integrate nanoscale milling capabilities with full-spectrum acquisition, Pillatsch et al. [170] developed the FIB-TOF detector system for FIB-SEM platforms. This system integrates the nanoscale milling capability of high-brightness FIB with the full-element detection sensitivity of TOF-SIMS (Fig. 10(e)), enabling simultaneous collection of complete mass spectra for each pixel during ion beam scanning to efficiently construct 3D chemical composition datasets. Its successful application in multilayer AlGaAs/InGaAs quantum well structures demonstrate the platform's exceptional compositional resolution capabilities, providing a powerful tool for cross-scale chemical visualization of multicomponent materials such as battery electrodes.

Multi-modal characterization, by integrating the complementary strengths of TOF-SIMS with other analytical techniques, has elevated battery interface analysis from 2D to 3D, from static to dynamic monitoring, and from isolated information to comprehensive correlations. This new paradigm not only significantly expands the dimensions and depth of interface research but also establishes a robust methodological foundation for precisely understanding interface evolution mechanisms and guiding interface engineering design. As the maturity of combined techniques and automation levels continue to advance, their application prospects in future battery research will become even more extensive.

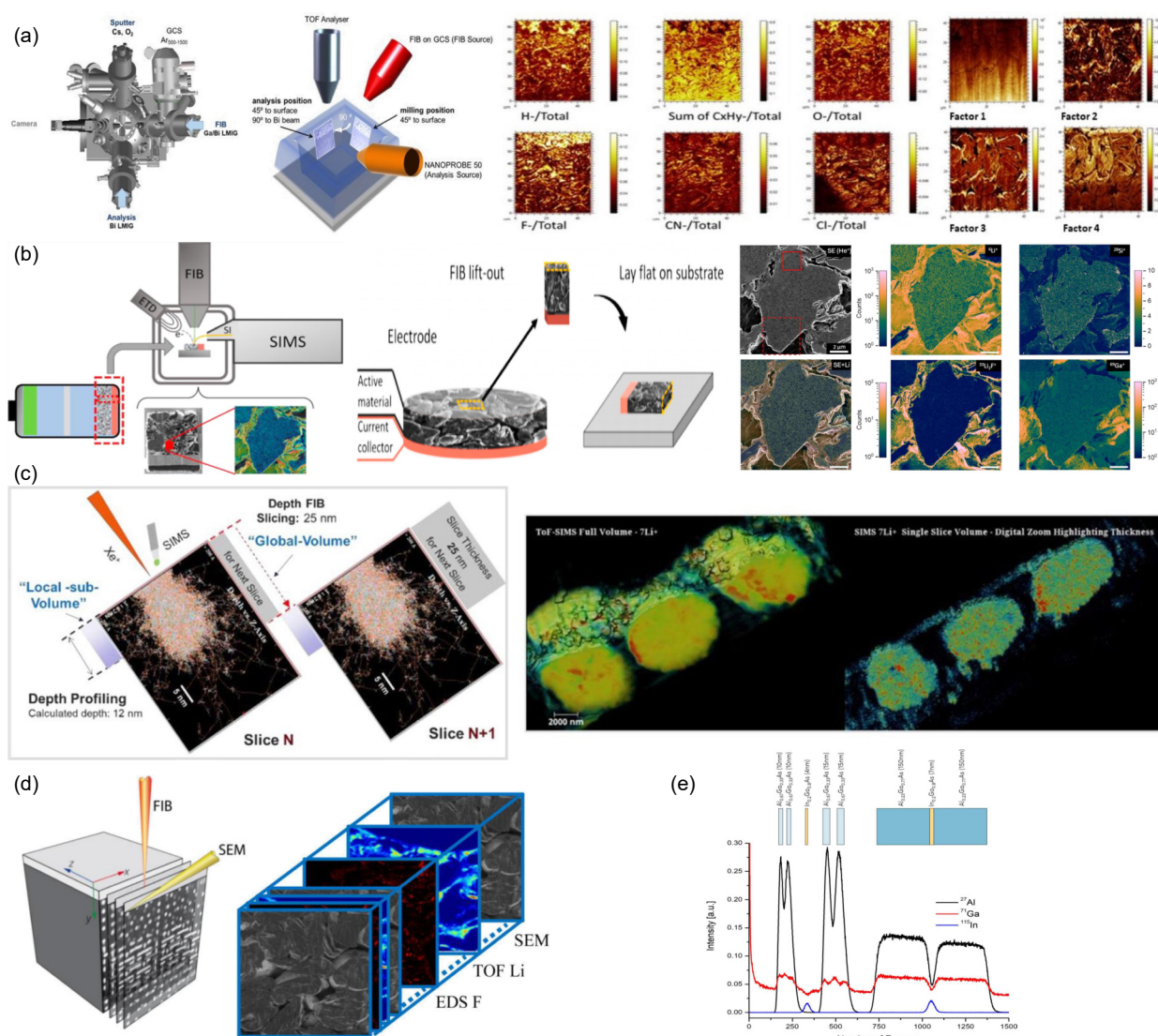


Figure 10 (a) Schematic diagram of the combined FIB and TOF-SIMS apparatus and 2D image of the test sample. Reproduced with permission from Ref. [166], © 2020 Oxford University Press. (b) Schematic Diagram of FIB-SIMS Sample Preparation Steps and Chemical Imaging. Reproduced with permission from Ref. [167], © 2024 American Chemical Society. (c) SIRM simulation of ion range overlaid with schematic of "Local Sub-Volume" and "Global Volume". Reproduced with permission from Ref. [168], © 2025 Oxford University Press. (d) Schematic image of serial sectioning workflow. Reproduced with permission from Ref. [169], © 2023 Oxford University Press. (e) FIB-SIMS measurement of a multilayer sample consisting of several AlGaAs layers and two InGaAs quantum wells. Reproduced with permission from Ref. [170], © 2025 Oxford University Press.

6 Summary and prospects

In this review, we comprehensively describe the instrument structure, development history, working principle and core functions of TOF-SIMS, and systematically summarize the latest progress of the application of TOF-SIMS in secondary battery research, which involves the analysis of electrode surface modification layer, solid-liquid interfacial film analysis, and tracing the electrolyte decomposition paths and so on. These advancements provide a crucial theoretical foundation and technical support for revealing the evolution patterns of electrochemical interfaces and guiding the design of high-performance electrode materials. However, TOF-SIMS still faces the challenges of matrix effect, sputtering damage and data interpretation complexities, which limit its application in probing the dynamic evolution of nanoscale heterogeneous interfaces. To enhance the application value and practical utility of TOF-SIMS in battery research, it can be further explored toward the following aspects in the future (Fig. 11).

(1) Matrix Effects and Challenges in Quantitative Analysis: Multi-modal Technology Integration and Standard Database Construction.

The signal intensity in TOF-SIMS is not solely determined by the concentration of the target species but is significantly modulated by the local chemical environment of the sample. This "matrix effect" constitutes a fundamental challenge to achieving reliable quantitative analysis. For instance, oxygen components in metal oxide matrices can strongly suppress secondary ion yields of organic molecules, while highly conductive graphite matrices may enhance ionization efficiency for light elements like lithium. The matrix effects result in signal intensity differences of up to several orders of magnitude between materials, making absolute quantitative analysis nearly unfeasible. Although calibration using standards or empirical models can be employed for correction, these methods are highly dependent on a high degree of matching in chemical state and morphology between the standard and the analyte, severely limiting their applicability to complex

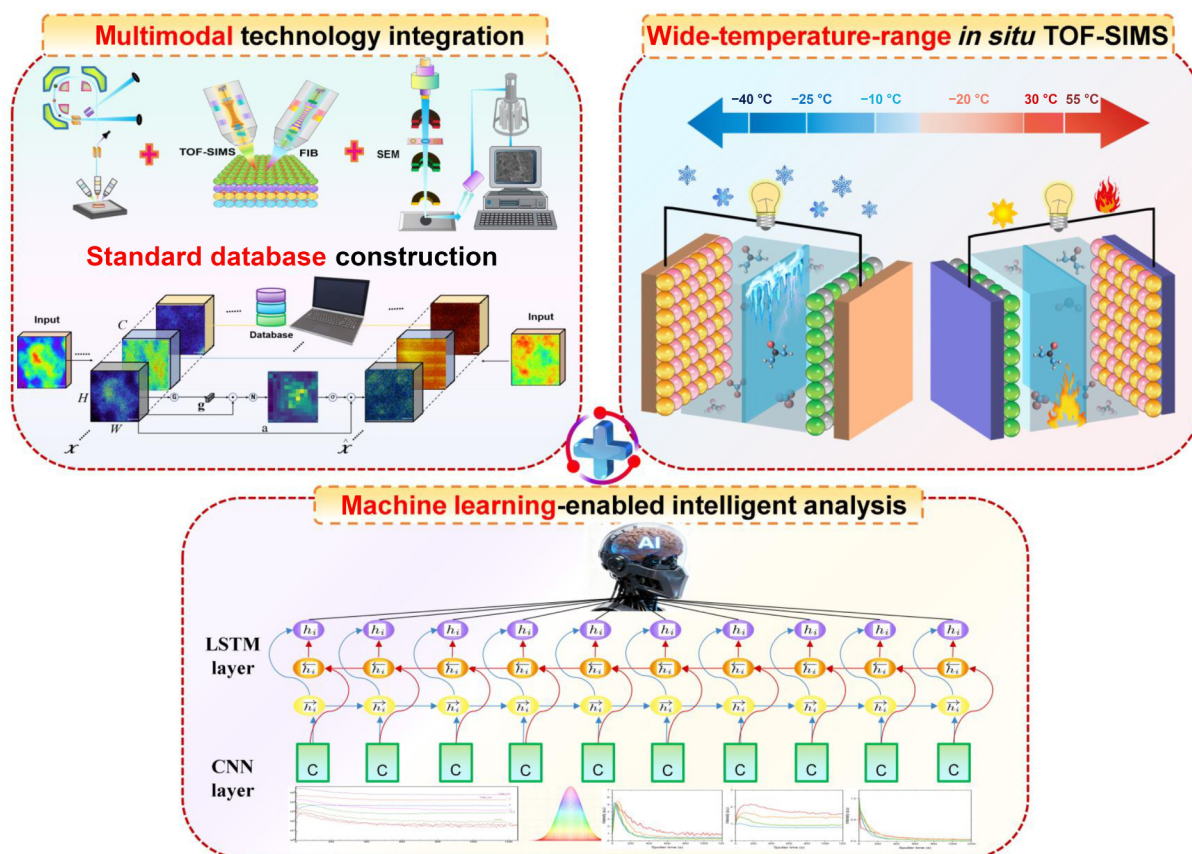


Figure 11 Prospects for future applications of TOF-SIMS.

heterogeneous systems like SEI. Furthermore, the complex fragmentation pathways prevalent in organic or polymeric systems add substantial uncertainty to mass spectrometry interpretation and elemental quantification.

To address this challenge, establishing battery interface specific standard samples and databases offers a viable solution. By systematically preparing model SEI/CEI films or electrode materials with known chemical compositions, dedicated databases incorporating "fingerprint spectra" and relative sensitivity factors can be built, providing a foundational scale for quantitative analysis. Practically, integrating TOF-SIMS with other techniques like XPS serves as an effective strategy for cross-validation. The semi-quantitative elemental chemical state information provided by XPS can act as an "anchor" for TOF-SIMS signal intensities, thereby significantly enhancing reliability in semi-quantitative comparisons. Furthermore, integrating machine learning models can enable algorithms to learn the variation patterns of ion yields in complex matrices. This facilitates intelligent correction of raw signals, thereby mitigating matrix-induced biases to a certain extent and enhancing the potential and accuracy of quantitative analysis.

(2) Intricacies of massive data interpretation: machine learning-enabled intelligent analysis.

The mass spectrometry data generated by TOF-SIMS typically contains thousands of fragment ion peaks, particularly when analyzing organic/inorganic hybrid interfaces in batteries. The accurate assignment of these spectral peaks highly dependent on researcher expertise and database matching, leading to highly subjective results and inefficient analysis. For instance, when analyzing electrolyte decomposition products, the mass overlap between $C_2H_3O^+$ (m/z 59.01) and LiF_2^+ (m/z 58.99) often requires

high-resolution mode for differentiation, inevitably sacrificing detection sensitivity. Furthermore, while traditional multivariate methods like principal component analysis can preliminarily extract information about spatial heterogeneity at interfaces from chemical imaging data, their applicability to complex heterogeneous systems is limited. These methods offer low automation, and the analysis process remains highly dependent on manual intervention.

To overcome this challenge, integrating machine learning and deep learning algorithms to transition data analysis from "experience-driven" to "intelligence-driven" has become an inevitable trend [171]. Specifically, the advantages of incorporating artificial intelligence algorithms manifest across three aspects:

Automatic assignment and chemical classification of mass spectrum peaks. Models based on the convolutional neural network (CNN) can automatically identify and assign characteristic fragment peaks in complex mass spectra, effectively resolving overlapping peaks. Combined with transfer learning strategies, these models can rapidly adapt to spectrum analysis across different battery systems, significantly enhancing throughput and objectivity.

Pattern recognition and failure prediction in chemical imaging. Chemical imaging data from TOF-SIMS can reflect interfacial inhomogeneity, but traditional analysis methods are difficult to quantify the degree of heterogeneity. Unsupervised learning algorithms can automatically identify and cluster chemically distinct regions within the images, such as lithium dendrite nucleation sites and electrolyte decomposition hotspots, thereby enabling the quantification of interfacial inhomogeneity. Furthermore, by integrating supervised learning algorithms like Random Forest, quantitative correlation models can be established

between the interfacial chemical distribution and macroscopic battery performance, facilitating the early prediction of performance degradation.

Dynamic Modeling for 3D Depth Profiling. TOF-SIMS depth profiling analysis data of battery interfaces contains dynamic evolution information, but traditional methods often interpret through empirical fitting. Temporal models based on the recurrent neural network (RNN) or the long short-term memory (LSTM) network can effectively capture the non-linear evolution of component distributions as a function of sputtering depth, simulating the dynamic evolution of interfacial structures. This method can be further coupled with computational methods such as phase-field simulations, providing a data-driven theoretical basis for predicting interfacial stability.

(3) Challenges in interface research under extreme conditions: wide-temperature-range *in situ* TOF-SIMS technology.

Precise characterization of battery interface behavior under extreme conditions is crucial for understanding and improving battery performance at high and low temperatures. However, applying TOF-SIMS to this field faces significant challenges, with the core contradiction being the compatibility between the instrument's fundamental ultra-high vacuum requirement and the integration of temperature control systems. Dramatic temperature fluctuations can induce thermal stress deformation in both the sample stage and the vacuum chamber, potentially compromising vacuum integrity and, more critically, causing misalignment of sensitive ion optics. This directly degrades signal quality and analytical reproducibility. More critically, the challenge lies in preserving the fidelity of interfacial chemical states. During the transfer of the sample from the extreme environment to the analysis position, the critical challenge lies in completely "freezing" transient structures—such as solidified electrolyte phases at low temperatures or high-temperature interfacial side-reaction products—to prevent their relaxation or alteration, which is essential for obtaining authentic chemical information. Additionally, numerous practical difficulties exist in experimental operation. For instance, in cryogenic experiments, water condensation readily contaminates the sample surface, while temperature-induced thermal drift can severely blur the spatial accuracy of high-resolution chemical images.

To address these challenges, developing an *in-situ* sample stage with an integrated precision temperature control module offers an effective solution. By combining high-efficiency heating/cooling modules, active thermal shielding, and high-precision temperature sensors, it enables rapid and stable temperature cycling from cryogenic to high temperatures while ensuring compatibility with ion optical systems. This technology allows direct TOF-SIMS analysis under targeted operational conditions, facilitating real-time capture of transient chemical information through highly sensitive mass spectrometry imaging. Key processes observable are electrolyte phase transitions, evolving ion transport dynamics, and spatial distribution of SEI/CEI components. When combined with depth profiling analysis techniques that mitigate beam damage at low temperatures, this method holds promise for resolving 3D interfacial chemical structures closer to the native state, thereby systematically revealing the microscopic mechanisms of battery failure under extreme conditions. Despite its broad potential, this technological pathway still faces several bottlenecks, including maintaining vacuum integrity under extreme temperature conditions, precise suppression of sample surface condensation, and real-time compensation for thermal drift. Overcoming these limitations will propel extreme-environment TOF-SIMS into an

authoritative tool for deciphering battery interface behavior across wide temperature ranges, thereby providing critical scientific foundations for interface design and material innovation of next-generation batteries.

Acknowledgements

This work was supported by the Key R&D Program of Heilongjiang province (2023ZX04A01), the National Key R&D Program of China (2021YFC2902905), The Key Project of Chongqing Technology Innovation and Application Development (2022TIAD-DEX0024, 2023TIAD-KPX0007, 2024TIAD-KPX0003), Beijing Nova Program, Chongqing Outstanding Youth Fund (2022NSCQ-JQX3895), and the National Natural Science Foundation of China (22109010).

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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