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Microelectrodes for Battery Materials

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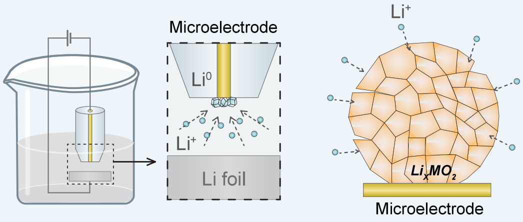
ABSTRACT: **The ability to measure current and voltage is core to both fundamental study and engineering of electrochemical systems, including batteries for energy storage. Electrochemical measurements have traditionally been conducted on macroscopic electrodes on the order of 1 cm or larger. In this Perspective, we review recent developments in using microscopic electrodes (<100 μm) for the study of battery materials. Microelectrodes allow us to explore spatiotemporal regimes that are not accessible with macroscopic electrodes. Temporally, microelectrodes can generate ultrahigh current densities, enabling the distinction between solid electrolyte interphase (SEI) kinetics and metal deposition kinetics. Spatially, they confine electrochemistry to single particles, allowing us to study their intrinsic properties. We outline future opportunities for the use of microelectrodes for future studies of battery systems. We propose their use for analyzing the electrochemistry of other reactive metals and exploring the potential of combining them with in situ imaging techniques.**



KEYWORDS: *microelectrodes, batteries, energy storage, electrochemistry, solid electrolyte interphase*

INTRODUCTION

Batteries are a critically important technology toward the transition to a clean and renewable energy future. Batteries are based on the electrochemical redox of solution and/or solid species. Due to differences in the electrochemical potential, these redox reactions enable energy to be stored and delivered on demand, with applications in electric vehicles, grid storage, and beyond.

The ability to measure current and voltage forms the basis of studying electrochemical systems. In conventional batteries, such measurements are conducted on macroscopic electrodes (millimeters or larger) containing a current collector, redox-active materials, conductive additives, and binders infiltrated with a liquid electrolyte.[1] These porous electrodes combine a high electrochemical surface area for high power density and efficient packing of redox-active species for high energy density. This combination of high energy and power density makes porous electrodes ideal for commercial battery applications.

Although macroscopic porous electrodes are commonly used in research, their inherent heterogeneity makes it very difficult to understand the intrinsic electrochemistry of energy storage materials.[2] An alternate strategy is microelectrodes, also called ultramicroelectrodes. While different variations of microelectrodes have been utilized, the most common feature is the shrinking of the current collector from macroscopic (>5 mm) to microscopic (<100 μm) dimensions. These microelectrodes, invented in the early 1980s,[3,4] enable enhanced mass transport rates through radial diffusion, where the flux of electroactive species to the microelectrodes allows for faster achievement of steady-state conditions with reduced diffusion layers. Moreover, negligible ohmic loss and short response times on microsecond or even nanosecond time scales make them particularly useful for dynamically monitoring electrochemical processes.[5−8] The small dimensions of the electrode also allow for localized measurements of electrochemical currents and voltages. Microelectrodes have long been used in a variety of electrochemical systems including electrocatalysis,[9] sensing,[10] and neuroscience.[11]

Although microelectrodes have long been used in liquid phase electrochemistry, their use for battery materials is more limited. One substantial difference with battery systems is that most batteries not only require electron transfer but also involve changes in the chemistry of a solid. For example, intercalation reactions cause the addition or removal of guest ions within a solid host (e.g., Li into C_6), while electrodeposition reactions in metallic anodes form a solid metal from dissolved cations (e.g., Li^+ to Li).

In this Perspective, we review recent advancements in microelectrodes for battery materials. Our primary objective of this work is to introduce and outline the scientific questions

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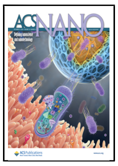

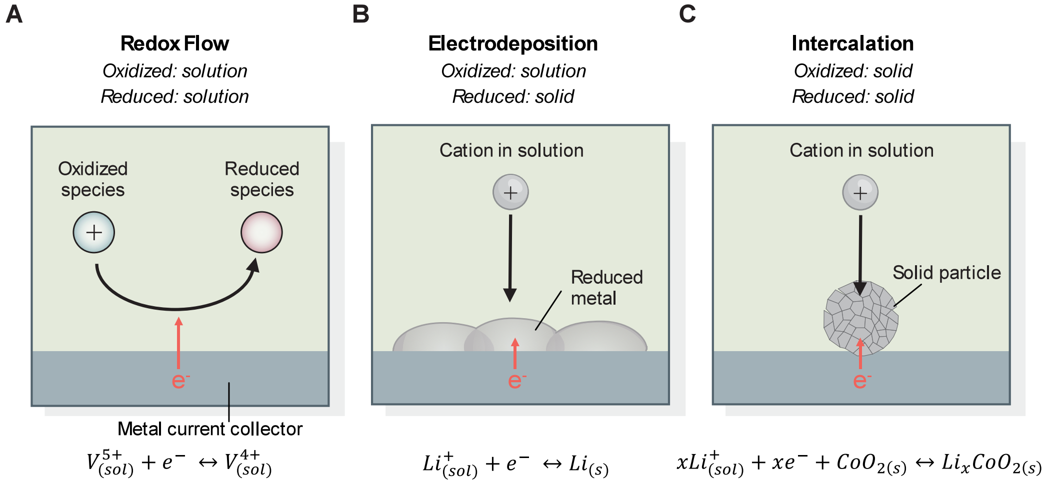

Figure 1. Categorization of battery reactions based on the phase of the oxidized and reduced species, with one example for each type. Solution-based species can be delivered by the liquid electrolyte, while solid species will remain on the microelectrode. (A) Redox flow cells rely on charge transfer from the metal to a dissolved species in solution. The species remains dissolved in solution before and after redox. (B) Electrodeposition reactions convert a dissolved species (e.g., Li^+) into a solid species (e.g., Li). For metallic deposition, the solid is formed upon the reduction of the cation from solution. Metal-air electrodes combine the cation with dissolved oxygen to form a solid, such as NaO_2. (C) In intercalation reactions, one or more solid particles must be placed on the electrode. Alloying or conversion electrodes can be also considered in this category because the oxidized and reduced phases are both solid. When used in microelectrodes, the solid particle must be attached to the microelectrode; in contrast, the solution species can be delivered to the electrode via the electrolyte in redox flow and electrodeposition reactions.

that can be solved using microelectrodes. We review papers that can serve as examples for the problems that can be addressed using microelectrodes. Finally, we outline our perspective on future opportunities for microelectrodes.

Our Perspective broadly reviews the use of (ultra)-microelectrodes for energy storage and incorporates recent advances in microfabrication and electrodeposition. Some previous related review papers have focused on single-particle chemistry of battery materials.[12,13] This article will not cover on-chip batteries or microbatteries[14−16] because their primary purpose is to integrate energy storage onto other functional devices, like microelectronics. In contrast, we aim to highlight the use of microelectrodes to enable fundamental studies of battery materials.

ELECTROCHEMICAL REACTIONS IN BATTERIES

Batteries rely upon the change in the redox upon the transfer of an electron and often the insertion of an ion like lithium. In Figure 1, we categorize the three types of reactions based on the phase (solution or solid) of the redox species. Because solution species can flow while solids are usually anchored in space, this method of delineation describes how to implement microelectrodes for the study of battery systems.

The first type of battery reaction is based on the redox reaction of ions or molecules dissolved in solution (Figure 1A). Here, an electron is transferred between the solid and the ion or molecule in solution, resulting in electron transfer and resulting electrochemical redox of the solution species. This type of reaction can be implemented as redox flow batteries, where the solvent containing the dissolved redox species are mechanically pumped to be delivered to the membrane. Both inorganic ions like vanadium[17] and organic molecules like quinones[18] can be used in redox flow batteries. Redox flow batteries generally have low volumetric energy density due to the low solubility (<10 M) of the redox species in solution compared to that of solid phases. In the context of microelectrodes, this system is also the simplest to implement because only the microelectrode needs to be fabricated, and the liquid phase enables the delivery of the redox species to the current collector. Redox flow systems are also the most similar to electrocatalysis systems where microelectrodes have long been implemented.

The second type of reaction is based on reversible electrodeposition from a solid phase from dissolved ions and molecules (Figure 1B). Here, one redox species is a solid, while the other is an ion dissolved in solution. In metal electrodeposition, the oxidized metal ion dissolved in solution (e.g., Li^+, Na^+, and Zn^{2+}) is reduced at the current collector, while the reduced metal (e.g., Li, Na, and Zn) is deposited as a solid in the current collector. A related reaction is the formation of a solid metal oxide (e.g., NaO_2) from dissolved metal cation and oxygen gas in a metal-air battery.[19] Like the case for electrodeposition, this reaction also deposits a solid phase upon electrochemical redox of dissolved materials. In the context of microelectrodes, the solid phase is directly deposited on the current collector.

The final type of reaction is based on solids as both the reactant and the product species (Figure 1C). These types of reactions are dominant in batteries and include nearly all materials used in commercial Li-ion batteries. In addition to intercalation reactions, they also include conversion[20] and alloying[21−24] reactions because the reactant and product phases are solid. Although the ion like Li^+ is delivered through the liquid electrolyte, these reactions necessitate the use of solids as both the oxidized and reduced species.

In this Perspective, we focus on electrodeposition and intercalation reactions. Redox flow systems are most similar to classical aqueous electrochemical systems that involve electron transfer to a dissolved species. There exists substantial literature[5−8] and even textbooks[25] on microelectrodes in such systems. In contrast, microelectrodes for electrodeposi-

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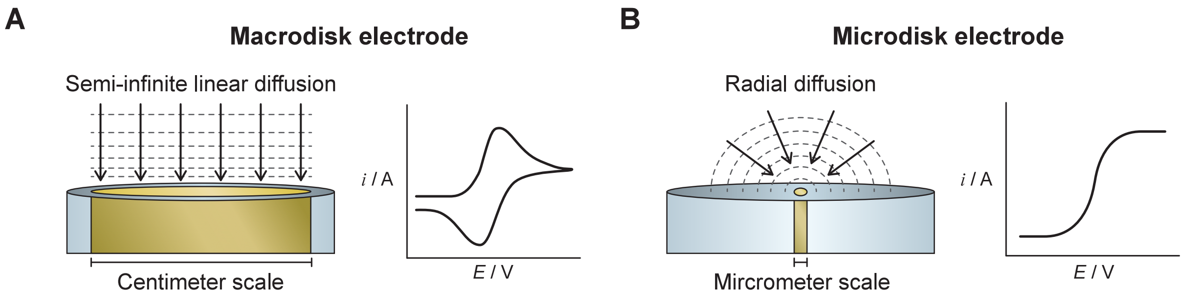

Figure 2. Microelectrodes reduce the current collector from centimeters to millimeter length scale and could yield different reaction kinetics. (A) At a macrodisk electrode, the thickness of diffusion layer is small relative to the electrode diameter, and semi-infinite linear diffusion occurs perpendicular to the electrode surface with a peak-shaped cyclic voltammogram. (B) At a microdisk electrode, where the diameter is smaller or comparable to the thickness of diffusion layer even in short time scales, a sigmoidal steady-state cyclic voltammogram can be recorded, which is indicative of mass transport-limited phenomenon governed by the radial diffusion. This allows for the measurement of transients at considerably shorter time scales with reduced ohmic loss.

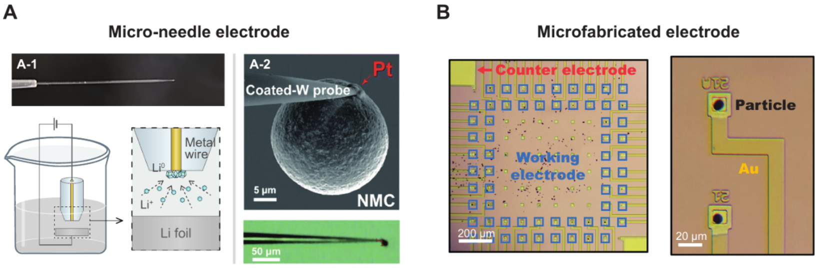

Figure 3. Fabrication of microelectrodes. (A) Microneedle electrodes, which are also called ultramicroelectrodes (UME), comprise a tungsten or platinum needle often coated with glass or a polymer. They can be used directly for electrodeposition or can be used to attach a particle for intercalation. A-2 Reprinted with permission from ref 35. Copyright 2018, Royal Society of Chemistry. (B) Microfabrication approaches can be used to create an array of microelectrodes on a single substrate, where particles can be attached. Adapted with permission from ref 36. Copyright 2023, Royal Society of Chemistry.

tion and intercalation reactions are more different due to the inclusion of solid redox-active materials.

OBJECTIVE FOR MICROELECTRODES ELECTROCHEMISTRY

The key defining feature of microelectrode electrochemistry is the reduction of the size of the electrode from macroscopic (>5 mm) to microscopic (<100 μm) dimensions (Figure 2). This size reduction enables a localized measurement of current and voltage that enables unexplored measurement regimes. Key advantages of this approach for batteries include:

1). Microelectrodes enable higher current densities primarily due to the shorter diffusion lengths (Figure 2). For example, when the microelectrodes are smaller than 25 μm, current densities as high as 1000 mA cm^{-2} are possible, compared to <10 mA cm^{-2} for bulk electrodes.[26] In intercalation batteries, the combination of a fast intercalation material with shorter electrolyte diffusion lengths can enable charge or discharge at rates as fast as 1000 C, or a full discharge in a few seconds.[27,28] 1 C is the current to (dis)charge in 1 h. These higher densities enable the exploration of unexplored operating regimes.

2). Microelectrodes are comparable in size to redox-active battery particles, including the micron-sized layered oxide cathodes and graphite anodes used in most Li-ion batteries. This enables the measurement of individual battery particles without the influence of heterogeneity, transport limitations, or additives like carbon black or binders, which can yield a more precise understanding of their mechanisms.

3). Microelectrodes present opportunities for high-throughput measurements due to the inclusion of many electrodes in a single device. This can also yield autonomous workflows.[29]

When properly implemented, microelectrodes provide a method to incorporate spatial resolution into electrochemical measurements. Microelectrodes directly measure electrochemical current and voltage, which are the central functional properties of a battery; in contrast, most microscopic measurements are based on the scattering or spectroscopy of light, X-rays, or electrons, which measure other properties of battery materials and can be used to indirectly infer current and voltage.

Scanning probe electrochemical techniques, such as the scanning electrochemical microscopy (SECM) and scanning electrochemical cell microscopy (SECCM), also provide localized electrochemical measurements.[30] SECM can be considered a microelectrode mounted on a scanning stage,[31,32] while SECCM localizes the liquid electrolyte using a nanopipette.[33,34] Despite these similarities, we will not review these scanning probe techniques in this work because they have been substantially reviewed in other works.[31,33]

TYPES OF MICROELECTRODES

There have been two primary types of microelectrodes based on their fabrication method. The first method is to use a sharp metallic needle that is several tens of micrometers in diameter at the tip. These needles can be integrated into two- and three-electrode electrochemical cells. The second method is the use

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of microfabricated "chips" based on semiconductor processing techniques.

Microneedles. Microneedles, also termed ultramicroelectrodes, are constructed by encapsulating tungsten or platinum wires within a glass capillary tube and epoxy resin such that only the "tip" of the needle would be exposed to the electrolyte (Figure 3A-1). Glass has the properties of perfect insulation, inertness, and transparency, which is the best choice to be embedded with metallic wires. Moreover, glass can be mechanically stretched by using a puller,[7] which will serve to thin both the glass and the underlying metal wire. This enables the formation of submicrometer cross-sectional areas. To secure the exposed electrochemically active area, flawless metal-to-glass sealing is required. The sealing must be done from one end to the other progressively to prevent air trapping between the fine capillary jet and the metal interface.

When immersed in an electrolyte and ionically connected to a reference- and counter-electrode, these needles can be directly used for electrodeposition for lithium and other alkali metals.[26,37−39] Additionally, solid intercalation particles including graphite,[27,40,41] $LiCoO_2$,[42−46] $Li_4Ti_5O_{12}$,[47] $LiMnO_2$,[43,48,49] $LiFePO_4$,[28,43] and various types of layered oxide cathodes.[35,50−54] Microneedles have also been used to study lithium insertion into Si.[21−24] One challenge in using microneedles for intercalation materials is maintaining the electrical contact between the needle and the particle over the course of the experiment. Depositing Pt using a focused ion beam[35,50] provides one way to improve the adhesion (Figure 3A-2). Alternatively, nanoimpact electrochemistry[55] relies on the collision between suspended particles and a microelectrode. The electrochemical currents can be collected during the collisions;[56,57] however, these collisions are too short for substantial charge and discharge of battery particles.

In microelectrode chemistry, the needle size and geometry play critical roles in electrode performance, particularly affecting response time scale and measurement accuracy. Inadequate microelectrode radius and geometry can lead to increased impedance and capacitance, impacting the quality of the measurements. Therefore, selecting the appropriate needle size and optimizing the geometry are essential steps to minimize these effects and ensure reliable and precise results in transient measurements using microelectrodes. In this manner, various preparation methods, including electrode sharpening, polishing, and sealing, have been continuously developed to support these efforts, even for nanometer-sized electrode preparation.

Microfabricated Electrodes. A second approach is to use semiconductor processing approaches to construct microfabricated electrodes (Figure 3b);[29,36,58] these devices, also called microelectrode arrays, have been used for measuring neuron action potentials in neuroscience.[11] Optical photolithography techniques are used to pattern metallic microelectrodes like Au or Al on a substrate,[29,36] typically silicon or silicon oxide due to its widespread use in microelectronics. Larger millimeter-sized contacts, or "pads," are fabricated at the edge of the chips to enable a connection to a potentiostat; interconnects, or "wires," electrically connect the pads to the microelectrodes. A larger counter-electrode contact can also be constructed on chip. For redox flow or electrodeposition, the microelectrode can be directly used as the working electrode.[29] For ion insertion reactions involving a solid, particles need to be manually assembled onto the microelectrodes.[36,58,59] Finally, a liquid electrolyte is implemented to ionically connect the microelectrodes to the on-chip counterelectrodes, thereby completing the electrochemical circuit. Detailed methods are given in ref 58.

One advantage of microfabrication is that it enables the definition of tens, hundreds, or even thousands of individually addressable microelectrodes on a single chip. By multiplexing these measurements, a single chip provides an opportunity for high-throughput and potentially automated experiments. One recent example is the Electrolab, an autonomous testbed for the study of redox flow molecules using microfabricated electrodes.[29] Microfabrication requires semiconductor processing "clean room" equipment that is not available at all universities and research sites; however, some commercial vendors like MultiChannelSystems supply microfabricated electrodes. Beyond commercial products, recent advancements in 3D printing have demonstrated the ability to print microbatteries.[60] This approach could also enable the fabrication of microelectrodes without requiring clean room microfabrication facilities.

SCIENTIFIC CHALLENGES ADDRESSED BY MICROELECTRODES

Microelectrodes present expanded opportunities for advancing the fundamental scientific understanding of battery materials. In this section, we identify and summarize some of the major scientific problems that have been addressed by using microelectrodes.

Electrodeposition. The electrodeposition of lithium (Li) metal is necessary for lithium metal batteries, which have much higher energy density than conventional Li-ion batteries using graphite negative electrodes.[61] However, the simultaneous formation of a surface corrosion film termed the solid electrolyte interphase (SEI) complicates the deposition process, which results in a poor understanding of Li metal electrodeposition and the lack of commercial Li metal batteries. While a number of past studies have attempted to rationalize Li deposition morphologies in different electrolytes, a general framework for understanding and predicting Li deposition morphology remains elusive due to the coupled growth of SEI and Li.[62] A paradigm shift in understanding Li electrodeposition requires that these two processes be decoupled. However, SEI formation occurs simultaneously with Li electrodeposition because metallic Li is extremely reactive, immediately reacting with the liquid electrolyte to form the SEI.

Several works have employed microelectrodes to overcome the problems of uncompensated IR drops and to reveal unexplored interfacial phenomena between Li and the electrolytes.[26,38,63] It is known that either ether solvent[64] or trace amounts of water in the electrolyte medium[65] can cause severe data distortion due to IR drops, hindering data interpretation. In this context, Aojula et al. proposed that the use of microelectrodes is effective in studying electrolyte kinetics in various electrolyte systems, allowing for the investigation of fast coupled chemical reactions on a freshly deposited Li surface.[66] Additionally, Verbrugge & Koch proposed the strategy for successfully minimizing chemical reaction between fresh Li and electrolytes by reducing the contact time between deposited Li and solvent-containing electrolyte through ultrafast Li plating (e.g., 1 A cm^{-2}).[63] Moreover, Boyle et al. effectively correlated Li plating kinetics to Li morphology and cyclability using transient ultramicroelectrode voltammetry.[39] This approach under an

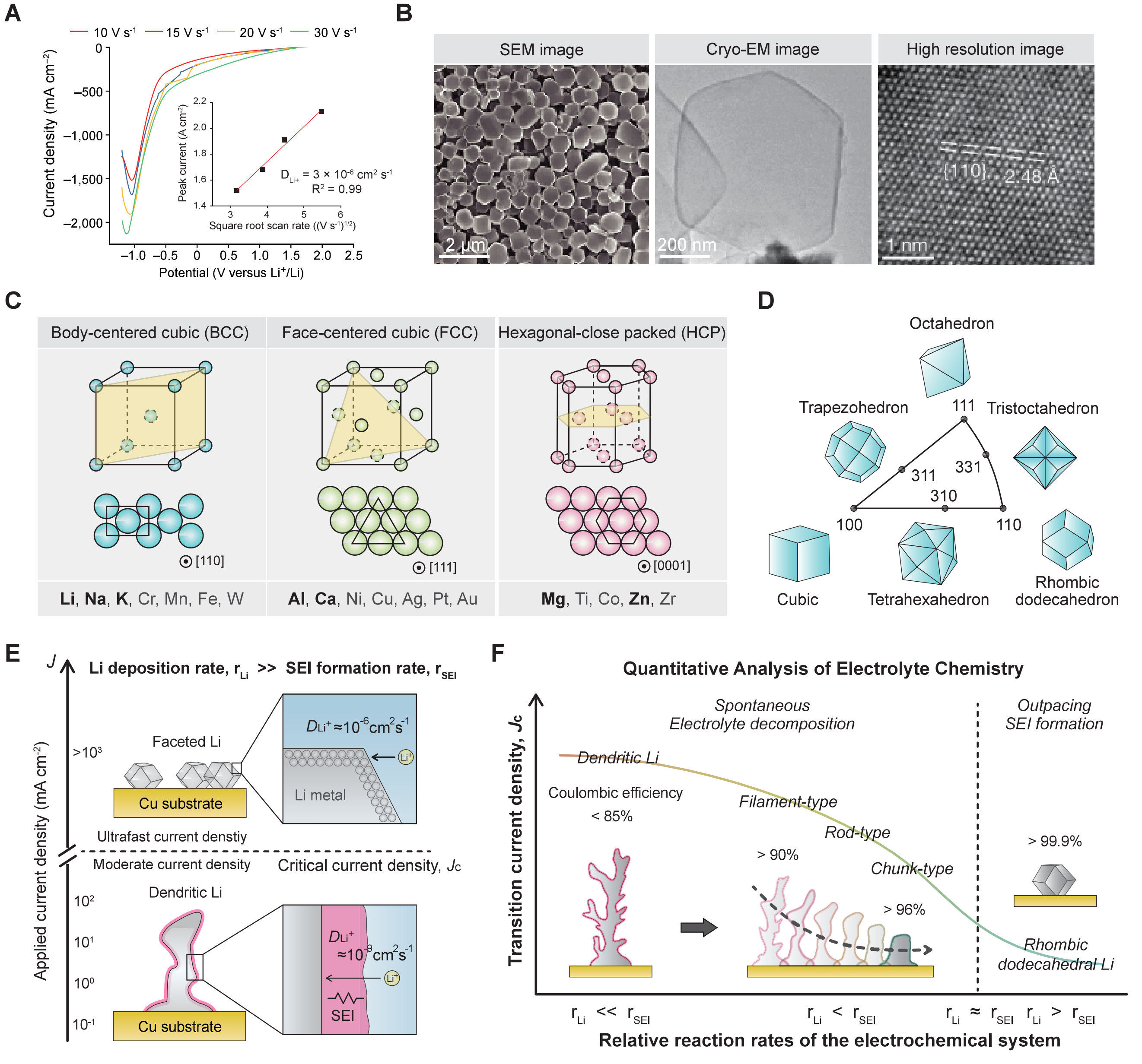

Figure 4. Applications of the microelectrode electrochemistry for various metal battery systems. (A) Linear sweep voltammetry (LSV) profiles of Li electrodeposition with an ultrafast scan rate from 10 to 30 V s^{-1}. Inset shows that the peak current density scales linearly with the square root of scan rate, with a Li diffusivity of 3 × 10^{-6} cm^2 s^{-1}. Adapted with permission from ref 26. Copyright 2023, Springer Nature. (B) The observation of faceted Li polyhedra deposited on UME at 1,000 mA cm^{-2}. Adapted with permission from ref 26. Copyright 2023, Springer Nature. (C) Crystal structures of various metals and their close-packed orientations. (D) The morphologies of various polymorphs consisting solely of a family of close-packed planes. (E) Scheme for morphological transition of the deposited Li, which is dictated by relative kinetics between the Li deposition rate and SEI formation rate. (F) Quantitative analysis of electrolyte kinetics correlating the transition current density with Li morphology.

ultrafast scan rate enables the measurement of the charge transfer kinetics by placing the time scale of the measurement shorter than the time scale of passivation by an SEI.[37] Therefore, these previous approaches encompass a strategy for understanding and differentiating Li plating from the SEI influence.

Recently, Yuan et al. decoupled Li deposition from SEI growth using an ultramicroelectrode geometry (Figure 4A) and surprisingly observed that the diverse Li morphologies in the model electrolytes all transition to a well-defined faceted polyhedron at ultrafast current densities (Figure 4B).[26] This result seems counterintuitive, as previous studies showed Li dendrites grow increasingly ramified at a higher current density, yet it aligns with expectations if Li deposition truly proceeds independently from SEI formation. Cryo-EM quantitatively identifies this morphology to be that of a rhombic dodecahedron, which matches the theoretical Wulff structure prediction of a body-centered cubic (BCC) crystal in the absence of a surface film. Furthermore, Yuan found that this well-defined faceted morphology persists independent of electrolyte chemistry or the current collector substrate, which indicates that outpacing SEI influence can eliminate the effect of these parameters on Li deposition morphology. This work aligns well with previous studies,[67,68] which reported that this

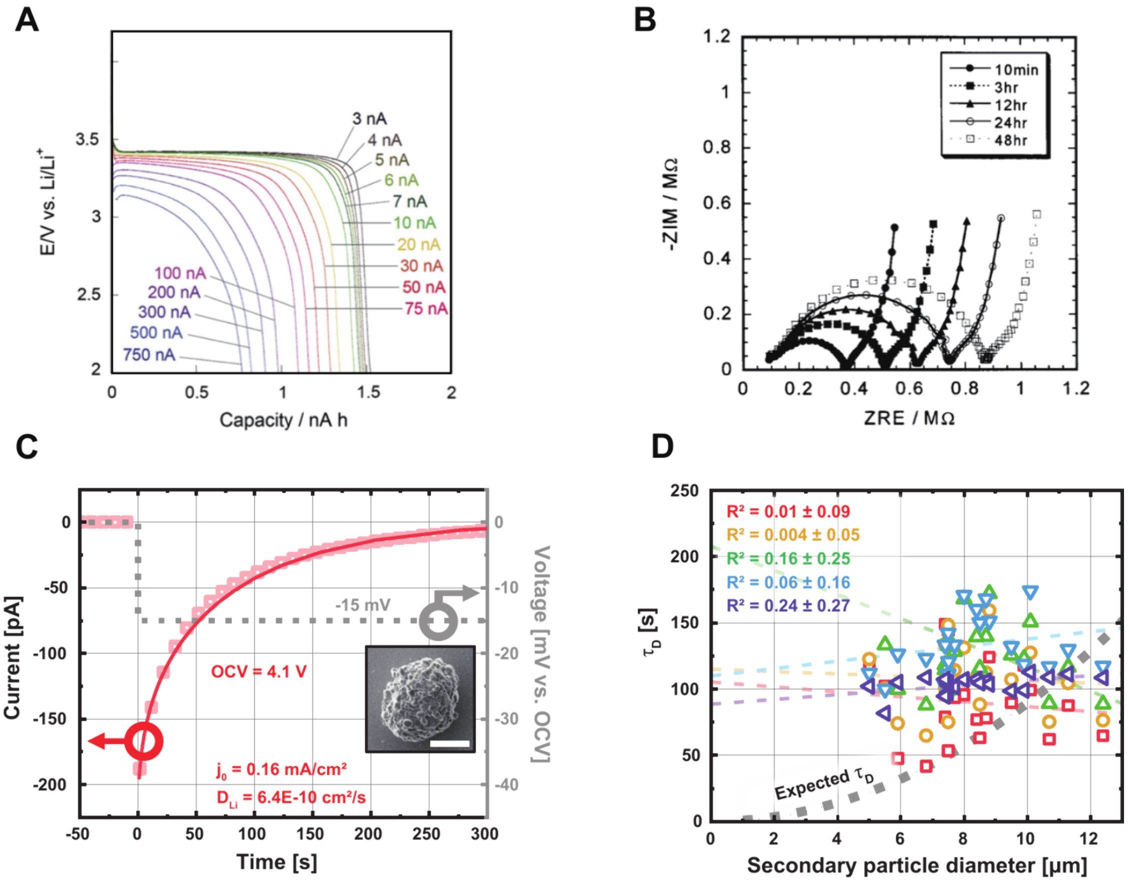

Figure 5. Single-particle electrochemical measurements in microelectrodes. (A) Constant current cycling of a single $LiFePO_4$ particle shows charge and discharge rates as high as 750 C (∼5 s). Reprinted with permission from ref 28. Copyright 2012, Elsevier. (B) Electrochemical impedance spectroscopy conducted on a single $LiCoO_2$ particle over time. Reprinted with permission from ref 42. Copyright 2001, IOP Publishing. (C−D) Potentiostatic intermittent titration technique (PITT) conducted on NMC particles to reveal that the diffusion time is independent of the diameter of the NMC secondary particle. Reprinted with permission from ref 36. Copyright 2023, Royal Society of Chemistry.

faceted morphology tends to appear on lithophobic substrates, where surface migration of Li adatoms is activated. Specifically, the single crystal Cu substrate exposing (111) crystallographic orientation leads to Li nucleation driven by the surface energy of Li itself, without any additional interfacial energy from the substrate, the electrolyte, or SEI layer.[67] This work challenged two long-standing axioms of Li electrodeposition: (1) high current densities promote dendritic Li growth, and (2) electrolyte chemistry governs Li deposition morphology. Instead, these UME studies reveal the intrinsic morphology of Li metal to be a nondendritic rhombic dodecahedron, which is independent of electrolyte chemistry and matches the theoretical Wulff construction of a BCC crystal. By outpacing SEI formation and decoupling it from Li metal growth, UME geometries open up expanded opportunities to explore how reactive metal deposition fundamentally proceeds without the influence of a surface corrosion film and its impact on battery operation. These unexpected findings will transform how the field thinks about Li electrodeposition and provide further insights for avoiding key failure modes during fast-charging of Li metal batteries.

Ultramicroelectrodes electrodeposition can be expanded to study the structure of other reactive metals, potentially impacting future technologies, by decoupling them from the SEI influence. Figure 4C illustrates the crystal structures of different metals and their corresponding closed packed crystallographic orientations. Since the surface energy of metals is lowest for their close-packed planes, the polymorph consisting solely of a family of close-packed planes (such as {110} for Li) will exhibit corrosion-resistant properties. Consequently, for Li, Na, and K, the rhombic dodecahedron represents the most stable morphology, while the octahedron is the most stable for Al and Ca (see Figure 4D). In contrast, hexagonal-close-packed (HCP) metals do not have their stable polymorphs consisting of {0001} close-packed planes, making a plate-like hexagonal column with a high aspect ratio of width to height (i.e., a flat plate with {0001} base) highly probable for minimizing total surface energy. These insights intrigue us to explore a wide range of possibilities to transform the most stable polymorphs and increase the reversibility of electrodeposition of metal ions.

Microelectrode may serve as a means of bridging morphological transition and electrolyte chemistry. When the applied current density exceeds a critical current density, the rate of metal deposition outpaces the rate of SEI formation, leading to the morphological transition (see Figure 4E). Since the electrolyte chemistry determines Li deposition kinetics and SEI formation kinetics, we believe that the current density required to decouple Li metal deposition from SEI formation will vary depending on the electrolyte formulation. Therefore, electrolyte decomposition kinetics can be quantified by measuring transition current densities across both conventional

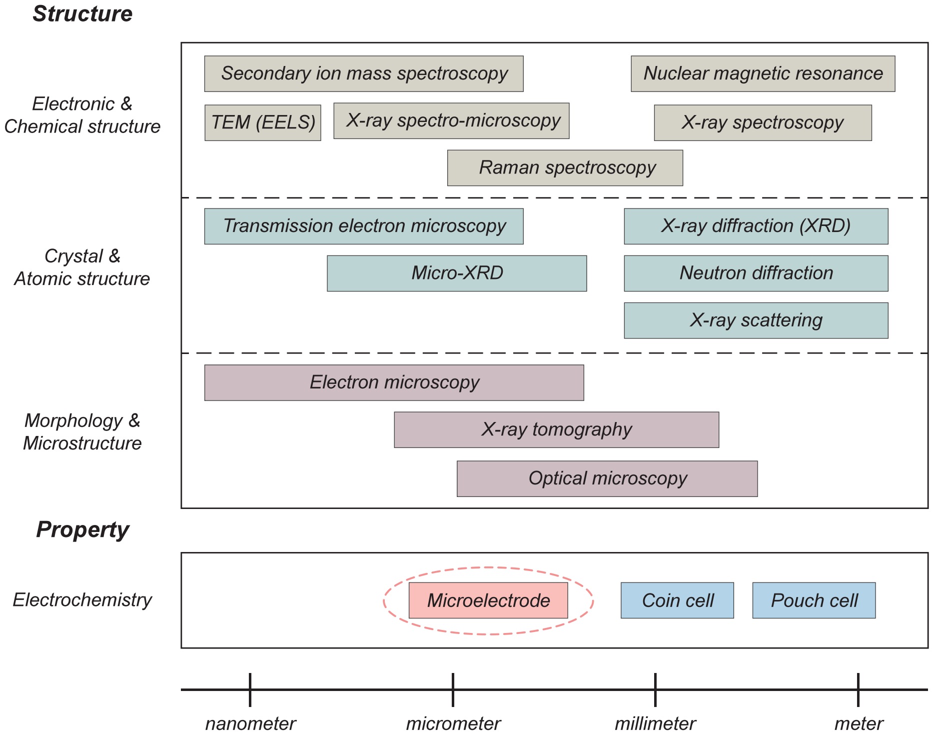

Figure 6. Examples of characterization techniques at multiple length scales. Microelectrodes bring the measurement of electrochemical properties from the millimeter to the micrometer length scale, thereby complementing the large number of structural characterization probes at multiple length scales.

and previously reported high-performance advanced electrolytes (Figure 4F). In addition, this capability also allows us to distinguish between electrochemical electrolyte decomposition and spontaneous corrosion of Li in the electrolytes,[69] both of which contribute to Coulombic efficiency but are challenging to differentiate during battery operation. Through an understanding of the intertwined relationship between transition current densities and Coulombic efficiency, this proposed quantification method for electrolyte chemistry has the potential to guide the development of electrolytes (and associated SEI layers) aimed at minimizing Coulombic efficiency losses.

Intercalation Electrodes. Microelectrodes have been used to conduct single-particle electrochemical experiments on anode and cathode materials in Li-ion batteries.[12] Such single-particle experiments take advantage of a well-defined single-particle geometry and the absence of additives. In Figure 5A, Munakata et al. showed that a single $LiFePO_4$ particle can undergo extremely fast cycling rates, up to 500 C,[28] or about 7 s; Dokko et al. conducted similar research on graphite to show cycling rates up to 1000 C,[27] or about 4 s. Like the case for electrodeposition, such research has revealed the extremely fast kinetics of individual intercalation particles in the absence of electrode-level transport limitations.

Other research has used microelectrodes to study the reaction rates and solid lithium diffusion kinetics. Typical approaches to measure the exchange current density (j_0) and the lithium diffusivity in the solid (D) include the potentiostatic intermittent titration technique[35,36,50] (PITT), electrochemical impedance spectroscopy,[35,42,52] and quasi-Tafel analysis.[51,54] Due to the well-defined geometries, lack of particle size distribution, and the absence of additives and binders, such microelectrode experiments should be considered the "gold standard" for identifying reaction and diffusion parameters to be used in continuum physical models. Research by Dokko et al. used electrochemical impedance spectroscopy to show the changes in the charge-transfer resistance over time[42] (Figure 5B).

Recent work by Min et al. quantified reaction and diffusion parameters of 21 particles using the microfabricated microelectrode array.[36] This work showed that smaller particles have the same diffusion and reaction time constants as larger particles, which can be explained by particle cracking and resulting electrolyte penetration.[70] This work showed that a statistical approach of analyzing multiple single-particle electrochemistry data sets can reveal unexplored mechanisms and, in this case, resulted in refined models that incorporated electrolyte penetration.[71]

FUTURE OPPORTUNITIES

We see microelectrodes as an emerging opportunity for fundamental research into battery systems. Although they have long been used for obtaining accurate and precise electrochemical measurements, recent research has shown their potential to explore previously unexamined within both electrodeposition[26] and intercalation[36] materials. In this section, we propose future opportunities for research in microelectrodes for batteries.

New Materials and Chemistries. Microelectrode measurements have thus far been conducted on lithium intercalation cathode and anode materials, lithium metal electrodeposition, and redox molecules.[29] These represent simpler model systems that facilitate the development of microelectrodes as a technique. However, with repeated demonstrations by multiple groups, there is potential for the use of microelectrodes in innovative areas of batteries.

Examples of unexplored microelectrode electrodeposition include other metals like sodium, potassium, zinc, as well as metal-air batteries; Figure 4 describes some of our predictions for other reactive metals. Examples of solid ion insertion materials include conversion materials[20] and sodium-ion battery electrodes, which have not been as well studied as intercalation materials and silicon. This platform may also facilitate studies of solid-state batteries, although the mechanical contact between the microelectrode and the solid electrolyte could present challenges.

Correlative in Situ Characterization at Matching Length Scales. In recent years, there has been substantial development for in situ microscopy at the micro- to nanoscale using electrons,[72] X-rays,[73,74] and optical[75−77] microscopy. These measurements enable observation of changes in the state-of-charge or other physical properties during battery cycling at the micro- to nanoscale. However, one weakness of such measurements is that the field of view for microscopy is much smaller than the size of the macroscopic electrodes used for electrochemical cycling. For this reason, the microscopic observations are not conducted on the same length scale as the electrochemical features. While imaging techniques to probe a macroscopic battery cell are starting to be developed,[78] they do not have the spatial resolution to resolve the dynamics within individual particles.

Microelectrodes can bridge this length scale by localizing the electrochemical signature to an area comparable to the field-of-view of the microscopic observation. We envision this as more practical for in situ optical and potentially X-ray microscopy, which often images areas in the tens of microns. While this will require the development of advanced electrochemical cells, it could substantially increase the ability to correlate electrochemical and spectro-microscopic signals.

Structure−Property Relationships at the Microscale. Over the last decades, a number of techniques have been developed to probe the chemical structure, electronic structure, crystal structure, and microstructure of energy storage materials from the nanometer to the macroscopic length scale[79−81] (Figure 6). While these advanced techniques have been able to elucidate the structure of materials at different length scales, they are usually correlated to electrochemical data taken at the millimeter or higher length scales, typically using macroscopic electrodes.

Microelectrodes are able to bridge this gap by enabling electrochemistry at the micrometer length scale and potentially even the nanometers in the future. By virtue of their small size and high surface-area-to-volume ratio, microelectrodes enable precise and localized property measurements essential for understanding materials and electrochemical systems. This capability unravels intricate processes at the microscale that dictate the performance of electrochemical systems, pushing boundaries with existing instrumentation.

High-Throughput and Autonomous Experimentation. By embedding multiple microelectrodes onto a single chip, a microelectrode array can enable high-throughput and autonomous approaches. Multiplexed microelectrode arrays can potentially enable much faster experimental preparation compared to macroscopic electrochemical cells. Multiplexed measurements using microelectrode arrays with 256 (or more) electrodes are commonly conducted in the field of neuroscience,[11] with companies like Axion Biosystems and Multi-ChannelSystems providing commercial benchtop solutions. Combining high-throughput microelectrodes with post-mortem ex situ characterization like scanning electron microscopy could be especially effective at increasing experimental throughput. Such high-throughput measurements can potentially lead to autonomous experimentation, with the Electrolab as one example of a redox flow battery system.[29]

If the high-throughput capability can be expanded, they can potentially be used for the process control and manufacturing of battery powders. One possible avenue is to inspect a sample of individual battery particles from a batch to assess the quality of the batch process. This will convey information about the distribution of electrochemical properties among particles, which will be a substantial advance over current metrology processes that primarily quantify physical properties such as the particle size.

CONCLUSION

Conventional battery materials research has typically been conducted on centimeter to millimeter scales. While these scales allow for easier observation, they make it difficult to distinguish fundamental behaviors due to interference from unwanted mechanisms. Fundamental research and advanced engineering of battery materials and systems require accurate characterization and measurements across many length and time scales. Microelectrodes are an emerging characterization method that can enable more accurate electrochemical measurements across different regimes.

This Perspective highlights the significant findings enabled by microelectrodes and their further potential as a measurement tool. The improved temporal electrochemical data obtained from microelectrodes could inform the design rule for electrolytes that prevents SEI formation and improves Coulombic efficiency. Moreover, single-particle electrochemical analysis using microelectrodes could aid in determining a more strict capacity degradation mechanism in cathode particles. These research needs are driven by the growing demand for rechargeable batteries. We envision that microelectrodes can expand understanding and knowledge of more advanced battery chemistries.

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Notes

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