

Received: 6 June 2021

Revised: 17 August 2021

Accepted: 18 August 2021

# The potential of scanning electrochemical probe microscopy and scanning droplet cells in battery research

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## Funding information

German Research Foundation (DFG), Grant/Award Number: 390874152; European Union's Horizon 2020 research and innovation program, Grant/Award Number: 957189

## Abstract

Spatially resolved characterization of electrode surfaces or electrode–electrolyte interfaces is of fundamental interest in battery research to unravel the complex underlying physicochemical processes. Scanning probe microscopy (SPM) techniques and derived methods have recently gained importance in *in situ* or *operando* studies of battery electrodes. This minireview provides an overview on well-established and advanced SPM methods such as scanning electrochemical cell microscopy (SECCM) and hybrid atomic force microscopy–scanning electrochemical microscopy (AFM-SECM) and their future potential for *in situ/operando* studies providing correlated structure/reactivity information. Although, most studies so far are focusing on lithium (Li)-ion batteries, the potential for post-Li battery chemistries is clearly evident. Future approaches for rapid performance assessment using scanning droplet cell electrochemistry in combination with advanced scanning probe microscopy are proposed and contrasted with the emerging challenges in the characterization of novel battery chemistries, as SPM methods have not yet been much used in this research area.

## KEYWORDS

AFM-SECM, battery, post-lithium, SDC, SECCM, SEPM, SPM

## 1 | INTRODUCTION

Globally increasing energy consumption by a growing world population paired with the threat of climate change requires a transition away from fossil energy production.<sup>[1]</sup> Research efforts in renewable energy topics including light-driven water splitting (i.e., artificial photosynthesis), fuel cells, and novel battery chemistries require a fundamental understanding of processes that occur at interfaces and formed interphases. Future energy storage demands related to, for example, electric vehicles and grid-scale energy storage systems may need novel post-lithium

battery chemistries based on earth-abundant elements. These battery chemistries include monovalent, bivalent, or trivalent ions such as Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, and Al<sup>3+</sup> based systems offering improved safety and cycle life. This topic is currently extensively studied for sustainable electrical energy storage,<sup>[2–4]</sup> as concepts known from Li-ion batteries cannot be directly transferred to post-Li systems, even in the case of monovalent ions such as sodium and potassium. For each of the listed and currently explored battery chemistries, known challenges arise with phenomena such as dendrite growth, degradation of electrolytes and electrode materials, solid electrolyte interphase (SEI)

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formation, non-uniformity in stripping/plating processes, and so on, all of these processes are currently investigated with *ex situ* and *in situ/operando* spectroscopic and microscopic methods,<sup>[5–7]</sup> as to date many of these processes are still not well understood. Among the microscopic characterization techniques, scanning probe microscopy (SPM)—pioneered in the 1980s<sup>[8]</sup> with the introduction of scanning tunneling microscopy and shortly thereafter with the introduction of atomic force microscopy (AFM)<sup>[9]</sup>—are highly suited to study processes that occur at interfaces and interphases, as recently reviewed.<sup>[10–12]</sup> Although it should be noted that their use is by far less compared to electron microscopy or spectroscopic techniques, as performing experiments at battery electrode and data interpretation might be challenging. AFM and AFM-based derived techniques such as electrochemical (ec)-AFM, Kelvin probe force microscopy (KPFM), electrochemical strain microscopy (ESM), quantitative nanomechanical AFM (QNM-AFM), and so on, provide information on surface potentials, nanomechanical properties, but also on changes in volume, the formation of cracks, phase transformations, electron transport, reactions at the interfaces, and changes in surface morphology of electrode materials with nanoscale resolution.<sup>[6]</sup> To date, most AFM studies have been performed at Li-ion batteries (LIBs). For example, the effect of electrolyte additives such as fluoroethylene carbonate was studied in respect to the SEI formation at silicon oxide/carbon composite anodes<sup>[13]</sup> and Li precipitation and SEI evolution at all-solid-state batteries.<sup>[14]</sup> The effect of electrolyte decomposition at various carbon anodes for LIBs was recently reviewed.<sup>[15]</sup> With a future focus on earth-abundant post-Li-ion battery chemistries, SPM techniques may also play an important role in investigating interface phenomena at novel electrode materials.

Among the scanning electrochemical probe microscopy (SEPM) techniques, scanning electrochemical microscopy (SECM),<sup>[16]</sup> scanning micropipette contact method (SMCM), and scanning electrochemical cell microscopy (SECCM), which are based on micro- and nanopipettes,<sup>[17,18]</sup> have been employed to study intercalation and deintercalation processes and factors influencing SEI formation on LIB anodes, as recently reviewed by Kumatani and Matsue.<sup>[19]</sup> AFM-derived hybrid techniques<sup>[20]</sup> enable that morphological and structural changes are correlated with electrochemical information at the sub-micro- to nanoscale. With most AFM instrumentation nanomechanical properties such as elasticity, friction, and adhesion, as well electrical properties can be recorded.<sup>[21]</sup> In recent years, AFM manufactures provide installations of their instruments in gloveboxes for *operando* studies, which is a major advantage over vacuum-based imaging techniques such as electron microscopy (scanning electron microscopy,

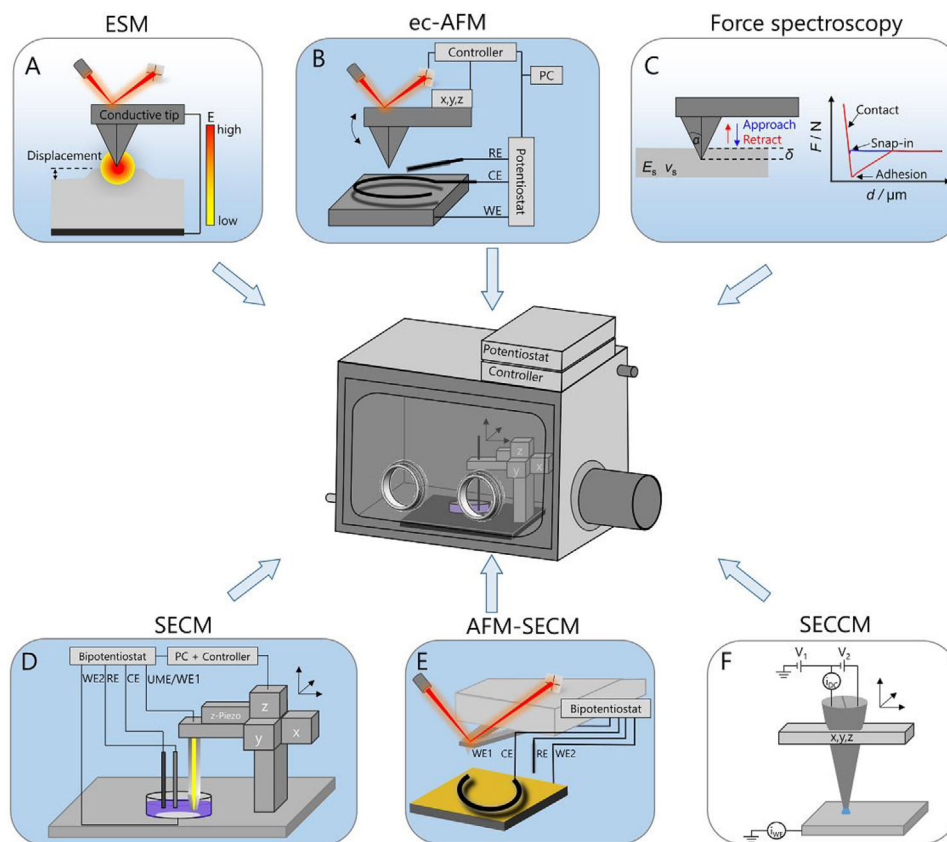
SEM and transmission electron microscopy, TEM), where reports on *operando* studies are still limited and mainly reported on all solid-state batteries<sup>[22,23]</sup>. High throughput electrochemical techniques like scanning droplet cells (SDCs), which were first introduced more than two decades ago,<sup>[24]</sup> gain attention for automated surface modification and screening of material libraries.<sup>[25]</sup> First SDC high-throughput approaches in battery research for pulsed Zn electroplating have been shown by Garcia et al.<sup>[26]</sup>

This minireview focusses on AFM-based and SEPM methods that are suitable for *in situ/operando* investigations of battery electrodes may in the future provide insight into electrochemical interface phenomena at novel battery materials. Other AFM-derived methods providing information on, for example, degradation of materials will be briefly described. Most AFM studies so far are studies on interfacial evolution in LIBs. Studies on other battery chemistries are still limited but may emerge in the near future. In the following, recent studies on battery materials and future potentials of SEPM - mainly SECM - and in particular of AFM-SECM will be reviewed and challenges will be discussed. SEPM may be used in combination with the scanning droplet cell for screening experiments to optimize and characterize novel battery electrode chemistries, which may then be characterized *in situ* with the SPM approaches discussed herein.

## 2 | OVERVIEW ON AFM AND SEPM METHODS IN BATTERY RESEARCH

### 2.1 | AFM-related methods

Figure 1 gives an overview on SECM, AFM- and pipette-derived SPM methods, which are currently employed in battery-related research. Methods based on conductive AFM probes (i.e., metal coated or modified with a thin conductive diamond layer such as boron-doped diamond) are used in conductive atomic force microscopy (c-AFM) and c-AFM derived techniques. At ambient conditions, c-AFM,<sup>[27,28]</sup> Kelvin probe force microscopy (KPFM),<sup>[29,30]</sup> scanning spreading resistance microscopy (SSRM),<sup>[31]</sup> and electrochemical strain microscopy (ESM)<sup>[32]</sup> have been employed mostly for all-solid-state battery systems.<sup>[6,33]</sup> Post-mortem studies of LIB anodes have been performed in ambient conditions and high vacuum (e.g., using SSRM). Changes in conductivity, surface potentials, aging of electrode materials, and surface deformation, for example, due to intercalation with nanoscale resolution are accessible via these techniques. Within the last decade, ESM (Figure 1A) is gaining attention in this field. A high frequency biased AFM tip—when in contact with the



**FIGURE 1** Schematics of the working principle of different SPM techniques housed in a glovebox for battery research. (A) ESM, (B) ec-AFM, (C) AFM force spectroscopy, (D) SECM, (E) AFM-SECM, (F) SECCM. The background color in the schematics indicates if the technique is suitable for measurements in solution (blue: measurements are only possible in solution; gradient: measurements are performed in air or in solution (A), (C)); white only a small liquid cell shown in blue (F) is formed)

sample—induces interfacial electrochemical processes and ionic currents through the solid leading to concentration gradients in the locally probed area of the sample, and thereby to surface displacements and strain. So far, ESM has been employed to study Li-diffusion in inorganic solid electrolytes for example in NASICON-type ceramics and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  as well as in Si and  $\text{LiCoO}_2$  as anode material where Li diffusion is dependent on grain orientation.<sup>[34,35]</sup> ESM studies were also reported to understand capacity fading and electrochemical degradation during galvanostatic cycling in a  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  thin film cathodes within an all-solid-state lithium-ion battery.<sup>[28]</sup> SSRM provides high-resolution information of change in conductivity by mapping the distribution of resistivity. SSRM measurements for LIBs revealed that capacity fading of layered Ni-rich cathode material could be associated with variation in electronic conductivity.<sup>[36]</sup> SSRM studies are mainly performed by comparing electrodes before cycling and after via post-mortem analysis of a cross-sectional area. For all AFM-derived methods, known issues with artifacts related to the AFM tip, scan-

ners, mounting, and so on<sup>[37]</sup> should be carefully evaluated in studies of complex samples like in battery research.

Among the in situ AFM techniques, ec-AFM (Figure 1B), where a potential is applied to a conductive sample, inducing processes at the electrode/electrolyte interface is attractive for battery-related research. Standard AFM cantilevers made from silicon nitride or silicon have been used to investigate anode or cathode materials cycled in electrolyte.<sup>[38–40]</sup> Changes in surface morphology due to SEI formation have been investigated.<sup>[41]</sup> For example, the structural changes during the SEI formation on exfoliated molybdenum disulfide flakes as anode material in sodium ion batteries revealed that as effect of the sodiation process permanent wrinkles were observed.<sup>[42]</sup> Also, dendrite growth and SEI formation at graphite anodes in dependence of ethylene carbonate (EC)-based and fluoroethylene carbonate (FEC)-based electrolytes were investigated via ec-AFM for Li-ion batteries.<sup>[38,43]</sup>

State-of-the-art AFM instruments provide the mapping of nanomechanical properties such as Young's modulus, energy dissipation, and adhesion via force spectroscopy

performed at each pixel. For example, PeakForce Tapping™ was used to determine the elasticity module of the SEI layer at a composite stable Li-anode with a protective layer composed of lithium fluoride and graphite fluoride for limiting the dendrite growth.<sup>[44]</sup> Alternatively, force spectroscopic measurements (Figure 1C) using conventional or colloidal AFM probes can provide quantitative information on the Young's modulus of battery components. Nanomechanical properties of the SEI have been determined at sodium-ion batteries using colloidal AFM probes. Force spectroscopy measurements at copper anodes gave evidence that softer layers are formed on more rigid layers with Young's modulus variations across three orders of magnitude.<sup>[45]</sup>

## 2.2 | SEPM methods

### 2.2.1 | Scanning electrochemical microscopy

SECM (Figure 1D), initially derived from electrochemical scanning tunneling microscopy (ec-STM)<sup>[46]</sup> and hybrid SECM techniques like SECCM have gained attention for studying battery processes.<sup>[19]</sup> The ability to perform *operando* studies on evolving heterogeneities in respect to electroactivity, surface modifications due to degradation of electrolytes during cycling, and the influence on the electrochemical performance of electrode materials and fluxes towards and from electrodes with high resolution may contribute to address some major scientific challenges in Li-ion batteries (LIBs).<sup>[47,48]</sup> So far, SECM has been used to study both bulk<sup>[49,50]</sup> and surface processes<sup>[47,51]</sup> at anodes and cathodes of LIBs. Local electron transfer kinetics correlate to the effectiveness of the SEI in blocking electrons and thus preventing further decomposition of the electrolyte, yet at the same time ensures high stability (cycling) for (de)intercalation. Using SECM, heterogeneities during *in situ* SEI formation could be visualized<sup>[47,48,52–56]</sup> via different redox mediators such as ferrocene or 2,5-di-*tert*-butyl-1,4-dimethoxy benzene (DBDMB). The latter provides a stable response up to potentials of 4.1 V versus Li/Li<sup>+</sup>.<sup>[48]</sup> *Operando* SECM at Si anodes revealed the formation of electrical insulating SEI during (de)lithiation.<sup>[57]</sup> SECM experiments in substrate generation/tip collection mode were performed to map ionic transport, e.g., to determine the transport of Li<sup>+</sup> ions at the interface of a LiCoO<sub>2</sub> electrode.<sup>[50]</sup> The achievable resolution in SECM is, among other factors, dependent on the size of the SECM probe, which are usually micro-sized disc electrodes. Hence, the achievable resolution is usually not comparable to the AFM-based methods. Further challenges might be related to finding suitable redox mediators, which are stable in the required potential window.

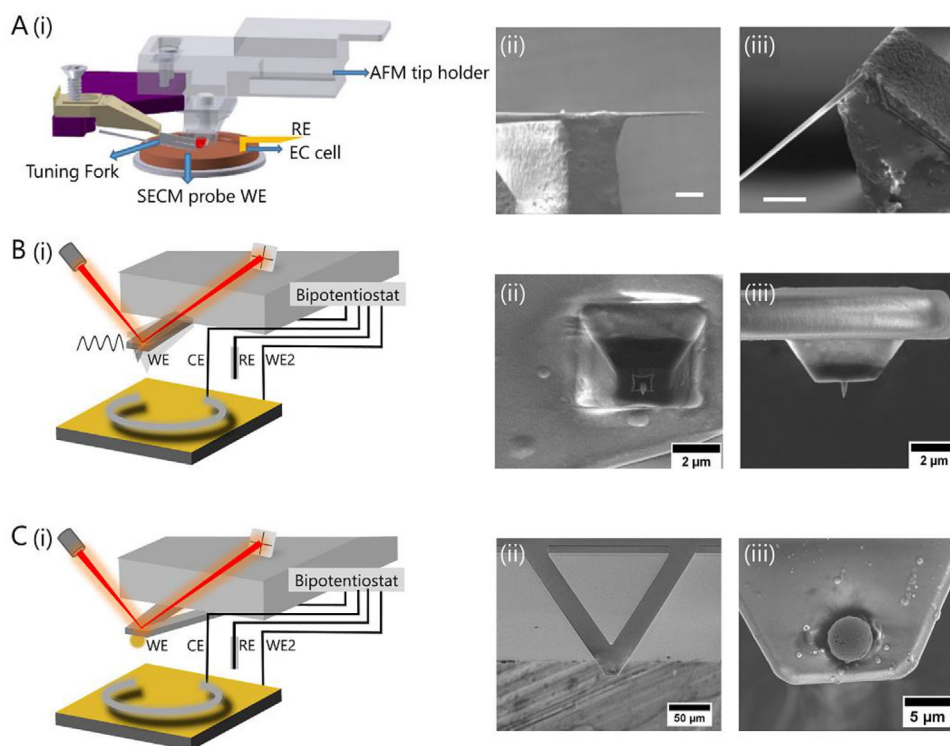
Possible convolution of the electrochemical reactivity and topographic effects when real battery electrodes are investigated may be an issue in constant height SECM.

### 2.2.2 | Scanning electrochemical cell microscopy

In SECCM (Figure 1F) or SMCM, a local (sub-)microscopic electrochemical cell is formed that is defined by the area of meniscus in contact with the substrate electrode, as recently reviewed by Unwin et al.<sup>[58]</sup> A significant advantage is that nanoelectrochemical measurements on conductive materials show reduced background noise as well as reduced capacitive contributions, as only a small region is probed with the formed electrochemical cell at any given time. SECCM was used to map the heterogeneity of a LiFePO<sub>4</sub> electrode in LiCl solution, which could be correlated to topographical features.<sup>[59,60]</sup> Initially, studies on the heterogeneity of LiFePO<sub>4</sub> particles using SMCM were presented by the groups of Schougaard and Mauze-roll in a collaborative effort.<sup>[61]</sup> The same groups studied dispersed LiFePO<sub>4</sub> particles in different electrolytes such as propylene carbonate and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonate)imide (EMI-TFSI) in respect to the potential window.<sup>[62]</sup> More recently, SECCM in a glovebox was employed to study the kinetics of polycrystalline LiCoO<sub>2</sub>,<sup>[63]</sup> Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> thin-film electrodes,<sup>[47,48]</sup> and single LiFePO<sub>4</sub> particles to visualize the distribution of the diffusion coefficient at grain boundaries.<sup>[60]</sup> SECCM was also utilized to study the effect of ZrO<sub>2</sub>-coatings on LiCoO<sub>2</sub> thin-film electrodes in respect to inhomogeneities.<sup>[63]</sup> Moreover, single particles may be studied, and their electrochemical behavior can be correlated to the particle size, crystallinity, and structure using *ex situ* electron microscopy methods, as recently shown for individual LiMn<sub>2</sub>O<sub>4</sub> particles, which are considered a promising material for Li-ion cathodes.<sup>[64]</sup>

### 2.2.3 | AFM-SECM

Nanopipette-based SPM techniques are advantageous when imaging soft surfaces like living cells, lipid bilayers, hydrogels, etc. as they operate in a “non-contact” regime. Whereas, AFM has specific advantages for studying hard samples, as physicochemical property maps with nanoscopic resolution can be obtained. Using conductive AFM cantilevers coated with an electrically insulating layer—except the very tip—or recessed micro-/nanoelectrodes integrated into an insulating AFM tip leads to the concept of hybrid AFM-SECM, as illustrated in Figure 1E, which has been introduced about



**FIGURE 2** Schematics for combined AFM-SECM measurements. (A) (i) Tuning fork-based AFM-SECM; (ii) SEM images showing the probe attached to the QTF, (iii) final nanoprobe electrically connected via focused ion beam (FIB) deposited platinum (scale bar: 100  $\mu\text{m}$ ). Adapted with permission from Reference.<sup>[69]</sup> Copyright 2017, American Chemical Society. (B) (i) Illustration of a dynamic mode or PeakForce Tapping™ SECM operation. (ii) AFM-SECM probe with recessed frame electrode, top view, and (iii) side view. (C) (i) Scheme of conductive colloidal AFM-SECM for quantitative electrochemical force spectroscopy; (ii-iii), SEM images of a conductive colloidal AFM-SECM probe bearing an Au-coated spherical electrode at an insulated AFM cantilever

20 years ago.<sup>[65–67]</sup> Hybrid AFM-SECM probes can be fabricated either by standard microfabrication processes, such probes are nowadays also commercially available<sup>[68]</sup> or by lab-bench approaches using insulated etched microwires.<sup>[66,67,69]</sup> Available probes can be grouped, for example, according to their resulting shape into probes with recessed (i.e., ring, disc, recessed disc and frame) or protruding (i.e., conical, triangular, spherical, etc.) electrodes, as recently reviewed and summarized by Patel and Kranz and Shi et al.<sup>[20,70]</sup> Redox processes mapped with the integrated electrode can now be directly correlated to the recorded topography and nanomechanical properties.

AFM-SECM is nowadays also commercially available as “add-on” module for AFM instruments. Although only a few studies have been reported in the literature, an implementation of AFM-SECM to study battery chemistries may enable unprecedented new insights, for example, for understanding the formation of electrochemical inactive regions during charging/discharging. A challenge for such measurements is related to the electrolytes used in battery research and the fact that the full AFM-SECM probe including the electrical contact is immersed in solution, which requires reliable insulation of the contact. Simpli-

fied schematics for combined AFM-SECM measurements using different AFM modes, along with differently shaped AFM-SECM probes are shown in Figure 2.

Non-contact AFM based on tuning forks with high stiffness allowing small oscillation amplitudes was demonstrated for AFM-SECM experiments.<sup>[69]</sup> Figure 2A(i) shows the simplified setup using an oscillating quartz tuning fork (QTF) without optical feedback, which has the advantage that photoexcitation experiments can be performed eliminating interferences. Probe fabrication is more laborious, as a pulled insulated wire is attached to a QTF using focused ion beam (FIB) via a series of Pt depositions,<sup>[69]</sup> as depicted in Figure 2A(ii) prior to FIB-induced Pt probe exposition. Electrochemical resolution of features down to 150 nm in size was reported. Tuning fork-based AFM-SECM has been reported for AFM-SECM in battery research.<sup>[71]</sup> For high-resolution imaging in contact mode, probe designs with protruding electrodes, whereby the AFM tip-integrated electrode is in direct contact with the sample surface may be problematic, as this may affect the electrode area due to wear or short-circuiting in case a bias is applied to the sample. To avoid such problems, topography and current

images are typically collected sequentially, first recording topography and nanomechanical data, e.g., in PFT mode, and then recording the electrochemical response in lift-mode without sinusoidal oscillation of the probe. Recessed AFM-SECM probes (Figure 2B(i)) have been used in PeakForce Tapping™ SECM,<sup>[72]</sup> as schematically shown in Figure 2B at soft patterned electrodes<sup>[73]</sup> and single gold particles.<sup>[74]</sup> Figure 2C(i) shows a simplified setup for measurements denoted as conductive colloidal AFM-SECM force spectroscopy.<sup>[75]</sup> Force spectroscopy measurements on SEI have been performed at molybdenum disulfide anodes in sodium-ion batteries<sup>[42]</sup> and LiFePO<sub>4</sub> electrode during aging.<sup>[76]</sup>

### 3 | SELECTED SEPM APPLICATIONS

In battery research, most electrochemical experiments including but not limited to cyclic voltammetry, electrochemical quartz microbalance (EQCM), electrochemical impedance spectroscopy (EIS), and so on are carried out in bulk solution. SEPM techniques offer unique ways in emerging battery chemistries to reveal the relationship between evolving structure and electrochemical activity.

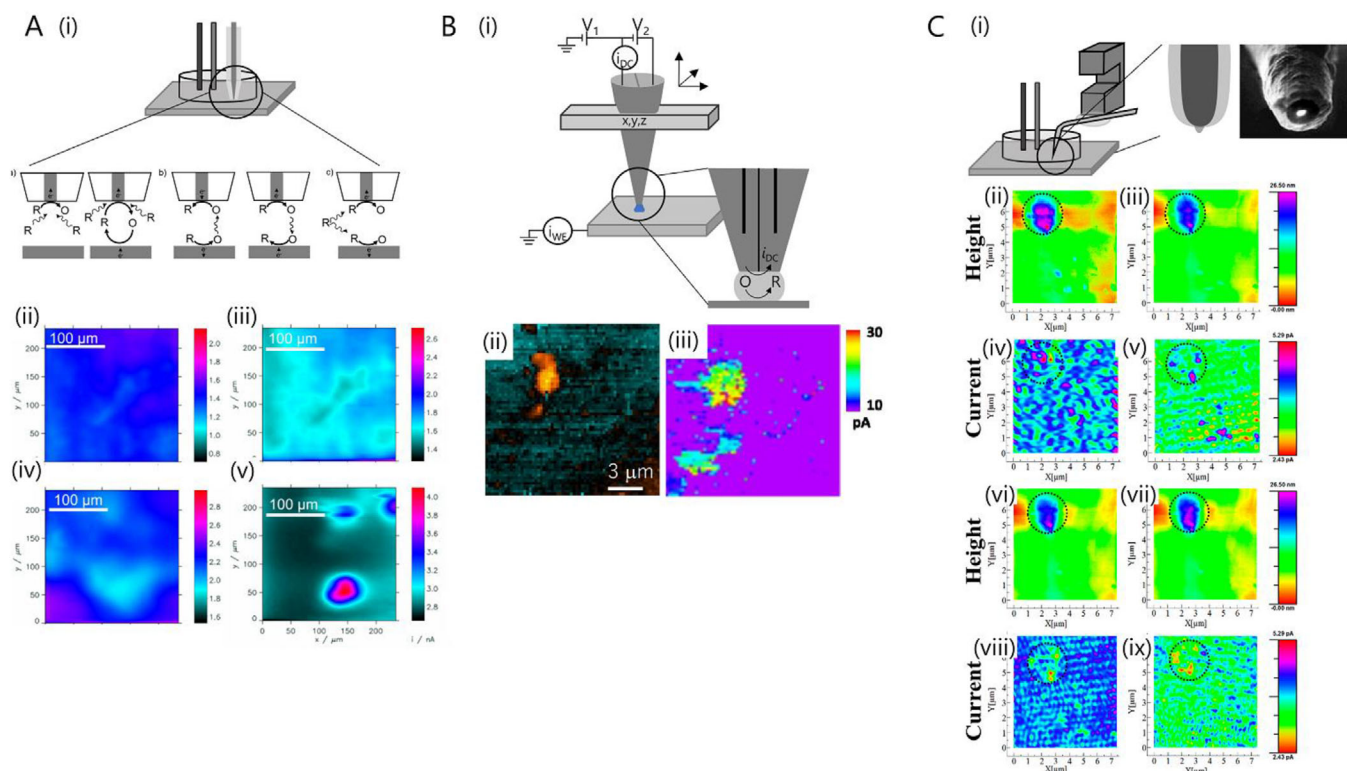
Sequential imaging approaches involving AFM and SECM have already been demonstrated in the past for studying SEI formation on glassy carbon electrodes,<sup>[47]</sup> and to map interfacial processes at redox flow batteries.<sup>[77]</sup> Ventosa et al. used SECM to detect changes due to intercalation during a cycling experiment at the TiO<sub>2</sub> electrode.<sup>[55]</sup> Cararelli et al. used intermittent contact alternating current scanning electrochemical microscopy (ic-ac-SECM) to characterize solid electrolytes in all-solid-state LIBs, which showed significant variation in resistances and allowed the simultaneous observation of both topography and impedance, respectively.<sup>[78]</sup> Wittstock and co-workers performed SECM studies on various electrodes for LIBs investigating in situ SEI formation.<sup>[48,52,53,79]</sup> Mass transport processes at porous LiFePO<sub>4</sub>/carbon composite electrodes for LIBs have been investigated using anthracene as redox active species rather than Li-ions to avoid complications related to Li electroplating.<sup>[80]</sup> Figure 3A(ii-v) shows a sequence of SECM feedback images of the evolution of the SEI on Li metal electrode in lithium perchlorate/propylene carbonate electrolyte<sup>[81]</sup> (please note the corrigendum to Figure 4<sup>[82]</sup>). Images have been recorded at (ii) the pristine Li metal and then at different charging cycles, (iii) after one charging cycle, (iv) after additional five cycles, and (v) after 11 charging cycles. By mapping the local current density distribution, the heterogeneity of the evolving SEI is evident. Only recently, SECCM inside a glovebox for the investigation of battery materials in non-aqueous electrolytes

was reported.<sup>[60]</sup> Besides facet-dependent diffusion coefficient on a Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> thin-film electrode, which cannot be evaluated using conventional electrochemical measurements LiFePO<sub>4</sub> particles were imaged (Figure 3B). SECCM was also used during (de)intercalation of Li to map the morphology of a LiFePO<sub>4</sub> cathode in an aqueous electrolyte. The authors could show that the electrochemical properties are strongly dependent on local structure and composition.<sup>[59]</sup> Local charging/discharging experiments can be performed at single particles at in situ conditions without the influence of neighboring particles which is highly interesting for composite electrode materials. Studies correlating structural changes mapped to local electrochemical phenomena are still scarce. Recently, Mahankali et al. used AFM-SECM to study Li–S interfacial redox reactions with nanoscale spatial resolution in real time.<sup>[71]</sup> Deconvoluted images of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> particles revealed both conducting and insulating regions. The authors monitored the contribution of the Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> particles toward the overall electrochemical activity during the oxidation process as depicted in Figure 3C(ii)-(ix). Changes in height and current along with phase images were recorded (not shown), which revealed a size-dependent oxidation process with smaller particles being oxidized at initial stages at lower overpotential.

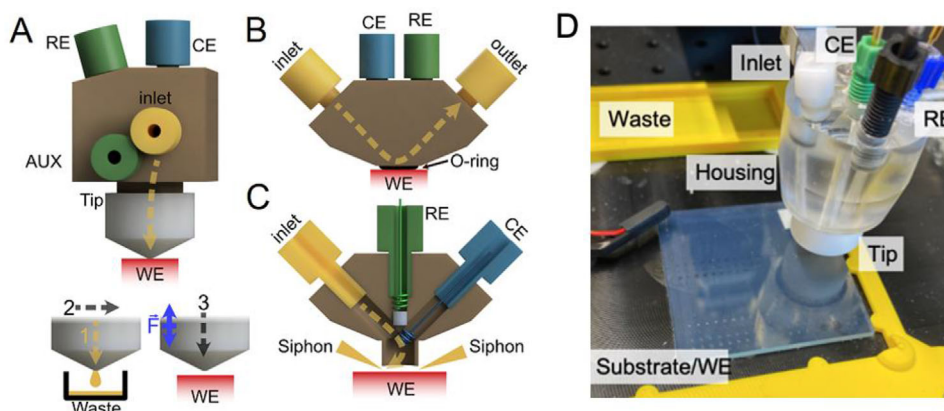
### 4 | SCANNING DROPLET CELL

For rapid screening and characterization of composite electrode materials, the use of SEPM techniques in combination with a SDC,<sup>[24,83]</sup> which offers higher throughputs at excellent repeatability without compromising precision, is highly interesting. Fundamental to any SDC is, that the reference electrode (RE), counter electrode (CE), and electrolyte inlet are miniaturized and fit into a small stage mounted housing. All SDC designs shown in Figure 4 have in common that only a small measurement area (MA) of the working electrode (WE) (or substrate) is exposed. This allows for the investigation of different MAs across a substrate, that is, if the WE has a composition gradient or different electrochemical protocols are employed.

The no-flow (NF)-type<sup>[84]</sup> design shown in Figure 4A uses a semi-soft PTFE tip that exposes a round 1-mm diameter area of the WE. The NF-type requires that the electrolyte needs to be exchanged after every experiment. In the future, this design may be beneficial for battery-related experiments. Before each experiment, the tip is lowered until a predefined force is reached to ensure a good seal. A similar approach is used in the interrupt flow IF-type<sup>[85,86]</sup> cell where an O-ring seals off the rest of the working electrode (Figure 4B) but a continuous electrolyte flow is maintained. Like for the NF-type cell,



**FIGURE 3** Schemes and applications of different SEPM techniques on battery materials. (A) SECM: (i) SECM modes used in battery-related studies: (a) negative (left) and positive feedback mode; (b) generation mode (substrate generation/tip collection, SG/TC (left) and tip generation/sample collection, TG/SC (right) mode); (c) redox competition mode. Lower panel: SECM feedback images before and after different charging-discharging sequences at a Li metal electrode: (ii) pristine, prior to cycling; (iii) after one charging cycle, (iv) after additional 5 cycles, and (v) after 11 cycles. Adapted with permission from Reference.<sup>[81,82]</sup> Copyright 2020, Wiley-VCH. (B) SECCM: (i) scheme, (ii) topography, and (iii) current images of a LiFePO<sub>4</sub> particle. The nanopipette was filled with 1.0 M LiClO<sub>4</sub>. The image was acquired by applying a constant voltage of 4.2 V versus Li/Li<sup>+</sup>. Adapted with permission from Reference.<sup>[60]</sup> Copyright 2020, American Chemical Society. (C) AFM-SECM: (i) scheme of setup using a tapered platinum wire sealed into a glass nanopipette as AFM-SECM probe as shown in the SEM image. (ii)-(ix) Imaging of Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> on carbon surface during oxidation: simultaneous height and current mappings of the Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> surface. (ii, iv) correspond to Li<sub>2</sub>S/Li<sub>2</sub>S<sub>2</sub> on glassy carbon before oxidation, (iii, v) at a potential of 2.5 V, (vi, viii) at 2.6 V and (vii, ix) 2.7 V versus Li/Li<sup>+</sup>, respectively;  $E_{tip} = 2.6$  V, Adapted with permission from Reference 71. Copyright 2019, American Chemical Society



**FIGURE 4** Schematic drawings of the three major types of scanning droplet cells with conceptual electrolyte flow indicated by yellow dashed arrows. All designs have in common that only a small WE area under the (A) tip bore hole opening (no flow, NF-type), (B) O-ring (the interruptible flow, IF-type), or (C) body opening is exposed to the electrolyte (continuous flow, CF-type). (D) Photograph of an SDC indicating the electrodes

sealing between the working electrode and the O-ring is achieved by a force-controlled touchdown. The continuous flow CF-type<sup>[86,87]</sup> design shown in Figure 4C also has a continuous flow, but the flow cannot be stopped between experiments. There is no sealing of the cell and overflowing the working electrode is prevented via siphons around the cell opening. Only a few examples using SDC have been demonstrated so far in battery research. Schuhmann and co-workers employed SDC with pulsed charging protocols to improve the number of charging cycles in LiFePO<sub>4</sub>/Li metal electrodes<sup>[88]</sup> and to prevent dendrite formation in Zn-metal anodes.<sup>[26]</sup> The same group recently reported pulsed SDC experiments for Li plating/stripping in non-aqueous electrolytes.<sup>[89]</sup> A major benefit of the use of SDCs is their potential to be fully autonomous due to facile full automation.<sup>[90]</sup>

## 5 | CONCLUSIONS AND OUTLOOK

This minireview provides a brief overview on the current state-of-progress in scanning (electrochemical) probe microscopy techniques suitable for *in situ/operando* studies of LIB and post-Li battery materials. Emblematic to SPM and SEPM methods is their capability to provide scientists with insights into physical and electrochemical properties at the nanoscale. This enables a fundamental understanding of processes at the electrode/electrolyte interface. Significant improvements with respect to probe fabrication and novel SPM operation modes have been made, which will foster a more rapid understanding of complex interfacial processes at battery electrodes and next-generation materials. In this context, given the achievable spatial resolution in topographical and electrochemical information, SECCM and AFM-SECM are certainly at the forefront contributing to future advancements in understanding and tailoring interfacial processes such as electron transfer, and so on. We anticipate that the combination with SEPM techniques such as SECM located inside the same glovebox may in the future allow for rapid high-throughput screening and characterization/evaluation of active materials accelerating the development toward the design of appropriate materials or material combinations in battery research.

## ACKNOWLEDGMENTS

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe) and was funded by the German Research Foundation (DFG) under Project ID 390874152 (POLiS Cluster of Excellence). F.R. and H.S.S have received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 957189.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study.

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**How to cite this article:** S. Daboss, F. Rahmanian, H. S. Stein, C. Kranz, *Electrochem. Sci. Adv.* **2022**, *2*, e2100122.  
<https://doi.org/10.1002/elsa.202100122>