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ToF-SIMS in battery research: Advantages, limitations, and best practices

Special Collection: Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis

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ABSTRACT

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful analytical technique whose application has great potential for battery research and that today is not used at its full potential. The goal of this article is to encourage battery researchers to add ToF-SIMS to their research toolbox and to incite ToF-SIMS experts to collaborate more strongly with battery researchers. It is, therefore, addressed to both new and experienced ToF-SIMS operators. First, an introduction to the analysis technique is given, in which the fundamental operating principle and the most common measurement modes are briefly explained. Additionally, we provide information on different machines commercially available. Based on this knowledge, we discuss the suitability of ToF-SIMS for battery research and highlight its method-specific characteristics for corresponding analytical tasks. We show that the high sensitivity of this analytical method (fractions < 10 ppm are detectable) combined with high flexibility for all analyzable materials (organic, inorganic, and hybrid) and sample formats (powders, thin films, electrodes, etc.) make ToF-SIMS particularly relevant for battery research, where the chemical nature of interfaces/interphases and traces of reaction products are of paramount importance. As practical guidance, we introduce and discuss the most common pitfalls when using ToF-SIMS for battery research and give hints on how they could be avoided or minimized. A major goal of this article is to review best practices, focusing on improving data quality, avoiding artifacts, and improving reproducibility.

I. INTRODUCTION

This article aims to raise the attention of the battery community to a powerful yet poorly utilized analytical technique, time-of-flight secondary ion mass spectrometry (ToF-SIMS), and to encourage SIMS experts to investigate the great potential of ToF-SIMS applied to battery samples. This article is, therefore, addressed to battery researchers with poor ToF-SIMS expertise, ToF-SIMS experts with poor battery-related knowledge, and anything in between. As a consequence, this section will briefly introduce key basic features of battery samples and ToF-SIMS, while Secs. II–VI will focus on the advantages, disadvantages, pitfalls, and best practices of ToF-SIMS applied to battery research.

Modern battery samples are typically 3D composites made of different components, each with its own physical-chemical properties and size/shape distribution. This is particularly true for battery electrodes, which are core components of any battery and whose performance is directly related to the materials used, their relative volume fraction, and their spatial distribution (i.e., the electrode microstructure).[1–8] Typical electrode components are active material(s) (AMs) [in which, e.g., Li-ions are (de-)intercalated], additives [mostly carbon conductive additive(s) to enhance electronic conduction and one or more binder(s) to enhance particles' contact], and the electrolyte, whose role is to allow ions to move from one electrode to the other while being electronically insulating.[9,10]

Interfaces are also of great importance in Li-ion and post Li-ion batteries, and both the chemical species present at the particles surface (e.g., residuals from the synthesis process or particles coating), and the (inter)phases formed during battery cycling strongly influence key properties as reversibility, battery cycle life, safety, and practical energy and power densities. Despite their importance, interface reactions, the composition and spatial distribution of interphases like the cathode- or solid-electrolyte interphases (CEI and SEI, respectively), and their relationships with the electrode and electrolyte formulations, particle surfaces, and cycling conditions are not fully understood yet, and they are therefore heavily investigated.[11,12] One key reason for this lack of knowledge is the difficulty of experimentally analyzing interphases. This is due to their small weight and volume fractions (Fig. S2),[50] their chemical composition (several different chemical components, making the concentration of each of them even smaller), and their spatial location (often buried inside the 3D electrode microstructure).

Typical analytical questions in battery research relate to the identification of interphases, the analysis of (electro)chemical reaction products at interfaces, the composite electrodes microstructure, and how all of those are connected to the electrode/cell performance, safety, and cycle life. Many instrumental analytics, like secondary and transmission electron microscopy (SEM and TEM), x-ray photoelectron spectroscopy (XPS), and energy dispersive x-ray (EDX), are commonly utilized to try answering those questions. However, either they do not provide information on the chemical composition (e.g., SEM and TEM) or they lack in terms of spatial distribution or sensitivity (e.g., XPS). On the contrary, ToF-SIMS is a highly sensitive technique that can detect chemical species at very low concentrations. Typically, the detection limit for elements is in the ppm range and for molecular fragments in the fmol range, depending on the ionization probability and secondary ion (SI) yield of the analytes as well as the applied primary ion beam and measurement settings. Furthermore, ToF-SIMS provides both high lateral resolution (down to 50 nm, with a practical limit around 100–150 nm for battery samples) and large field of views (up to several centimeters), as well as high mass resolution ($m/\Delta m > 30\,000$ FWHM) that allows distinguishing ion species with similar masses. SIMS is, therefore, particularly suited for surface and interface analysis, which is of great importance in battery research, and has already demonstrated its applicability and potential when combined with battery samples.[13–28] Nonetheless, ToF-SIMS is still rarely applied to battery research. Most of the published work focuses on the synthesis of new materials in combination with cell construction and electrochemical characterization. It is rather a rarity that works go beyond this and is also dedicated to analytical questions on decomposition processes. Therefore, with this article, we want to encourage battery and SIMS experts to collaborate more strongly to unlock a better understanding of both state-of-the-art (Li-ion) and developing (e.g., Na-ion, solid-state) battery technologies.

The rest of this article is divided into five parts: first, ToF-SIMS working principle, (dis)advantages, and the main instrument providers and setups are presented (Sec. II). Then, best practices for analyzing battery samples by SIMS are provided (Sec. III), together with the main pitfalls of this technique to be aware of (Sec. IV). Afterward, recent advancements in SIMS data processing are discussed (Sec. V). Lastly, the main information reported is summarized, and perspectives for the more widespread use of SIMS in battery research are given (Sec. VI).

II. ToF-SIMS WORKING PRINCIPLE AND (DIS) ADVANTAGES

In the field of surface analysis, ToF-SIMS has emerged as a powerful technique with several advantages. It offers valuable insights into the chemical composition and molecular structure of surfaces together with high spatial resolution. However, it is important to consider various factors and limitations to ensure an accurate interpretation of ToF-SIMS data. For this, the working principle of ToF-SIMS and its main advantages and drawbacks need to be well understood. Therefore, these key aspects are discussed in this section. In addition, main instrument providers and setups are reported.

A. Working principles

The basic operating principle of ToF-SIMS is relatively simple (Fig. 1) and described in the following. For more details on the operation principle, the underlying fundamental physical mechanisms, and technical details related to ToF-SIMS, readers are referred to Refs. 29–31.

(1) A primary ion beam is exploited as a primary ion source, and the primary ions are accelerated to bombard the sample surface located in ultrahigh vacuum ($\leq 10^{-8}$ mbar). As primary ion species, Bi_x^+ (monoatomic or clusters) is typically used for battery research. Considering that Bi is first liquefied to generate ion clusters, this primary ion gun is also referred to as liquid metal ion gun (LMIG).

(2) The primary ions hit the sample surface and induce a collision cascade that leads to the ablation of secondary species, such as electrons, atomic and molecular fragments, from the sample surface (typically the first monolayers). As a function of the material hardness, the so-called ion mixing effect (a result of the collision cascade) is more or less pronounced and can increase the depth of information. If (large) cluster ions are used as primary ion species, surface sensitivity is usually decreased.[32] As a rule of thumb: the larger the clusters, the lower the surface sensitivity. In favor, cluster ions show less implantation depth and less fragmentation of molecular samples.

(3) Whereas most of the generated fragments are neutral, the charged fragments, referred to as SIs, can be extracted by an electric field and subsequently analyzed in a ToF mass spectrometer system. The ToF determines the m/z of every ion analyzed by accelerating them through an electric field and measuring the time required to hit the detector after traveling through a field free flight tube. Knowing the speed of the ions and the analyzer length allows calculating the mass over charge ratio (m/z) of the analyzed SIs. In order to have a well-defined starting point for the time-of-flight analysis, either the primary ion or the secondary ion beam at the analyzer entrance must be pulsed. Besides the ToF, other kinds of mass analyzers like sector field, quadrupole or ion traps can be used, especially ion traps, like orbitraps, are powerful (Fig. S3).[50] They require longer analysis time but offer higher mass resolution ($m/\Delta m >$ 240 000) and accuracy, at the expense of spatial resolution.

It is important to note that ToF-SIMS is a destructive method that uses fragmentation information to draw conclusions on the existing surface chemistry. This means that the detected SIs are mostly not directly present in the detected form in the sample. Instead, they correspond to fragments of the existing compounds

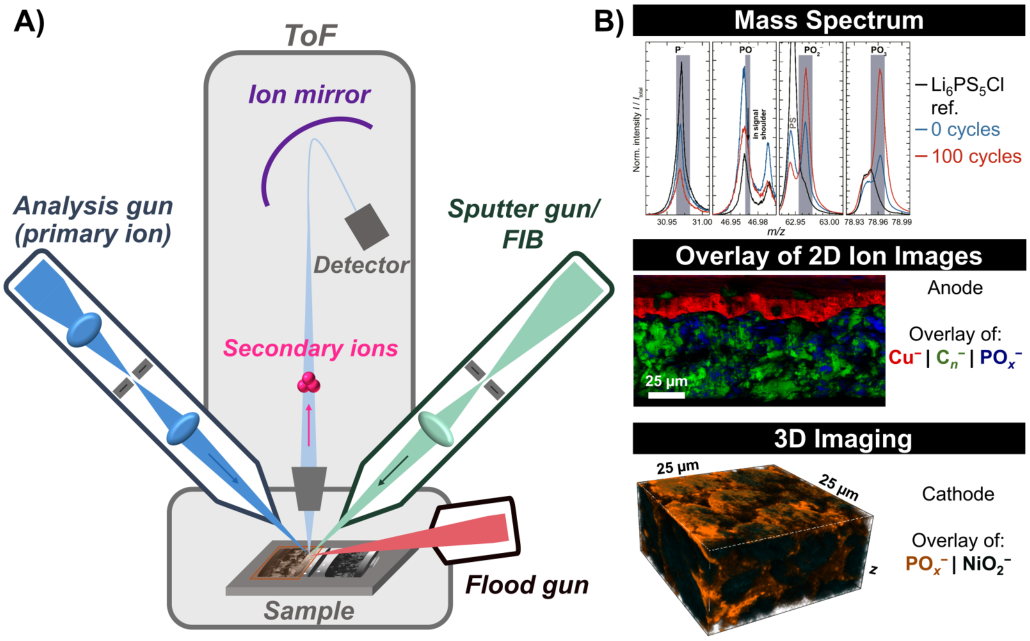

FIG. 1. (a) Schematics of the working principle of a ToF-SIMS. Primary ions (left) are focused and accelerated to bombard the sample surface. The bombardments lead to cascade phenomena causing fragments of the species present on the sample surface to get ionized, forming the SIs. These are extracted and accelerated through electric fields into the ToF analyzer (top), which determines the *m/z* ratio of each ion detected. A low-energy electron flood gun (bottom right) is used for charge compensation caused by primary ions hits. A sputter or FIB gun (right) can be used to ablate part of the sample to analyze its bulk composition. (b) Example of ToF-SIMS analysis data: (top) mass spectrum (here of a solid-state composite cathode), (center) 2D imaging of, e.g., electrodes cross sections (here: graphite anode), and (bottom) 3D imaging (here of a coated cathode active material). The top insertion of (b) was reproduced with permission from Walther *et al.*, Chem. Mater. **31**, 3745 (2019). Copyright 2019 American Chemical Society.

formed during the collision cascade and associated effects such as material recombination/mixing. However, from the composition and relative amount of the SI fragments, it is often possible to draw conclusions on the sample's chemical characteristics. The big advantage of ToF analyzers is that they have a high transmission [Eq. (1)] and single ion counting detectors can be used, which allows to reach the highest sensitivity. Consequently, the primary ion dose can be kept $<10^{12}$ ions/cm^2, allowing to scan the sample surface of inorganic materials about 100 times without removal of the first atomic layer (static SIMS).

In general, the intensity of the SIs can be determined by Eq. (1),[29]

$$I_s^x = I_p \times y_x \times a^{\pm} \times \theta_x \times \eta, \tag{1}$$

where I_s^x is the secondary ion current, I_p is the primary ion current, y_x is the sputter yield, $a^{\pm}$ is the ionization probability (either for positive or negative ionization), θ_x is the concentration of species x in the analyzed area, and η is the transmission of the SIMS machine used, i.e., the fraction of generated SIs that are collected and detected. The ionization probability is often directly connected to the so-called *matrix effect*, which describes the dependency of the ionization probability on the chemical environment. Since the ionization probability is typically unknown, ToF-SIMS is generally considered to be a semiquantitative method. However, drawing semiquantitative conclusions requires assuming that all the parameters in Eq. (1), except for θ_x, can be considered constant for the chemical fragments being compared, or that the differences can be compensated through appropriate data normalization. The latter underlines the importance of proper normalization (or data scaling) procedures, which will be further discussed in Secs. III and V. In addition, model samples with known composition can be used to build SI-specific calibration curves (SI intensity vs concentration), i.e., the so-called relative sensitivity factor (RSF) that allows converting SI intensity into concentration. However, this approach is particularly challenging when dealing with multiphase samples like battery electrodes, which typically contain several unknown degradation products, and it is possible for low concentrations only.

The linear relationships between the SI current and the ionization probability can be seen both as an advantage and as a disadvantage. On the one hand, it hampers a proper quantitative evaluation; on the other hand, it enables high sensitivity for compounds with high ionization probability. This can be a key to ease the detection of interfaces or interphase compounds at low concentrations, some of which have shown high ionization probabilities.[20]

ToF-SIMS can be combined with various other features, like a sputter gun (for instance, based on Ar^+, O_2^+, or Cs^+) or a

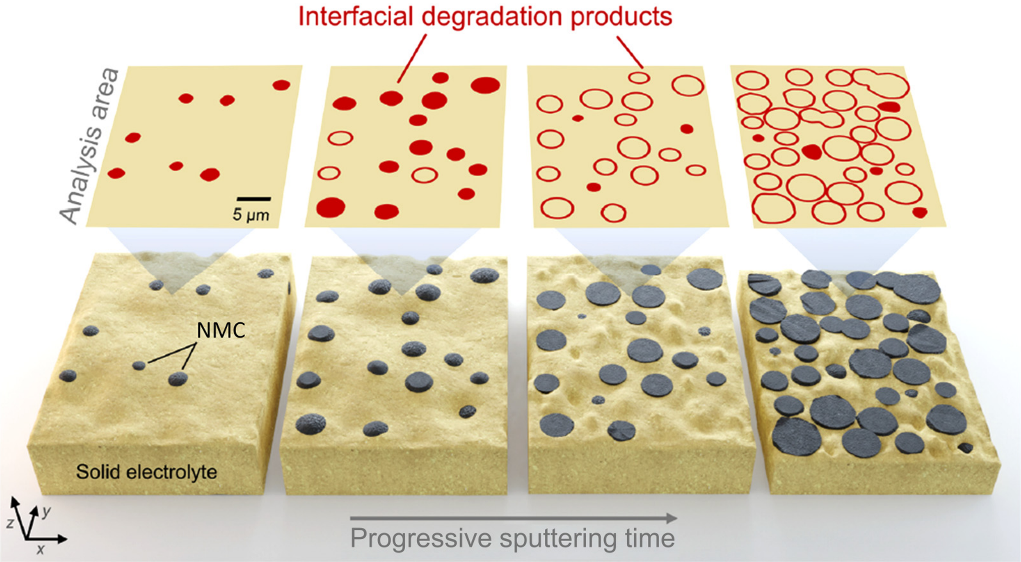

FIG. 2. Example of differential sputtering for the case of all-solid-state cathode using NMC as active material (dark particles) and Li_6PS_5Cl as solid electrolyte. Different sputter-resistance (in this case, lower for the solid-electrolyte phase) may lead to a relative increase in the volume fraction of the CEI interphase formed at the NMC/Li_6PS_5Cl interface (circles in upper image row), until a sputtering equilibrium is reached. Figure reproduced with permission from Walther, "Interfacial degradation in lithium thiophosphate-based composite cathodes for all-solid-state lithium-ion batteries," Ph.D. thesis (Justus Liebig University Gießen, 2021). Copyright 2021 Author(s), licensed under a CC0 license.

focused-ion beam (FIB) gun (Ga^+), as shown in Fig. 1. An alternating sequence of analyzing and sputtering/milling allows, for example, depth profiling and 3D tomography analysis. Therefore, ToF-SIMS can provide surface-sensitive data (static SIMS) as well as information on buried interfaces and the bulk (dynamic SIMS).

When performing a sputtering or a milling process, it is important to keep in mind that certain phases in the composite electrode might be more sputter resistant than others. This means that over sputtering the relative volume fraction of those phases may increase (Fig. 2) until a sputter equilibrium is reached. If some of the minority phases of interest show this characteristic, as found in Ref. 16 for the case of CEI formed on $LiNi_xMn_yCo_zO_2$ (NMC) plus argyrodite (Li_6PS_5Cl) cathodes, differential sputtering can be used as a convenient way to ease the detection of such a minority phase. However, if a quantitative evaluation of the phase fractions has to be carried out, the nonconsideration of possible differential sputtering may lead to erroneous results, tending to overestimate the volume fraction of the most sputter-resistive phase(s).

Figure 2 illustrates that long-term sputtering typically leads to roughening effects due to local differences in sputtering rates arising from compositional variations and different crystal orientations.

B. Advantages and disadvantages

1. Advantages

Key advantages of ToF-SIMS applied to battery research are (1) the possibility to obtain *surface-sensitive* chemically related information, (2) the capability to reach both *high mass* and *high spatial resolutions*, (3) *high sensitivity*, allowing to detect species at very low (<10 ppm) concentration, and (4) *analysis of the sample's bulk* by combination with a sputter or FIB gun. Figure 3 depicts the high sensitivity and relatively high spatial resolution achievable by ToF-SIMS and compares those with other imaging or surface analytical techniques, such as SEM or XPS.

In addition to these key advantages, other important SIMS features are briefly summarized in the following.

(5) *Investigating different types of electrodes and powders.* ToF-SIMS analysis flexibility with respect to electrode types is particularly important because battery research is characterized by different electrode formats (liquid- or solid-state electrolytes based, thin films, etc.), which are relevant for both basic and applied research. In addition, powders can be analyzed as well, although sample preparation in this case can be more challenging due to, e.g., embedding of the particles in a polymer matrix, as discussed in more detail in Ref. 34.

(6) *Analysis of organic, inorganic, and hybrid materials.* The capability to measure organic, inorganic, and hybrid materials simultaneously can be particularly useful in the context of battery electrodes, as they are typically composite materials in which both organic (e.g., binders or polymeric solid electrolytes) and inorganic (e.g., cathode active materials or ceramic solid electrolytes) materials are found.

(7) *Isotope analysis.* The capability of distinguishing between different isotopes can be useful for model experiments. Indeed, using isotope-enriched chemicals (e.g., ^2H instead of ^1H, or ^6Li instead of ^7Li) can allow identifying where those isotopes are

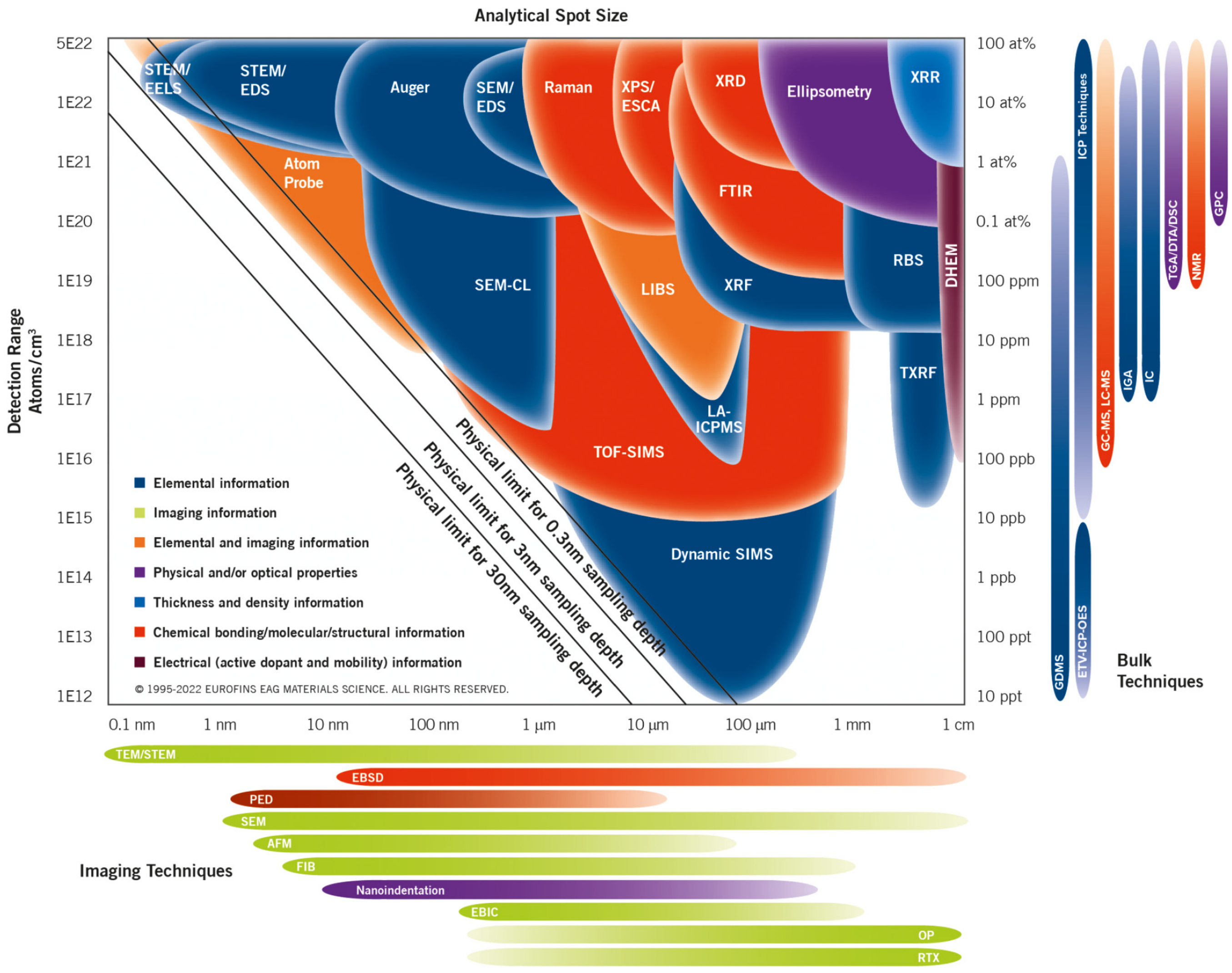

FIG. 3. Schematics comparing different analytical methods in terms of their detection limit, lateral resolution, and type of information obtained. It can be seen that no analytical method fulfills all criteria simultaneously to the same extent, but also how ToF-SIMS allows reaching both high sensitivity with relatively high lateral resolution. Reprinted with permission from https://www.eag.com/techniques/. Copyright Eurofins Scientific (www.eurofinsEAG.com).

located after synthesis, manufacturing, or cycling. Examples of this could be the identification of not reacted chemicals partially covering the AM particle's surface, track solvent degradation during cycling,[35] or Li diffusion into the AM particles.[36,37]

(8) *Analysis of positively and negatively charged SI.* The capability of measuring in both polarities allows the detection of species that are easier to charge positively and species that are easier to charge negatively, contributing to the particularly high sensitivity of this technique. Indeed, SIMS signal intensity is proportional to the ionization probability of the secondary species, i.e., the probability that a neutral molecular fragment is positively or negatively charged during the cascade phenomena occurring after the primary ions hit the sample surface [Eq. (1)].

2. Disadvantages

Despite its numerous advantages, ToF-SIMS, like any other analytical technique, has a number of drawbacks and limitations that require a combination of several analytical methods to compensate for their respective disadvantages. The main ToF-SIMS limitations are summarized in the following.

(1) *Lack of information on the oxidation state of the detected species.* The lack of information about the oxidation state can be overcome through XPS. XPS, on the other hand, can typically only detect concentrations greater than 0.1 at. %. The combination of these techniques is, therefore, particularly practical as it can compensate for most of their respective limitations.

(2) *Differentiation of chemical species with similar associated fragmentation processes and material crystal structures.* The formation of a given chemical species (e.g., the degradation of the electrolyte over electrochemical cycling) can be followed by ToF-SIMS only if the reagent(s) and the product(s) of those reactions lead to the formation of different SIs, or to a significant variation in their amount. Otherwise, with ToF-SIMS analysis, it would not be possible to clearly distinguish between reagents and products, whereas other methods, such as solid-state nuclear magnetic resonance, can achieve this.[38] In addition, changes in the crystal phase are typically not detectable by ToF-SIMS, while these are clearly observable through x-ray diffraction.

(3) *SIs shielding caused by the sample roughness/topography.* Another important parameter to keep in mind is the high roughness of typical battery samples. In ToF-SIMS analysis, this can cause shadow effects as well as different ion intensities due to different angles of impact of the primary ion beam, resulting in fewer SIs intensity being detected by the analyzer. This drawback, similar to the different ionization probability of different SIs, requires appropriate data scaling/normalization procedures, as will be discussed in Secs. III and V.

(4) *Limitation of lateral resolution and surface sensitivity.* Despite ToF-SIMS being able to reach relatively high lateral resolutions and its high surface sensitivity, it should be mentioned that other methods can outperform ToF-SIMS on both these characteristics. In particular, higher lateral resolutions can be obtained by electron microscopy (Fig. 3), while higher surface sensitivity can be obtained by low energy ion scattering.

(5) *Semiquantitative information.* It should be always kept in mind that SIMS is a semiquantitative method [Eq. (1)] and that quantitative information can be extracted only if devoted RSF values for calibration are previously determined, which however is often challenging (if not impossible) in the context of battery-related materials.

C. Instruments providers and measurement modes

Whereas in the 1970s and 1980s SIMS equipment was typically self-built at university group level, most of the SIMS machines in use today are commercially available. Most manufacturers sell stand-alone SIMS machines, which can, however, be customized to implement extra features for sample transfer, preparation, or to add other analytical methods. Table I offers an overview of the commercially available state-of-the-art SIMS devices. In general, all these machines can be utilized for the analysis of battery samples. Because battery materials are commonly air sensitive, a key factor is to assure suitable transport containers and procedures to avoid contaminations and reactions when transferring air sensitive samples from the glovebox to the SIMS.

Among all the analyzers listed in Table I, ToF analyzers are the most versatile, and they are suited for both static (surface characterization) and dynamic (depth profiling/3D analysis) SIMS. Moreover, ToF analyzers can analyze all masses within one analysis cycle at very high speed, fasting SIMS measurements, and unlocking fast imaging procedures. Accordingly, a relatively large number of ToF-SIMS devices are sold, which makes ToF analyzers the most frequently used ones in battery research. Hence, in this paper, we focus on ToF-SIMS.

In ToF-SIMS, the machine performance depends to a significant extent on the operating mode of the primary ion source. Different measurement modes can be used, typically to increase the mass resolution at the expense of the lateral resolution (or vice versa), with the most suited modes depending on the analytical task to be carried out. In the following, the main ToF-SIMS instrumental modes are listed and both their advantages and disadvantages are discussed.

High mass resolution mode. This measurement setting achieves high mass accuracy and resolution, thus allowing clear signal identification and discriminating between SIs with similar masses (in the order of 0.1 uma, but even smaller if using an Orbitrap as an analyzer), and high total ion counts. For samples with low roughness, mass resolutions $m/\Delta m$ of up to 30 000 FWHM can be achieved with a state-of-the-art ToF analyzer. ToF analyzers allow performing fast (typically a few minutes) surface measurements. The main drawback of this mode is very poor lateral resolution (several microns).

High lateral resolution mode. The imaging mode can be used to enhance the lateral resolution, allowing to, e.g., map the spatial location of both degradation products *and* main phases. However, higher lateral resolution comes at the expense of mass resolution and signal intensity, making it more challenging to assign different peaks to a given SI and to differentiate between two SIs having similar masses. In addition, due to lower primary ion currents, this mode leads to significantly lower SIs current and, therefore, longer measurement times (typically in the range of 1–2 h).

Delayed extraction mode. A third mode uses the same principle as MALDI (Matrix Assisted Laser Desorption Ionization) imaging and combines the advantages of the high mass resolution and imaging modes and is typically referred to as delayed extraction. This mode is similar to the imaging mode, but the extraction voltage, i.e., the voltage applied to accelerate the SIs into the ToF analyzer, is only applied after a given time delay. This produces a time-of-flight compensation for the initial SIs energy spread, leading to an improved mass resolution. The main disadvantages of this approach are that lower masses (typically <30 m/z) are not detectable and that SIs counts are further diminished (loss of SI yield of *ca.* 50% compared to the high lateral resolution mode), leading to even longer experiment times (typically half-day). The machines by Physical Electronics offer an imaging mode at high mass resolution, “HR^2”, that is superior to delayed extraction. It offers linear sensitivity and mass resolution as a function of m/z.

A very nice comparison of the measurement modes is given in Ref. 51. In addition, all these modes can be combined with a sputter gun or an FIB gun to analyze the sample’s bulk. The former case is typically performed for depth profiling, meaning that after each SIMS analysis a sputtering step is performed, allowing to measure the concentration evolution of the SI of interest into the sample depth. The sputtered region should typically be at least 2–3 times larger than the analysis area, to avoid edge effects during the SIMS measurement. Sputtering, however, due to its high current, leads to a significant sample charge, which may not be fully compensated by a flood gun (a flow of low-energy electrons applied to the sample surface). This problem can be solved by

TABLE I. Overview of commercially available stand-alone state-of-the-art SIMS devices in alphabetical order. Devices in which SIMS is installed as an add-on technology were not taken into account.

Manufacturer	Model name	Analyzer	Special feature	Literature reported application in battery research
Cameca	NanoSIMS 50L	Magnetic Sector	– High spatial resolution down to 50 nm – Parallel acquisition of 7 masses – Insensitive to sample roughness	Rare
	IMS 7f	Magnetic Sector	– Dynamic SIMS – High precision isotopic analysis – Parallel acquisition of 7 masses – Insensitive to sample roughness	Rare
	SIMS 4550	Quadrupole	– Dynamic SIMS – Insensitive to sample roughness	Rare
Hiden Analytical	SIMS Workstation	Quadrupole	Simple laboratory device	Unknown
	ToF-qSIMS	ToF & Quadrupole	Simple laboratory device	Unknown
	Hi 5	2× Quadrupole	– Parallel anion and cation detection – Insensitive to sample roughness	Unknown
Ionoptika	J105	ToF	– Designed for biological applications – Analysis of battery materials possible – Insensitive to sample roughness	None
Iontof	M6 (M6 Hybrid SIMS)	ToF & Orbitrap	– Versatile machine for inorganic and organic materials – Spatial resolution down to 50 nm – EDR technology for collecting only a fraction (e.g., 10%) of the selected ions and extrapolates the overall count rate avoiding oversaturation. – Several options for inert sample handling (transfer vessel, VCT, full scale glove box for loadlock) – High mass resolution with orbitrap analyzer	Numerous
	ToF 5	ToF	– Versatile machine for inorganic and organic materials	Numerous
Physical Electronics	nanoTOF 3	ToF	– Versatile machine for inorganic and organic materials – High tolerance for sample roughness – Powerful imaging at high mass resolution mode – MS/MS possible for unique identification of organic molecules – Option for inert sample handling (transfer vessel)	Few

separating the sputtering and analysis step by a pause (whose time can be controlled by the operator), in which only the flood gun is used for charge compensation purposes.

Although there is a clear interest in following concentration trends of SIs being analyzed, when using sputter guns for inorganic battery materials, it is usually possible to measure only the first few hundred nm in a reasonable amount of time, although a few microns can be achieved. Additionally, as mentioned above, effects such as differential sputtering and roughening effects play an increasingly critical role with higher sputter depth. Thus, if the core bulk of the sample needs to be analyzed, FIB, which is used to create a deep crater that is subsequentially analyzed through the SIMS, could represent a better choice. FIB cutting could be performed either in the SIMS chamber (in case a FIB gun was

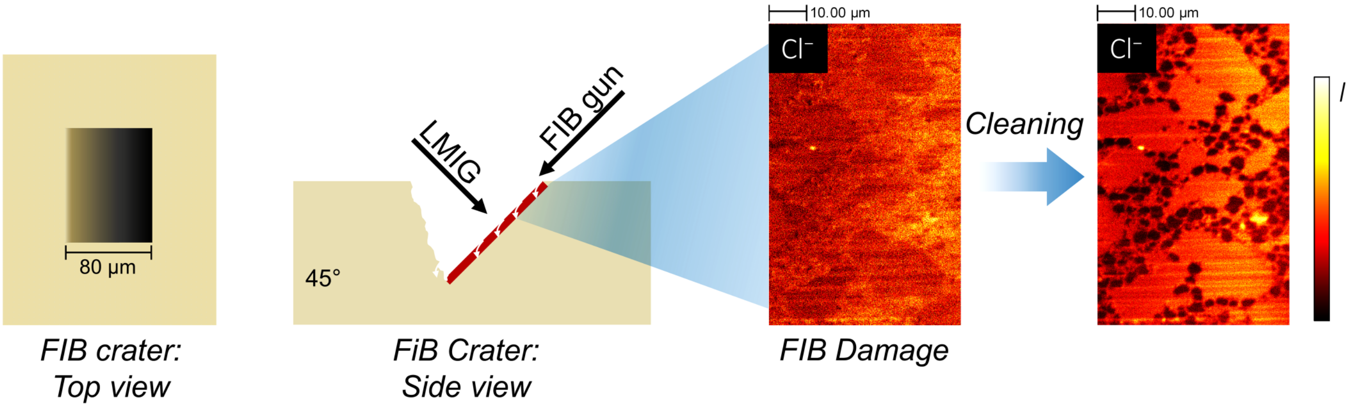

FIG. 4. Schematics of FIB damages created after milling and polishing a 45° crater, and the image quality improvement after a cleaning step performed by the primary ion gun (LMIG). The SI images were taken on a composite cathode using Li_6PS_5Cl as the solid electrolyte and NMC as the cathode active material. It can be seen that after cleaning, areas of the solid electrolyte and the active material can be well distinguished, whereas the chemical information was completely smeared out before cleaning, i.e., Cl^- was detected everywhere on the FIB crater sidewall.

included in the instrument) or in a FIB-SEM, which therefore implies an additional transfer step. The analysis of a FIB crater wall benefits from smoothing the surface as much as possible. For that purpose, in addition to the FIB milling, a polishing step, i.e., a second FIB step performed at lower current and with better beam focus, can be carried out. In addition, the use of FIB typically leads to sample damages, further requiring a cleaning step. Otherwise, the chemical information is completely smeared out and mainly defect species (due to recombination effects caused by the high-energetic FIB) are detected (Fig. 4). This can be performed, for example, using the primary ion gun in direct current (DC) mode and letting it scan the FIB crater for a few minutes to remove the damaged layer. In addition, in the last decade, new ion polishing systems have been established for superior cross section preparation (Sec. S6 in the supplementary material).[50]

Lastly, all these analyses can be performed either at room temperature or under cryogenic conditions. Cryogenic conditions may be needed for samples that are particularly damaged by the primary ion beam, possibly leading to artifacts, like in situ formation of degradation products.

Table II reports an overview of the strengths and weaknesses of the setups discussed above.

III. BEST PRACTICES

This section discusses best practices needed to obtain reliable and reproducible data using ToF-SIMS in the context of battery research and is divided into six parts: (1) measurement planning, (2) sample preparation, (3) sample handling and transfer, (4) statistics, (5) data processing and evaluation, and (6) information to be reported when publishing your results. These best practices were selected to be applicable to most kinds of battery samples. However, interested readers can find more detailed information on particularly sensible samples like lithium/sodium metal and polymers in Secs. S4 and S5 in the supplementary material, respectively.[50]

(1) *Measurement planning.* The experimental design should be planned as a function of the specific analytical needs. A good rule of thumb is to optimize the measuring conditions while trying to keep the design as simple as possible. Examples of this can be designing specific sample holders to analyze electrode cross sections (sample tilted at 90°), or using modified current collectors, like an easily removable current collector to analyze the degradation products formed at the electrode/current collector side. Other, more advanced experimental setups can allow, for example, to perform *operando* SIMS measurements, as recently reported by Yamagishi *et al.*[39] or to combine scanning probe microscopy (SPM) with SIMS to combine the SIs data with the sample surface topography, which can play a particularly important role for topographic samples. Last but not least, it should be underlined that multiple repetition (multiple analysis spots on each sample and multiple samples) is strongly beneficial to enhance the statistical representativity of the results and that, if different samples have to be measured at different times, appropriate storage should be ensured to make the measurements comparable.

TABLE II. Summary of the advantages and disadvantages of different measurement modes discussed in this section. All these modes can be combined with a sputter or FIB gun.

	Mass resolution	SIs intensity	Lateral resolution	Example of typical time
High mass resolution	+	+	–	From a few to 30 min
High lateral resolution	–	–	+	1–2 h
Delayed extraction	+	–	+	Half-day or more

FIG. 5. Schematics of the role of insulating tape in Li-containing battery samples. Without using it (right), application of the flood gun can lead to a potential difference between the sample holder and sample surface, causing unwanted metallic Li deposition.

(2) *Sample preparation*. This is a critical step and can take place both before transferring the sample into the SIMS, and after. First, during ToF-SIMS analysis, battery samples typically have to be electrically insulated. Insulation of battery samples is typically done by attaching them onto the sample holder with insulating tape. Otherwise, the application of the electron flood gun for charge compensation can lead to a difference in electrical potential between the sample surface and the metallic sample holder. If the sample contains mobile ion species such as Li^+, this difference in potential can then lead to metallic Li plating on the sample surface (Fig. 5), which must be avoided. The ion beams themselves can also cause undesired transport and reactions within the sample. In addition, other sample preparation steps, such as sample cutting, polishing, and cleaning (FIB crater, Sec. II C) or simple polishing with high I_p, may be required once the sample is transferred into the SIMS main chamber. Other sample preparation steps depend on the exact sample(s) and on the analysis to be carried out, but might include sample washing (for the case of cycled lithium ion battery (LIB) electrodes[40]), cutting (e.g., by application of FIB or other cutting and polishing procedures), current collector removal (to analyze the electrode surface that was in contact with the current collector during cycling), etc.

(3) *Sample handling and transfer*. The high reactivity of battery samples requires handling them in inert atmospheres. Sample preparation is typically performed in gloveboxes, and an appropriate transfer system is needed to avoid any atmospheric contamination while transferring the sample between the glovebox and the SIMS. As an example, thiophosphates, an important class of solid electrolytes, should always be transferred with a tight and devoted transfer system, as, for instance, the Leica VCT 500. In addition, it should be noted that not only O_2 and H_2O (which level is strictly controlled, typically at <0.1 ppm, in a glovebox) but also N_2 can be detrimental, in particular, for Li or Na metal samples, leading to the formation of a passivation layer containing lithium or sodium nitride.[41] Therefore, both storage and transfer are very likely to cause surface reactions, the reason for which surface cleaning procedures are required. In the case of very reactive samples, the fact that the transfer module should be free of surface adsorbates is often overlooked. Cleaning is usually done by baking under vacuum. Any contamination in the glovebox from stored outgassing chemicals must also be considered.

(4) *Statistics*. Acquiring data from multiple sample analysis areas and multiple (in principle identical) samples is key to ensuring that the results obtained are statistically valid, and ToF-SIMS analysis is no exception. Even if this could be challenging for very long measurements (e.g., delayed extraction), it is easy to acquire data from several analysis areas with high mass resolution measurements ($n \geq 5$ and $n = 10$–15 can be easily reached). Therefore, the latter option is particularly suited to collect statistically trustable data, which can be easily visualized and compared by, for example, box or violin plots.[15] We, therefore, strongly recommend considering experimental designs that allow surface analysis rather than choosing time-consuming and (sometimes) unnecessarily complicated experimental setups—even if they might be fancy.

(5) *Data processing and evaluation*. Data evaluation depends on the applied measurement mode (mass resolution, imaging, or depth profile) and can be performed both via commercial software (typically provided by the instrument provider), *open-source* or *in-house* codes. However, what should always be done is assigning the main peaks of interest to given SIs. Afterward, the identification of the main peaks of interest (i.e., the most relevant ones for the analysis to be carried out) can be performed either manually or by statistical approaches for dimensionality reduction, like principal component analysis (PCA), multivariate curve resolution, or maximum autocorrelation factor. The use of statistical approaches for dimensionality reduction can be particularly useful when considering that SIMS spectra are typically composed of hundreds of different peaks, many of which are likely secondary or uninfluential for the analytical task to be carried out. In short, dimensionality reduction approaches allow identifying the peaks explaining most of the differences between the samples analyzed, and combining them in new variables, enabling to identify the difference between the analyzed samples in a much smaller (e.g., 2D, 3D, 4D) space.[42]

Among these approaches, the most known one is PCA, whose objective is to explain a maximum variance of the dataset collected (e.g., all the spectra collected for all the samples analyzed) through a linear combination of the original variables (e.g., all or a selection of the identified SIs). Linear combination of the original variables leads to the creation of new variables, called principal components (PCs) in the context of PCA. Each PC is mathematically defined in a way to describe as much data variance as possible (meaning that the PC1 describes a higher share of the initial data variance compared to PC2, which describes a higher share of the initial data variance compared to PC3, etc.). All PCs must be orthogonal to each other (meaning that they describe a different portion of the original data variance). For a very accessible, yet rigorous, explanation of the working principle behind PCA, the readers are referred to Ref. 43.

An important step of data evaluation is data normalization (or scaling). This is particularly important for battery samples, considering that the choice of the analysis area can lead to different results due to the sample topography and heterogeneity. Therefore, if possible (typically in high mass resolution mode), multiple points should be measured on a variety of samples to obtain statistically relevant results. The number of data points per sample (e.g., $n = 5$–10 for surface spectra) and the number of samples (e.g., $n = 3$) strongly depend on the sample heterogeneity, and it should be estimated on a case-by-case basis. Several procedures can be used for scaling the data. The simplest way is to scale the SI count of each peak (peak area) by the total number of SIs detected during the measurement. Another, conceptually similar, approach consists in scaling by the SI count associated with a given species. In the context of battery electrodes, a possible choice for the reference peak could be a peak specifically associated with the active material. In both cases, however, data are scaled by using SIs collected over the entire region of analysis, therefore falling short in accounting for the heterogeneities inside the region of analysis, e.g., the active material-related SIs signal being much higher in a subregion where an AM particle is located and lower in subregions containing pores. More advanced scaling procedures can be used for overcoming this limitation, as will be discussed in Sec. V.

TABLE III. Summary of parameters to be reported in any SIMS-related scientific publication.

	Information to be reported
General to all measurement modes	– Primary ion source (e.g., Bi), species (e.g., Bi$^+$, Bi$_3^+$), energy, and aperture used. – Primary ion current. – Operation mode (high mass resolution, imaging, etc.). – Analysis area (e.g., 150 × 150 μm^2). – Raster size (e.g., 256 × 256 pixels). – Number of frames per analysis scan. – Number of primary ion shots per pixel (e.g., 1 shot/pixel). – Stopping condition used (e.g., a primary ion dose limit of 10^{12} ions/cm^2, or the number of scans). – Polarity (positive or negative). – Time for each SI detection (e.g., 60 μs, this time is directly proportional to the maximum *m/z* ratio detected). – Charge compensation (if the flood gun has been used or not). – Mass resolution. – Main chamber pressure.
Imaging-specific	– Estimated lateral resolution. – Delay extraction time (if delayed extraction is used).
Depth profiling-specific	– Sputter gun source (e.g., Ar) and acceleration voltage. – Pausing time between sputtering and analysis used for charge compensation purposes. – Sputter current. – Crater size (e.g., 400 × 400 μm^2). – Number of sputter frames/sputter time per step.
Sample preparation and transfer	1. Sample storage and preparation (e.g., insulating tape). If FIB is used for the sample preparation: • FIB source (e.g., Ga), energy, and aperture used. • Crater sidewall angle (e.g., 45° or 90°). • Crater size (e.g., 70 × 70 μm^2) • Raster size (e.g., 512 × 512 pixels). • Dwell time (e.g., 180 ms/pixel). • Number of cycles. • Crater sidewall polishing and cleaning procedure. 2. Sample transfer procedure.
Data evaluation	– Software. – Additional information related to data processing and scaling.

(6) *Report of SIMS analysis results.* Finally, when reporting results in a scientific publication, all relevant information on how the SIMS measurements were performed should be reported to allow the readers to both reproduce and better interpret the results. Table III summarizes the information that should be reported in any experimental section of a SIMS-related scientific publication.

IV. PITFALLS

During measurements or sample handling/transfer, several pitfalls may lead to errors, possibly causing wrong data interpretations and conclusions. Two pitfalls have been already discussed in Sec. III, being (1) plating of lithium metal caused by not having insulated the sample, and (2) gases reacting with the sample, like N_2 or solvent gases, possibly present in the glovebox used to prepare the sample. Other pitfalls can be grouped into (3) wrong instrumental handling, (4) SI signal artifacts due to sample specificities, (5) nonconsideration of the matrix effect, and (6) sputtering artifacts.

(3) *Instrumental handling.* The most common mistake in terms of instrumental handling is probably the generation of oversaturated signals during the measurement. Oversaturated peaks make it impossible to use that signal to compare different samples. Furthermore, it can represent a problem even if this signal is not directly used as a comparison metric. Indeed, SIMS data need to be scaled for proper comparisons, and the most common approach relies on scaling the SI count of each peak by the total number of SIs detected during the measurement. However, if even only one peak in the mass spectrum is oversaturated, the total number of SIs is underestimated and, more importantly, this underestimation may be different for different samples or for different regions of analysis. Thus, if such oversaturation occurs and the data should be scaled by the total number of SIs or by the oversaturated peak itself, the measurement parameters should be changed. This could be done by decreasing the I_p to avoid oversaturation, or estimation of the SI intensity during the measurement by collecting only a fraction of the associated SIs [e.g., by enhanced dynamic range (EDR) technology]. With EDR, only a fraction (e.g., 10%) of the selected ions is collected and the overall count rate is extrapolated to avoid oversaturation. To do this, selected ions are sent through an attenuation unit in the time-of-flight analyzer. Therefore, the advantage of this approach is that it does not increase the measurement time (for equal total SI counts), contrary to decreasing the I_p. Other options might also be using the total ion signal excluding the oversaturated peak(s) or changing the measurement polarity (from negative to positive SIs, or vice versa).

(4) *SI signal artifacts*. Analysis of battery samples can be challenging due to their composite nature, requiring to handle different materials having different properties, potentially each with its own specific challenges. For example, melting of polymer partly filling the electrode pores, or halide redeposition during a sputtering or FIB step (consider cryogenic conditions in such cases). Another challenge is the typical surface roughness and topography of battery samples, which can bury interfaces of interest and shield some of the SIs generated by the primary ion beam (Sec. II B). This problem can be minimized by smoothing the electrode surface as much as possible (for instance, through calendering or uniaxial pressure) or creating polished FIB crater surfaces. The importance of the sample topography is the main reason for which more advanced setups allow combining SPM and SIMS (Sec. II C), or devoted data scaling procedures, can be particularly convenient.

(5) *Nonconsideration of the matrix effect.* The relationship between signal intensity and the matrix effect (which significantly affects the ionization probability) can cause inexperienced users to misinterpret high SI intensities as high concentration and vice versa. It is, therefore, useful to remind that ToF-SIMS is a semi-quantitative technique, and if quantitative results are needed it is required to either build devoted RSF values or combine ToF-SIMS with other techniques, like XPS.

(6) *Sputtering artifacts*. In addition, sputtering can lead to specific artifacts, such as material mixing, or particles morphology change [Fig. 6(b)] caused by different sputter rates originating from the orientation of the sputter beam and from the particle topography [Fig. 6(a)], or by different sputter rates of different materials or crystal phases. This is also important when embedding powders in, e.g., a polymeric matrix. Indeed, the sputter rate of the embedding material often differs drastically from the sputter rate of the examined particles, leading to preferred sputtering of the former. If the difference is too large, the embedding material is completely sputtered away and the results are similar to a nonembedded sample (triangle formation of particles by preferential sputtering), as discussed in Ref. 34. Finally, sputtering can also hinder proper analysis of mobile carriers, e.g., positively charged mobile ions in the crystal structure of the particle of interest. This can be attributed to repulsion between a positive mobile carrier and positively charged sputtering ions, which can cause the mobile species to be repelled away.[44]

V. RECENT ADVANCEMENTS IN DATA PROCESSING

ToF-SIMS is an extremely powerful analytical technique that is far from being used at its full potential in the context of battery research. In this section, we present some of the advanced data processing procedures currently being tested and developed.

As mentioned in Sec. III, the most classical data scaling procedures (i.e., dividing all the SI signals by the total ion count of the area underneath a reference peak) are based on SIs collected over the entire region of analysis, not accounting for local heterogeneities. Analyzing smaller regions could minimize this limitation, but at the expense of representativeness. An alternative approach consists in scaling the results on a pixel-by-pixel basis, rather than using the spectrum obtained from the entire region of analysis. In other words, for each peak, it is possible to scale the intensity of each associated pixel by the total ion count collected from that same pixel (or by the SI associated with a reference species collected on that pixel). Afterward, the scaled values for each pixel are summed to reconstruct data representative of the entire region of analysis. This approach can, therefore, combine the representativeness brought by the analysis of a relatively large area with the higher accuracy offered by the consideration of local heterogeneities. Two fully automated and *user-friendly* (no coding experience needed) codes, one performing a spectra-based and the second one performing a pixel-by-pixel-based data scaling, are published together with this article. These codes are designed for being

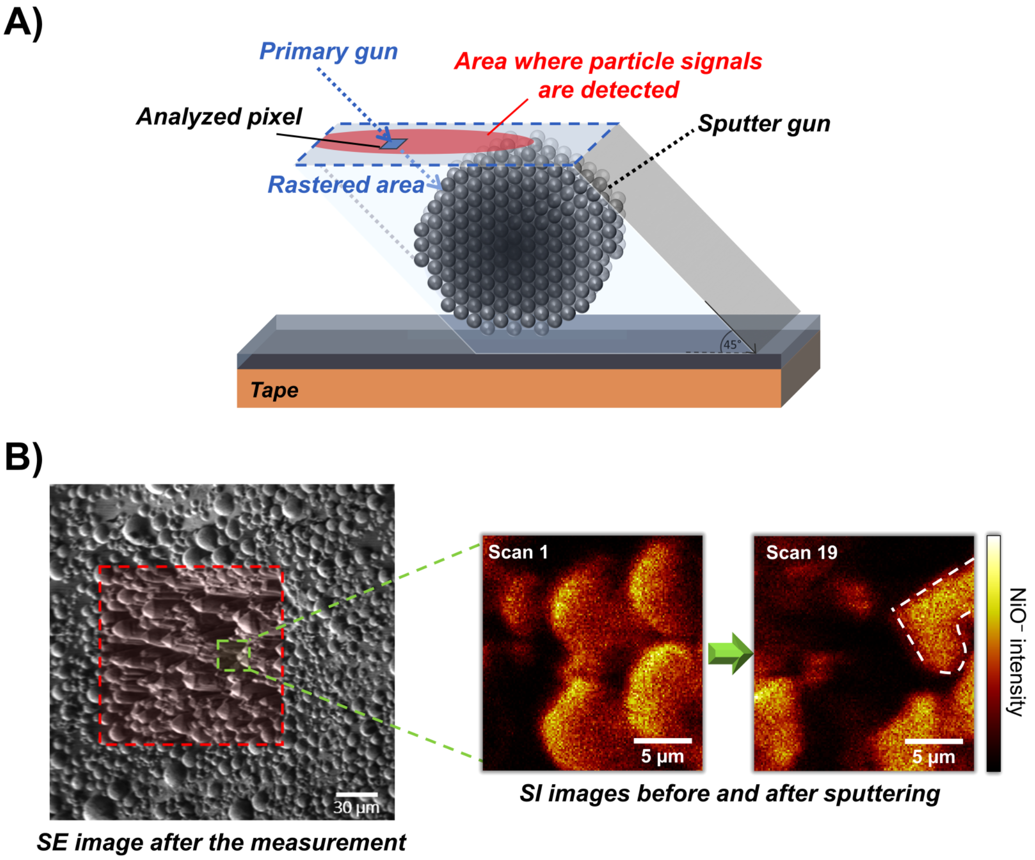

FIG. 6. (a) Schematics showing that, as a function of the analysis beam (primary gun) orientation and the particle topography, the particle is detected only in a part of the scanned area. In addition, as a function of the sputter gun orientation and particle topography, different regions of the particle may experience different sputter rates, leading to changes in the particle shape over sputtering. This phenomenon is better illustrated in (b), where the change of NMC particle shapes before sputtering (scan 1) and after 18 sputtering steps (scan 19) is shown.

applied to experimental procedures in which several spots of the same samples were analyzed, automatically offering the associated statistics and plotting those in the form of box plots.

Another application of ToF-SIMS that has not been sufficiently explored yet is the characterization of electrode microstructures through SIMS. Indeed, with an appropriate experimental setup, SIMS can be used to analyze electrode cross sections, and the different phases (AM, additives, degradation products) can be identified by the detection of SI(s) associated with those phases, allowing to obtain segmented images without the need of devoted procedures based on, e.g., image contrast or trained machine learning (ML) models.[45] Similarly to other microstructural characterization approaches, such as x-ray tomography of (FIB-)SEM,[46,47] SIMS-based microstructures can then be used to determine electrode properties at the bulk level (interfaces, volume fractions, tortuosity, etc.) and at the single particle level (particles shape, coverage, interfaces, etc.).[44] The main advantage of the SIMS-based approach, however, is that it unlocks the identification of minor but critical phases like the SEI and CEI, allowing to map their spatial distribution. To the best of our knowledge, to date there is no other analytical technique capable of analyzing large areas and sampling the spatial distribution of both the main and SEI/CEI phases into the electrode microstructure. The main disadvantage of this approach is that the analysis is limited to 2D microstructure characterization because of long measurement times. Indeed, imaging a representative (hundreds of μm long) segment electrode of the cross section with high lateral and relatively high mass resolution (delayed extraction mode) can require up to 24 h of measurement, making unrealistic the analysis of several 2D slices (similarly to FIB-SEM) to reconstruct the 3D microstructure. This limitation, however, can be overcome by recent ML-based strategies, which have already been demonstrated to allow the reconstruction of realistic 3D microstructure using as input representative 2D slices.[48,49] The combination of high-resolution SIMS images of electrode cross sections and ML procedures to reconstruct the associated 3D electrode microstructure will be discussed and presented in a forthcoming publication from our research group.

Improved image resolution can also be obtained during the data processing step. An easy but not often utilized approach consists in multiplying (pixel-by-pixel) images associated with different SIs, all originating from the same compound/phase. An example of

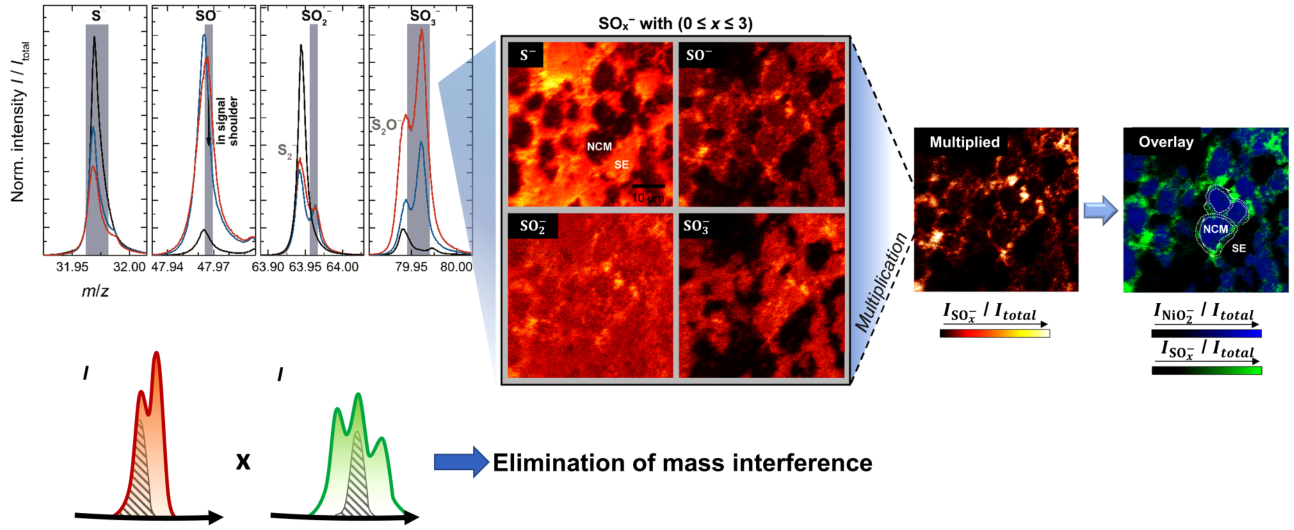

FIG. 7. Example showing how the multiplication of different SI images (all originated from the same phase) can lead to a much sharper spatial identification of this phase. Here, the case of SO_x^- species $(0 \leq x \leq 3)$, all originated from the CEI, is reported, together with the multiplied image of all SO_x^- images and an image overlay between the multiplied SI image and the NiO_2^- image (SI specifically originated from the AM, here NMC), showing a perfect match, therefore demonstrating the correctness of the procedure utilized. Part of this figure was reproduced with permission from the supporting information of Walther *et al.*, Chem. Mater. **31**, 3745 (2019). Copyright 2021 American Chemical Society.

such an approach is depicted in Fig. 7 for the case of SO_x^- species $(0 \leq x \leq 3)$, all originating from the CEI, and showing how the combination (multiplication) of those images unlocks a much sharper identification of the CEI spatial location. In this example, due to mass interferences the signals of the SO_x^- species cannot be clearly separated from other signals in the mass spectrum. Thus, due to insufficient mass resolution and accuracy of the mass peaks, the SI images not only map the lateral distribution of the desired species, but also the lateral distribution of the mass interferences. Nevertheless, pixels in which SO_x^- species can actually be identified show a high intensity for all SO_x^- species related SI images. In contrast, pixels in which no SO_x^- species are present, even if a certain intensity is detected due to mass interferences for a given SO_x^- species, show a low or no intensity for the others. By multiplying the different SI images pixel by pixel, mass interference can be compensated, resulting in a sharper and more accurate image. In other words, multiplication of SI images emphasizes what the signals have in common and weakens what they differ in.

Lastly, another advanced but yet unexploited experimental approach is to utilize sputter damages to estimate the molecular stability of the species being analyzed. Since battery research is often accompanied by the search for more stable compounds and phases, rapid and simple experimental approaches to test the consequences of a material change are highly desirable. This could be achieved by checking the ratio (and their evolution over sputtering) between long and short fragments originated by, e.g., two different solid electrolytes (unmodified vs modified). Indeed, if one of the two solid electrolytes shows a significantly higher fraction of long fragments over sputtering, this may be the first indication of higher molecular stability. Since surface analysis is already sufficient for this analytical task and only takes a few minutes, this is an easy and quick approach for this kind of study.

VI. SUMMARY AND CONCLUSIONS

The main goals of this article are inviting the battery community to utilize ToF-SIMS for analytical purposes, and reviewing good practices in the field of battery materials research to exploit ToF-SIMS at its full potential, accounting for its advantages, disadvantages, and technical characteristics. The discussion was divided into four parts: working principles, (dis)advantages, and main measuring modes of ToF-SIMS (Sec. II), best practices (Sec. III), main pitfalls (Sec. IV), and recent advancements in data processing (Sec. V).

Section II starts discussing the advantages brought by ToF-SIMS and why battery researchers should be interested in this analytical technique. The main advantages of ToF-SIMS can be summarized as

(i) High surface- and chemical-sensitivity;
(ii) High mass and spatial resolutions;
(iii) Low detection limit (<10 ppm);
(iv) Sample bulk can be measured when combining ToF-SIMS with a sputter or FIB gun;
(v) All types of electrodes and powders are measurable;
(vi) Organic, inorganic, and hybrid materials can be analyzed;
(vii) Possibility of distinguishing between different isotopes;
(viii) Possibility of analyzing both positively and negatively charged SIs.

These numerous advantages can unlock, e.g., a more accurate determination of the chemical nature and associated spatial location of degradation products generated during battery cycling or storage, which is key for a better understanding of the key role of battery interfaces and interphases.

The main disadvantages of ToF-SIMS can be summarized as

(i) Lack of advanced chemical information, e.g., on the oxidation state of the detected species;
(ii) Differentiation of chemical species is possible only if the SIs generate through the associated fragmentation process are different;
(iii) SIs shielding caused by the sample roughness/topography;
(iv) Limitation of lateral resolution and surface sensitivity;
(v) Semiquantitative information.

Since any analytical technique inevitably has a number of drawbacks, and ToF-SIMS is no exception, several analytical approaches should be combined to compensate for their respective weaknesses. Good analytical techniques to be combined with ToF-SIMS are XPS (analysis of the oxidation state) and (FIB-)SEM (improved spatial resolution). Both are already largely employed for battery research.

ToF-SIMS machines can be purchased by different companies (Table I), and several operating modes can be used, being high mass resolution and imaging modes (or approaches aiming to combine the advantages of both, like delayed extraction) the most common ones.

Section III is focused on best practices when applying ToF-SIMS to battery samples. For measurement planning, they should be kept as easy as possible while optimizing measuring conditions and reducing possible sources of error. Sample preparation steps of battery samples, e.g., surface cleaning or insulating the samples before the analysis, are essential to avoid lithium plating caused by the flood gun used during measurement. An appropriate sample handling is also important to avoid contact of the battery samples with oxygen, moisture, solvent gasses and, in case of metallic lithium and sodium, N_2, which could react with the samples and generate artifacts in the final results. In most cases, in battery research, working in a glovebox while handling battery materials is standard. Furthermore, during sample transfer from the glovebox into the SIMS instrument possible contacts with the external atmosphere should also be avoided. For data processing and evaluation, one should choose a proper data normalization/scaling procedure and eventual dimensionality reduction procedures to better interpret the obtained results. Information about how to report ToF-SIMS data when publishing the results can be found in Table III.

Section IV deals with common pitfalls behind ToF-SIMS measurements in the context of battery research, as listed in the following:

(i) Lithium metal plating for samples that were not insulated from the sample holder;
(ii) Gases reacting with the samples during sample preparation or transfer;
(iii) Wrong instrumental handling, such as not accounting for oversaturated signals, which would make the most common data scaling procedure, i.e., scaling by total ion counts, incorrect;
(iv) SI signal artifacts due to sample specificities, as surface roughness;
(v) Nonconsideration of the matrix effect;
(vi) Sputtering artifacts, such as particle shape modification of species evaporation and re-deposition (e.g., halides).

Finally, Sec. V discusses some promising advances in data processing. In addition to pixel-by-pixel multiplication of images to remove mass interferences, normalization to account for local heterogeneities (an *open-source* and *user-friendly* code for this is published in this article) is discussed in more detail. Further, the combination of ToF-SIMS-based cross-sectional electrode images with the devote ML method is shown to capture the 3D battery microstructure in terms of both major phases and spatial location of degradation products.

Overall, we hope that this paper can be seen by the battery community as an opportunity to introduce a new powerful analytical technique in their research toolbox, which we believe has great potential to unlock a deeper analysis of battery degradation products and their relationships with, e.g., electrode and electrolyte formulations, storage conditions, and cycling protocols.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Teo Lombardo and Felix Walther contributed equally to this paper.

Teo Lombardo: Conceptualization (lead); Writing – original draft (lead); Writing – review & editing (equal). **Felix Walther:** Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Christine Kern:** Data curation (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Yannik Moryson:** Investigation (equal); Writing – original draft (equal). **Timo Weintraut:** Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Anja Henss:** Writing – review & editing (equal). **Marcus Rohnke:** Conceptualization (lead); Funding acquisition (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The ToF-SIMS automatic scripts for data normalization (both spectra- and pixel-by-pixel-based) and the associated documentation can be found in the "ToF-SIMS data normalization and analysis" subfolder in Github repository at https://github.com/teolombardo/User-friendly-scripts-for-experimental-battery-researchers, Ref. 52.

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