

Battery Research: Characterizing the Future



Essential
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Briefings

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Front cover: atomic force microscopy image of a cross-sectioned cathode with lithium metal oxide, carbon and polymer filler. 15x15 μ m scan. Image © Bruker.

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CONTENTS

4 INTRODUCTION

6 INSIDE A LITHIUM-ION BATTERY

11 CHARACTERIZING BATTERY
MATERIALS

26 FUTURE FOR BATTERIES

About Essential Knowledge Briefings

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INTRODUCTION

Dramatic changes in the world of batteries over recent decades have helped usher in our modern technological world. Today, many of our electronic devices, from laptops to smartphones, are powered by rechargeable lithium-ion (Li-ion) batteries, and they could soon extend into many other areas as well. This includes transport, through the ongoing development and adoption of electric vehicles.

As the metal with the lowest density and a very high electrochemical potential – and therefore the highest energy-to-weight ratio – lithium is an ideal material for batteries. The first lithium batteries were developed in the 1970s, powered by a metallic lithium anode. Although more powerful and longer lasting than the alkaline battery, these first lithium batteries were non-rechargeable, limiting their use.

Adoption of a lithium cobalt oxide cathode and a graphite anode led to the first rechargeable Li-ion battery, which was commercialized in 1991. Li-ion batteries are now the gold standard for rechargeable batteries, hence their ubiquity in portable electronic devices.

Yet there is significant room for improvement. Although less susceptible than other battery types, Li-ion batteries still suffer from ‘self-discharge’, whereby chemical reactions inside the battery reduce its stored charge (by up to 3% per month). Li-ion batteries also exhibit limited capacity, inaccurate estimates of remaining charge, and are notoriously expensive to produce. Furthermore, they can suffer from the growth of crystalline needles of lithium, known as dendrites, from the anode. If these dendrites grow to reach the cathode, they can

short-circuit the battery, potentially causing it to catch fire or even explode.

Scientists are actively investigating various ways to overcome these issues – from producing improved Li-ion batteries by synthesizing better battery materials to developing next-generation battery technologies that might one day replace Li-ion batteries as the gold standard. But doing this requires precise, sensitive techniques for analyzing and characterizing these materials and technologies.

This EKB will introduce the main analytical techniques used to characterize Li-ion battery materials. In particular, it will focus on nanoindentation, a very common method for measuring the mechanical properties of materials, and atomic force microscopy (AFM) characterization, which works by ‘touching’ the surface of materials with a mechanical probe to map their topography and properties with nanoscale resolution. The EKB will explain how these techniques and their various modes work, and will detail how they are used for analyzing battery materials and what kind of information they can produce. It will also present two case studies to illustrate how the techniques are being applied by working scientists in the laboratory.

Looking to the future, it will explore what new lithium-based battery technologies are in the pipeline – including metal, sulfur and air-based technologies – and the specific challenges associated with their characterization. It will look at novel characterization approaches that may overcome these challenges, and explore the ultimate applications of more powerful batteries, from powering electric vehicles to storing renewable energy.

INSIDE A LITHIUM-ION BATTERY

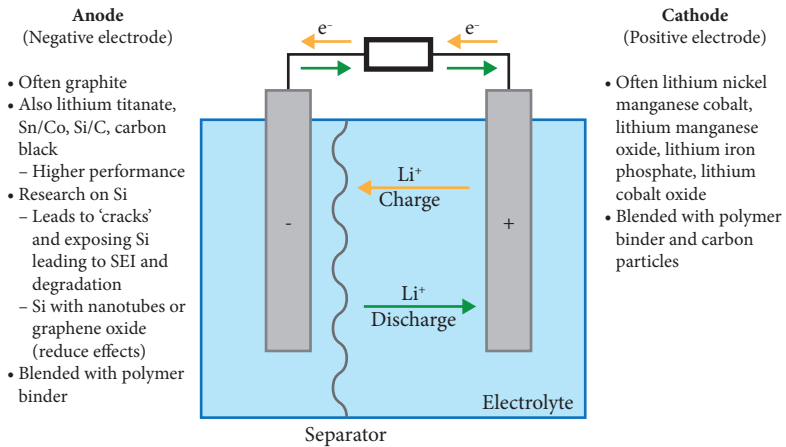
Like all rechargeable batteries, a Li-ion battery is, in essence, a device for converting chemical energy to electrical energy and vice versa. It consists of four main components (see Box 1 for more detailed descriptions).

1. The anode (negative electrode), usually made from graphite, plated onto a copper current collector.
2. The cathode (positive electrode), made from a transition metal oxide, plated onto an aluminium current collector.

Both of the electrodes allow lithium to be reversibly incorporated (intercalated) into their interiors without significantly changing the crystal structure.

3. The electrolyte, a material that conducts lithium ions (Li^+) between the anode and cathode; it may be liquid or solid.
4. The separator provides a barrier between the anode and the cathode, while still allowing the exchange of lithium ions from one side to the other; in a Li-ion battery, it is often made from polyolefin.

Figure 1 shows a battery in use. In a charged state, lithium atoms are stored between the carbon layers of the graphite anode. When the battery is powering a device, lithium atoms lose an electron and are deintercalated at the anode, becoming lithium ions that dissolve into the electrolyte. At the cathode, lithium ions from the electrolyte are intercalated into the metal oxide cathode, gaining an electron. This process



Intercalation = Li inserted into the electrode

Separator = permeable membrane allowing flow, but no short circuit

Figure 1. How a Li-ion battery works

causes electrons to travel around an external circuit from the anode to the cathode, generating an electric current. During charging, the reverse process occurs, with an applied charge powering the transfer of lithium ions and electrons from the cathode to the anode.

Lithium has always been of interest as a battery material, as it is a very electropositive element (3.04V), producing the greatest possible cell potential (the difference in voltage between the anode and the cathode). Lithium also has a low density and one of the smallest ionic radii for any single charged ion. These factors confer a high gravimetric capacity (the amount of charge it can store, 3608mAh per gram), and therefore a high energy density.

Given these properties, an anode made of pure lithium metal would confer the highest possible energy density. However, in trying to create rechargeable lithium batteries in

the 1980s, scientists discovered that repeated charge/discharge cycles using lithium metal anodes cause the rapid growth of dendrites on the lithium metal anode. This often resulted in early lithium batteries short circuiting, which could lead them to catch fire and occasionally explode.

Anode

The anode is generally made of a thin graphite film, deposited onto an aluminium current connector. The layered structure of graphite allows lithium atoms to be intercalated between the layers of carbon, with six carbon atoms required to intercalate each lithium atom.

Cathode

The cathode is made of a lithium ion transition metal oxide, plated or bound onto a copper current connector. Commonly used cathode materials include lithium cobalt oxide (LiCoO_2) with a layered structure, lithium manganese dioxide (LiMn_2O_4) with a spinel structure, and lithium iron phosphate (LiFePO_4) with an olivine structure.

Electrolyte

The electrolyte is commonly a lithium ion-conducting liquid or paste consisting of lithium salts dissolved in mixtures of linear and cyclical carbonate solvents. Additional additives, such as vinylene carbonate, may be used to improve battery lifetime. Electrolytes are not chemically stable when in contact with the electrodes during initial charging and form a composite layer known as the solid electrolyte interface (SEI), which is conductive to lithium ions, electrically insulating, and mechanically robust and elastic. Formation of the SEI is a normal process during the first uses of a battery, and the SEI serves to protect the electrode and electrolyte from degradation.

Nevertheless, the formation and subsequent dynamics of the SEI are highly complex. Repetitive charge/discharge cycles can lead to SEI fracture or uncontrolled growth as a result of 'parasitic reactions' between the electrode materials and the electrolyte. In both cases, this can reduce battery efficiency and may lead to catastrophic failure if lithium plating begins to occur on the SEI surface. As such, there is great research interest in electrolyte additives that can prevent the deposition of solids at the electrode/electrolyte interface and in the use of solid electrolytes that don't form an SEI.

Separator

The separator serves three main purposes in a Li-ion battery: to physically separate the cathode from the anode; to prevent dendrites that grow on the anode from reaching the cathode and short-circuiting the battery; and to facilitate lithium ion transport. The ideal separator would have infinite electronic resistivity and zero ionic resistivity; in a Li-ion battery, these properties are generally achieved by using a polymer such as polyolefin. The separator is also a key safety feature of the battery – during thermal runaway, pores in the separator should collapse as the temperature increases, stopping ionic conductance and shutting down the cell. Another key safety feature of the separator is its resistance to puncture by conductive material (such as dendrites) or by small conductive particles introduced in the interelectrode space during manufacture.

Box 1. The components of a Li-ion battery

After many frustrated efforts, research switched focus from lithium metal to materials such as silicon or graphite that can reversibly incorporate lithium ions into their structure. Although such materials decrease the energy density of the battery, they reduce the growth of dendrites and thus paved the way for the safer rechargeable Li-ion batteries that are in common use today.

As anyone who has ever used a portable electronic device will know, a Li-ion battery will gradually degrade over its lifetime, reducing the amount of charge it can hold. This degradation is measured by two quantities: capacity fade and resistance increase (aka power fade).

Structural changes to the electrode microstructure, as well as parasitic reactions at the SEI, can cause both of these problems. Repeated intercalation and deintercalation of lithium into the electrodes causes strain in the crystal structure and can lead to deformation, cracking and, ultimately, failure. In addition, the lithiated graphite anode and the unlithiated metal oxide electrode are highly reactive, and both can react with the electrolyte in complex ways, increasing the resistance and lowering the battery capacity.

The formation and dynamics of the SEI are key to this process. Initially, the SEI forms a thin film that prevents electrolyte molecules from reaching the electrode but allows lithium ions to pass through. While this lowers the capacity of the battery slightly, it is essential for preventing the electrodes from degrading over many charge/discharge cycles.

Over the lifetime of the battery, however, the SEI layer grows, as parasitic reactions occur at both the cathode and

anode. These reactions cause the deposition of solid products (which can contain lithium) at the electrode surface, increasing the thickness of the SEI. These solid products can block lithium ions from reaching the electrode and may also reduce the number of mobile lithium ions in the electrolyte. When lithium ions can no longer reach the electrodes, the likelihood that dendrites will grow on the surface of the SEI increases, potentially leading to catastrophic cell death.

This all shows that the electrical properties of a battery are highly dependent on the numerous complex chemical reactions occurring within the battery, which, in turn, depend on the molecular structure and morphology of the battery components. Hence there is a pressing need for increasingly sophisticated methods for studying and optimizing the chemical and structural properties of Li-ion batteries. In particular, there is a need to match the chemical and structural properties to changes in electrical properties under normal battery operating conditions.

Until recently, this has proven difficult to achieve given the highly volatile nature of the electrolytes and the reactivity of the electrodes. However, the development of more advanced *in situ* and *in operando* methods is now making such characterization possible. Many attributes of Li-ion batteries are of interest to scientists, and these may be thought of broadly as mechanical, morphological, electrical and electrochemical. Investigating how these attributes vary within all components as a result of manufacture, external conditions or use is a critical aspect of battery research.

CHARACTERIZING BATTERY MATERIALS

The performance of any battery, whether in terms of its capacity, lifetime or energy density, is ultimately down to the intrinsic properties of the materials that comprise its anode, cathode, electrolyte and SEI. Various characterization techniques can be used to interrogate the physical and chemical properties of these materials, as well as their internal electrochemical processes and degradation mechanisms.

The composition and crystalline structure of battery materials can be assessed using techniques such as electron-dispersive X-ray spectroscopy and electron microscopy. The chemical environment of the electrodes can be probed via a range of spectroscopy techniques, including Raman spectroscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS).

There are also several widely used techniques for assessing the electrochemical properties of a Li-ion battery. These include simple cycling tests, which determine how many times the battery can be charged and discharged until it deteriorates; electrochemical impedance spectroscopy, which involves applying a small voltage to measure impedance at a given frequency; and galvanostatic intermittent titration, which uses current pulses to determine the thermodynamic properties of electrode materials.

Traditionally, lithium-ion characterization approaches have been applied *ex situ*; however, newer *in situ* and *in operando* characterization techniques allow materials to be characterized while the battery is in use. These include Mössbauer spectroscopy, a technique related to nuclear magnetic resonance

spectroscopy, and a type of spectroscopy called X-ray absorption near edge structure, which relies on the absorption of X-ray photons.

This EKB, however, will focus on ‘surface-sensing’ imaging approaches, especially AFM and a similar technique called nanoindentation. Other important battery imaging techniques briefly touched on will include scanning electron microscopy (SEM), transmission electron microscopy (TEM), hard X-ray microscopy and optical profiling.

Atomic force microscopy

AFM allows the visualization of materials at subnanometer scale. In simple terms, it involves scanning a probe over the surface of a sample. Minor changes in the texture of the material lead to deflections of the probe, which are detected by a laser beam to generate a detailed image of the surface topography (Figure 2).

More specifically, a cantilever with a very sharp tip is scanned over the battery material. As the tip approaches the surface, close-range attractive forces between the surface and the tip cause the cantilever to bend towards the surface. When it gets even closer, increasingly repulsive forces cause the tip to bend away from the surface. The deflection caused by these forces is recorded by bouncing a laser off the back of the cantilever onto a position-sensitive photodetector, with any deflection altering the position of the laser beam. A map of surface topography can be built up directly from these recorded deflections, by comparing the deflected signal with a reference signal known as the setpoint.

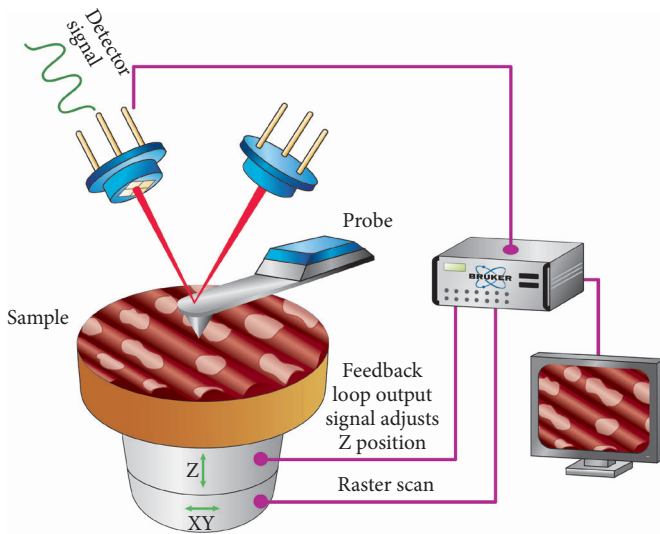


Figure 2. Schematic of basic scanning probe microscopy operation

AFM operates in several primary modes (Figure 3). Two of these – contact mode and tapping mode – have proved particularly useful for characterizing battery materials. As its name suggests, in contact AFM the tip of the cantilever physically touches the surface as it scans along the material. Although simple, fast and sensitive, contact mode also has a major drawback. The lateral forces exerted on the sample as the tip is scanned across can be very high, potentially causing damage to both the tip and the sample.

It was to overcome this problem, as well as those caused by friction, adhesion and electrostatic forces, that tapping mode AFM was developed. Tapping AFM maps the topography of a sample by lightly tapping its surface with an AFM probe, which oscillates at its resonant frequency. The force of the intermittent contacts made by the tip with the sample

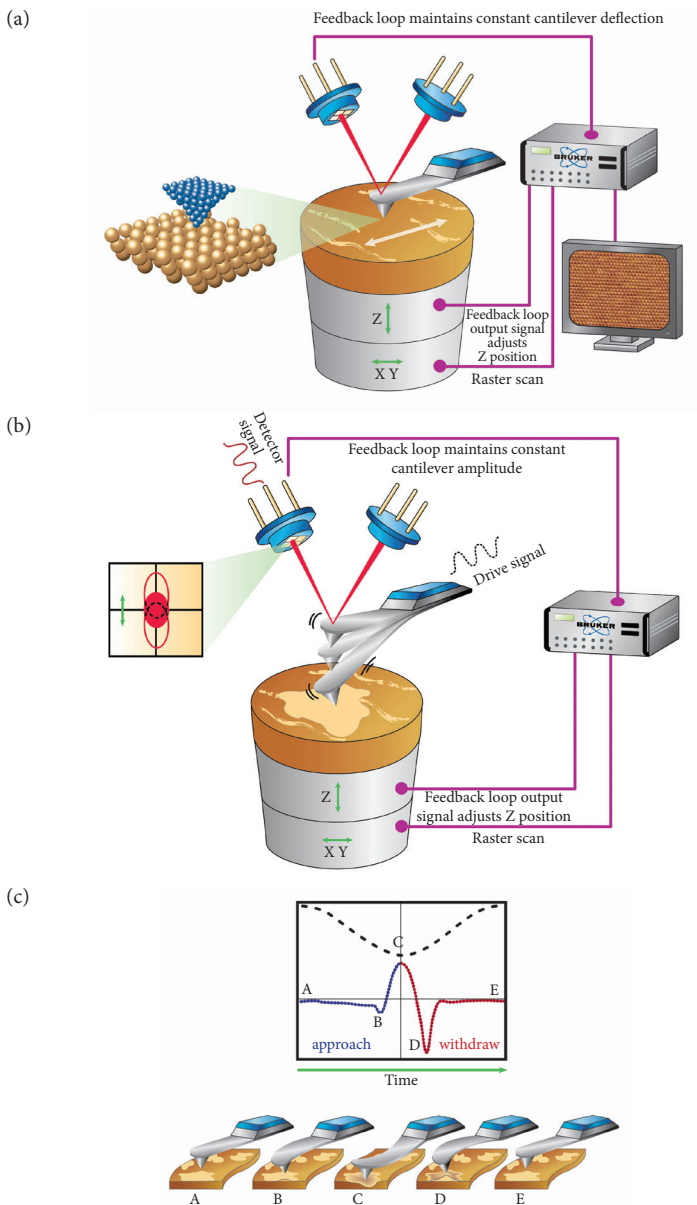


Figure 3. Schematics of primary AFM modes: (a) contact mode, (b) tapping mode, (c) PeakForce tapping mode

surface can be used to generate an image. PeakForce tapping AFM offers even greater sensitivity. Here, the probe periodically touches the sample surface in the same way as conventional tapping AFM, but it is oscillated in a sine wave pattern at a frequency that can be an order of magnitude less than the resonant frequency. Together with an intelligent algorithm that can determine the peak force experienced by the tip, this allows PeakForce tapping to measure piconewton scale interaction forces, making it particularly useful for studying battery materials.

Although these comprise the primary modes of AFM, there are many secondary modes that are also useful for characterizing battery materials (Table 1). While the primary modes focus on producing three-dimensional images of surface topography, the secondary modes probe various chemical, mechanical, electrical and electrochemical features of the surface, often by using specialized tips and cantilevers. These features can include surface hardness, friction and elasticity, adhesion, permittivity, conductivity, magnetism, surface potential, electrochemical reactivity and temperature.

Thanks to its ability to visualize individual atoms on surfaces, AFM is one of the most commonly used techniques for characterizing battery materials, able to work on a variety of sample types with a wide range of electrical or insulating properties. AFM can also work in liquids (*ie* electrolytes), as it does not require an electron beam or lenses.

Importantly, AFM can also be used for *in situ* battery analysis. This is generally performed in an oxygen- and moisture-free environment to protect battery components,

Mode	PF-QNM	SSRM	TUNA/PF-TUNA
Full name	PeakForce Quantitative Nanomechanical Property Mapping	Scanning Spreading Resistance Microscopy	Tunneling AFM PeakForce Tunneling AFM
Summary	Uses PeakForce tapping to simultaneously map nanomechanical properties and image sample topography	Combines contact mode AFM with a wide-range amplifier in order to measure spreading resistance, which relates to impedance and occurs with aging in Li-ion batteries	A form of contact-mode AFM that uses an ultra-low current measurement technique. Especially used to study low-conductivity samples. A variation of this technique called DataCube (DCUBE)-TUNA also allows simultaneous measurement of nanomechanical properties and electrical conductivity
Advantages	<ul style="list-style-type: none"> • High (atomic-scale) resolution • Non-destructive • Suitable for both very soft and hard materials • Fast and easy to use • Can study the variation of mechanical properties across a surface 	<ul style="list-style-type: none"> • Measures electrical properties in 2D • High resolution • Simultaneously maps topography and spreading resistance (and thereby carrier density) 	<ul style="list-style-type: none"> • High-resolution current mapping • Can be used for fragile samples • High sensitivity • Precise force control • No damaging lateral forces • Correlates nanomechanical and nanoelectrical properties
Mode	KPFM/PF-KPFM	EC-AFM	PF-SECM
Full name	Kelvin Probe Force Microscopy PeakForce Kelvin Probe Force Microscopy	Electrochemical AFM	PeakForce Scanning Electrochemical Microscopy
Summary	A form of conductive AFM operated in non-contact mode. KPFM produces a map of the work function (the minimum energy required to remove an electron) of surfaces, which in turn provides information about composition and electronic state	Combines AFM with electrochemical measurements. It can be used to perform <i>in situ</i> measurements in an electrochemical cell, and therefore investigate changes in the electrode surface during electrochemical reactions	Dual function probes contain a nanoelectrode on the tip of a typical AFM cantilever. PF-SECM can conduct quantitative nanomechanical property mapping and measure surface conductivity and electrochemical activities simultaneously
Advantages	<ul style="list-style-type: none"> • Can analyze the surface potential of a range of structures • High resolution • Measures surface potential and maps topography 	<ul style="list-style-type: none"> • See the effects of electrochemical reactions in real-time • Compatible with 1 part per million (ppm) environmental controls • Fast and easy to use • Specialised technique – designed for Li-ion battery research 	<ul style="list-style-type: none"> • Allows simultaneous topographic mapping and measurements of electrochemical, electrical and mechanical properties • High spatial resolution (under 100nm) of electrochemical mapping • Can be used for liquid electrolytes

Table 1. List of secondary AFM modes for characterizing battery materials

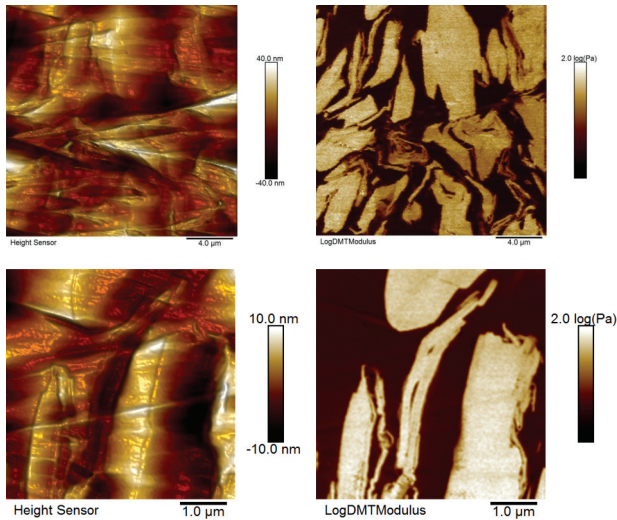


Figure 4. PeakForce QNM on anode. 20x20 and 5x5 μm scans

allowing it to provide measurements that reflect the real working conditions of Li-ion batteries.

AFM has been used extensively to study battery electrodes and their interface with the electrolyte (Figure 4), probing the formation of lithium dendrites and identifying regions prone to electrolyte breakdown. It has also proved effective for studying SEI formation (Figure 5), including assessing the thickness and stability of the SEI and identifying different types of SEI morphology. For example, it has been used to investigate how morphological changes to the SEI are affected by variations in temperature and voltage.

Nanoindentation

In many ways, nanoindentation is similar to AFM: it uses a nanometer-scale, rigid probe with known mechanical properties and specific geometry to indent a test material with unknown

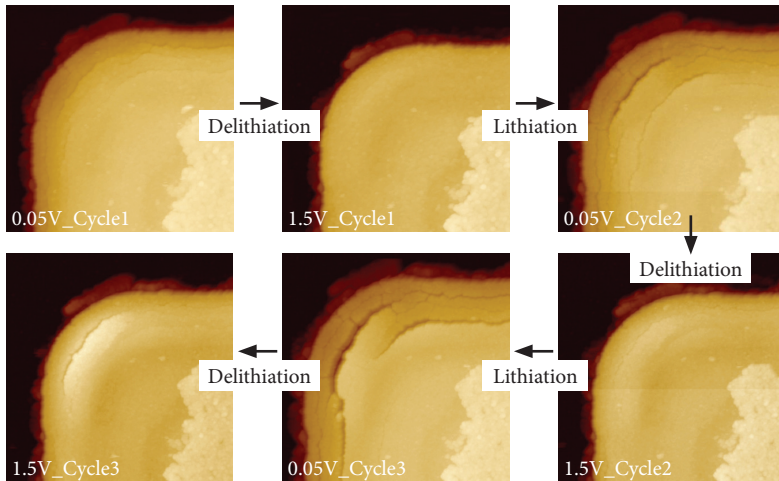


Figure 5. *In situ* observation of cracking and debonding of SEI

characteristics (Figure 6). However, nanoindentation is a cantileverless technique, which uses electrostatic actuation as a force control to move the probe. Instead of a LASER and mirror sensing of displacement, a three-plate capacitive displacement sensor is used.

By monitoring the load and displacement when pressing the tip of the probe into a surface and then subsequently withdrawing it, a load-displacement curve is generated. This curve can then be used to calculate the hardness, elastic modulus and various viscoelastic properties of the material under study.

The tip of the probe is usually made of diamond and, crucially, has a specific geometry. This geometry must be known, so that the area of the tip in contact with the sample can be calculated from the depth of penetration. Nanoindentation is a highly versatile technique and many variations exist to measure different mechanical properties. The main difference between these variations is in the way load is applied.

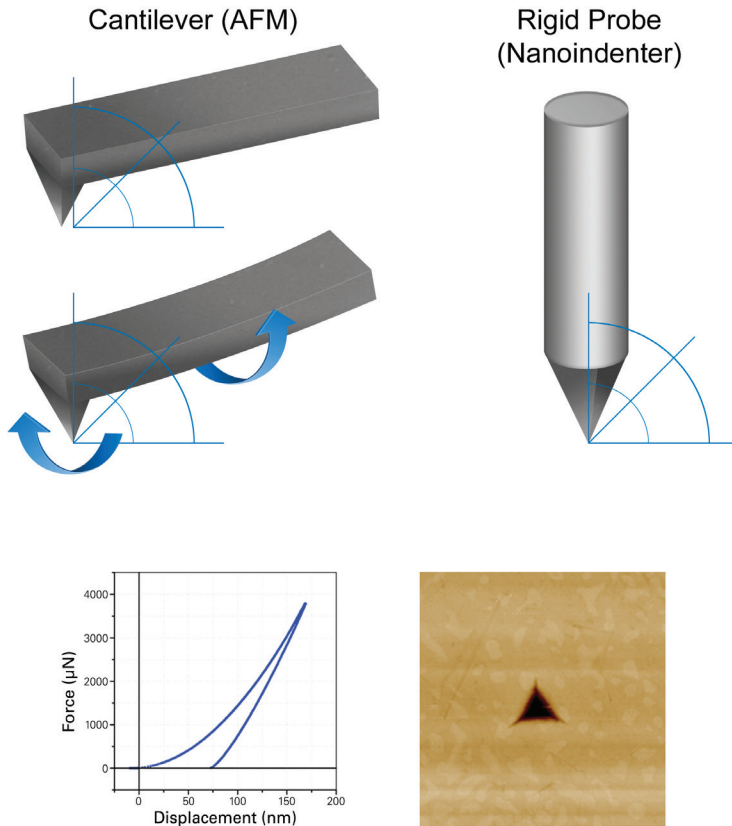


Figure 6. How nanoindentation works

The most basic form of nanoindentation is quasi-static nanoindentation. This uses a single load–hold–unload cycle and can be used to calculate stiffness and hardness measures based on the unloading portion of the load-displacement curve. The rate at which the load is applied (strain rate) can also be controlled in a technique called constant strain rate nanoindentation, which allows the strain-rate-dependent hardness of materials to be investigated.

For viscoelastic and plastic properties, there are several additional nanoindentation techniques. Creep nanoindentation measures the increase in displacement at a fixed load, while its close relation stress-relaxation nanoindentation measures the applied load needed to maintain a fixed displacement. Dynamic nanoindentation (nanoscale Dynamic Mechanical Analysis, or nanoDMA) superimposes an oscillatory force over a quasi-static loading profile, providing data on the viscous mechanical properties of a sample.

All of these techniques can be used on different components of Li-ion batteries, and provide mechanical and topological information about the surface (Figure 7). Many commercially available nanoindentation systems are specifically designed for *in situ* and *in operando* investigations, and are sealed in highly controlled inert atmospheres (oxygen and water both react energetically with many battery components).

To provide insights into changes in battery properties during charge/discharge cycles, *in situ* measurements must be made quickly to capture reaction dynamics. A recent advance that allows nanoindentation to achieve this is accelerated property mapping, in which a grid of quasi-static measurements are taken over a short time frame (400 individual indents in approximately 67 seconds). With this technique, variations in the mechanical properties of battery components over large areas can be mapped. For example, the homogeneity of SEI deposition can be monitored in real-time during charge/discharge cycles.

Nanoindentation can also be used to investigate the mechanical properties of separators. This is important, as small defects introduced during manufacture can affect the

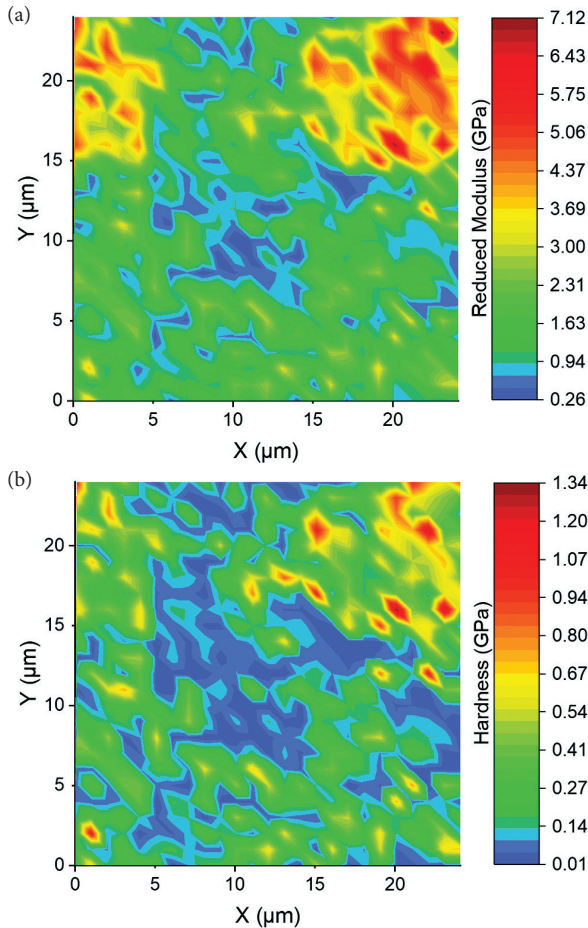


Figure 7. (a) Modulus and (b) hardness map showing variation in a lithium film deposited on the copper working electrode

resistance of the separator to fracture. Mapping the mechanical properties of the separator using nanoindentation can be useful for assessing whether any defects are present, and, if so, to then test the resistance to fracture. As the separator plays a crucial role in preventing short circuits, such testing is crucial for improving the safety of Li-ion batteries.

Other characterization techniques

As well as force-based techniques, optical, electron and X-ray based techniques are widely used in battery research. SEM and TEM use the interaction of electrons with a sample to image battery component surfaces at nanometer-scale resolution. When used *in situ*, these high-resolution techniques can show how the crystal or pore structure of the electrodes change with charge/discharge cycling. These techniques can also be used to determine mechanical performance of individual particles.

In situ SEM and TEM are, however, low throughput techniques, and involve complex beam-sample interactions that can complicate interpretation of the actual device performance.

X-ray based techniques, such as X-ray microscopy, provide information by analyzing the interactions of X-rays with samples. Numerous variations are available, depending on what aspect of the interaction is being monitored (*ie* absorption, diffraction, transition or scattering). X-ray based techniques provide slightly lower resolution than TEM or SEM, but have the advantages of not requiring vacuum conditions, being non-destructive and achieving high penetration depths. In addition, X-ray absorption properties can be used in XPS to provide chemical information about the sample. Increasingly, these techniques are being used to map changes in the chemical composition of the electrode and SEI.

Fourier-based infrared (FT-IR) and Raman spectroscopy are optical techniques that use, respectively, infrared electromagnetic radiation and the absorption/emission of scattered light to determine the chemical composition of a sample.

These techniques are particularly useful for battery research as they do not require vacuum conditions and are thus more easily adapted for *in situ* use. Raman and FT-IR have been used to identify changes in the chemical composition of electrolytes and the SEI, and to determine the composition of the products of parasitic reactions at the SEI, including identifying gaseous products.

There are also a number of optical profiling technologies for mapping surface topography. These use optical objectives with a fixed focal distance and a very shallow depth of field to take multiple images as the objectives are scanned across a sample surface. By knowing the point in the scan where each image is taken, the distance between the objective and the surface at each point can be determined, allowing the construction of a detailed representation of surface topography. As a non-contact technique, optical profilers are particularly useful for studying fragile surfaces, such as the separators in Li-ion batteries.

Finally, correlative techniques combine two or more of the analytical techniques discussed above. Combining multiple techniques to advance battery research is providing much needed holistic understanding of how electrical, structural and chemical properties are related, and how they influence the normal function, degradation or unsafe workings of Li-ion batteries.

CASE STUDY 1. Observing lithium dendrite growth in situ using electrochemical AFM

Lithium dendrite growth is one of the biggest problems affecting the safety of Li-ion batteries. But probing the initial stages of dendrite growth is difficult due to the reactive and fragile nature of lithium compounds, especially when studying growth at the SEI. A team of researchers from the USA and China has now found a way to overcome this problem by using in situ AFM.

'We applied in situ electrochemical atomic force microscopy (EC-AFM) to investigate lithium dendrite growth on the graphite anode,' explains team leader Cai Shen from the Ningbo Institute of Materials Technology and Engineering in China. The team used PeakForce tapping mode to probe the anode surface.

'Using PeakForce tapping, we can trace the morphological evolution of the electrode surface under potential control at even lower forces than conventional tapping mode, which protects the delicate surface of the electrode,' says Shen.

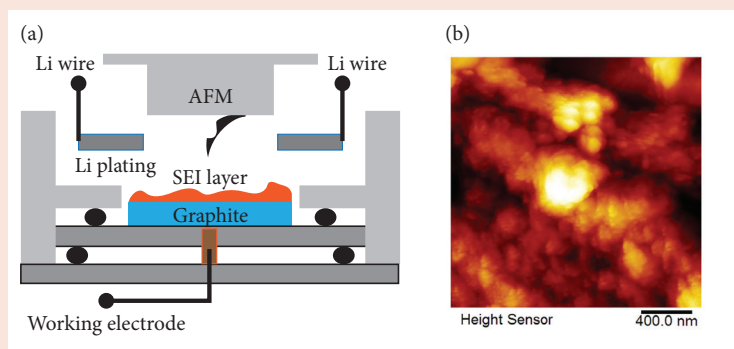
For this work, the team first deposited an SEI layer on graphite and then studied dendrite growth behavior by cycling with ethylene carbonate-based and fluoroethylene carbonate-based electrolytes. These experiments showed that lithium is only deposited on the graphite anode when cycled in an ethylene carbonate-based electrolyte.

'We found that lithium dendrites did not form on the surface of the graphite electrode when it was cycled in fluoroethylene carbonate electrolyte,' says Shen. This could be attributed to the fluorine in the fluoroethylene carbonate electrolyte, which

promotes the formation of a thick and compact lithium fluoride (LiF)-rich SEI film.

The researchers also used PeakForce quantitative nanoscale mapping (QNM) AFM, which can simultaneously map nano-mechanical properties and image topography, to quantify the mechanical strength of LiF. They showed that LiF is stiff enough to form a stable and robust SEI layer capable of suppressing lithium dendrite growth.

Importantly, these experiments were conducted in a glove box, where oxygen and water are kept below 0.1 ppm and a commercial liquid electrolyte can be applied. This makes it likely that their results closely reflect the situation for Li-ion batteries under genuine working conditions.



(a) Schematic illustration of *in situ* EC-AFM experiment; (b) AFM image of highly oriented pyrolytic graphite electrode after lithium plating in an ethylene carbonate-based electrolyte

Shen C, Hu G, Cheong L-Z, *et al.* Direct observation of the growth of lithium dendrites on graphite anodes by operando EC-AFM. *Small Methods* 2017;2:1700298. (<https://doi.org/10.1002/smt.201700298>)

FUTURE FOR BATTERIES

Novel lithium-based battery technologies

The demand for batteries with higher energy density, quicker charge/discharge capability and longer lifetimes is continually driving research efforts. Some of the most promising lines of research involve alternative lithium-based battery technologies, including Li-air, Li-sulfur and solid-state batteries. Li-air and Li-sulfur both have higher theoretical energy densities than current Li-ion batteries, which use graphite anodes.

The Li-air (aka Li-oxygen) battery uses a lithium metal anode with an aqueous or non-aqueous electrolyte and a porous carbon cathode, which acts as a catalytic surface for production of lithium peroxide (Li_2O_2) in the non-aqueous case or lithium hydroxide (LiOH) in the aqueous case. The Li-S battery, meanwhile, uses a lithium metal anode and a lithium sulfide (Li_2S) cathode. The main advantage of these technologies is that Li_2S , Li_2O_2 and LiOH can all store far more lithium per unit mass than traditional transition metal oxide cathodes, thus increasing the energy density of the battery.

However, these technologies face many challenges before commercial products matching the current capabilities of Li-ion batteries can become available. One is the use of lithium metal anodes, which raises the familiar problem of lithium dendrite growth and the consequent safety concerns. In addition, there are many unknowns regarding the precise chemical intermediates that form in the batteries, how parasitic reactions cause capacitance fade, and degradation mechanisms at the electrodes.

Solid-state batteries replace the liquid electrolyte with a solid version made from a lithium ion-conducting material.

The advent of solid electrolytes with high ionic conductivities could well be the key turning point for battery technology.

It is thought that solid electrolytes may prevent the formation of lithium dendrites, and even if dendritic growth did cause a short circuit (as evidence of dendritic growth along grain boundaries in solid electrolytes has been observed), solid electrolytes are inflammable – unlike volatile liquid electrolytes. Solid-state batteries could therefore resolve the major safety issues surrounding the use of lithium metal anodes, and are probably required for the commercial development of Li-air or Li-S batteries.

Novel characterization techniques

Characterizing these novel battery technologies generally involves many of the same techniques used with conventional Li-ion batteries (Figure 8). For example, in Li-air non-aqueous batteries, the deposition of solid Li_2O_2 can block the pores on the carbon catalyst, preventing electron transport. Monitoring this formation with *in situ* AFM (in contact or tapping mode) has shown that specific electrolyte additives can dramatically reduce this electrode blockage by modifying the morphology of the Li_2O_2 crystals.

In developing solid-state batteries, several promising groups of solid materials with high lithium-ion conductivity have been identified, including garnet-type lithium-ion conductors, lithium superionic conductors and lithium aluminium titanium phosphate. However, scientists have found that lithium dendrites can still form within these materials, and there is increasing evidence that grain boundaries in the

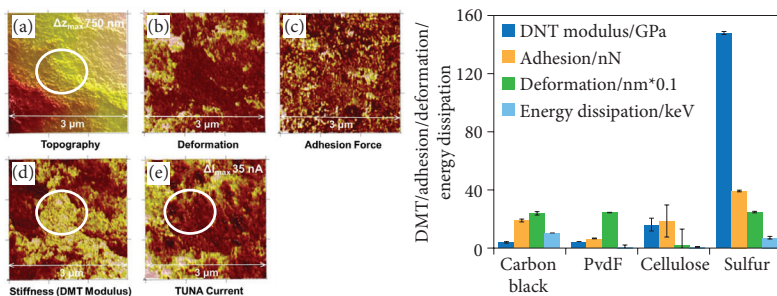


Figure 8. (Left) AFM images of a suspension-coated polyvinylidene fluoride sample before cycling. a) topography, b) deformation, c) adhesion, d) DMT modulus (stiffness), e) PeakForce-TUNA current. (Right) Statistical evaluation of mechanical properties of the basic materials used for preparing the cathodes. Figures from Hiesgen R, Sörgel S, Costa R, *et al.* AFM as an analysis tool for high-capacity sulfur cathodes for Li-S batteries. *Beilstein J Nanotechnol* 2013;4:611–24. © 2013 Hiesgen *et al*; licensee Beilstein-Institut. (<http://creativecommons.org/licenses/by/2.0>)

solid electrolyte are critical to this process. The precise mechanism is still poorly understood though, and many electrochemical, mechanical and structural factors require investigation before understanding – and ultimately control – of the process is possible.

No one single technique is sufficient to produce such an understanding, and so scientists are increasingly utilizing correlative techniques, where multiple types of measurements are made at once. SEM in combination with energy-dispersive X-ray spectroscopy and AFM, for instance, can map grain boundaries topologically, and provide chemical information and data on the local mobility of ions. AFM has also been combined with Raman spectroscopy to characterize lithium intercalation and degradation of the cathode, and to correlate these chemical properties with sample topography.

Bringing multiple techniques to bear on these research challenges will provide much needed understanding of the way in which electrical, structural and chemical properties

are related, and how they interact to dictate battery performance and degradation.

Future applications

There are many exciting applications for future lithium-based battery technologies. Smaller and more powerful Li-ion batteries will continue to drive the personal electronics market; beyond this, Li-ion batteries also have the potential to tackle sustainability issues, such as by powering electric vehicles.

Li-ion batteries are highly suitable for use in electric vehicles thanks to their high energy density, and, as part of continued efforts to tackle climate change and air pollution, the transportation industry is predicted to become a major market for Li-ion batteries. Although Li-ion batteries are already widely used in the current generation of electric vehicles, there remains much room for improvement. Future iterations will require even higher energy capacity, allowing electric cars to drive further on a single charge and utilize faster recharging (a typical electric car currently takes around four hours to charge).

Lithium nickel manganese cobalt oxide batteries are one of the most powerful types of Li-ion battery, and they currently dominate the electric vehicle market. But they could soon be overtaken by other battery types. Lithium iron phosphate (LiFePO_4) batteries, for example, have a much longer lifetime (over 10 years and 7000 charge cycles), while lithium vanadium oxide batteries have been shown to have double the energy density. Li-air batteries could also power cars, using a battery just a fraction of the size of conventional fuel tanks.

Looking even further ahead, Li-ion batteries could also be used for large-scale power supply – in renewable energy. The major stumbling block for renewable energy is the inability to store the huge amounts of energy produced by technologies such as solar and wind, for use at night and when the wind isn't blowing. This is where electrochemical energy storage has advantages over current solutions, such as pumped-storage hydroelectricity, due to its vast energy capacity and long lifespan.

There are ongoing research efforts to build a lithium-based battery with sufficient capacity to reliably store solar or wind energy over long periods of time. The US company Tesla recently built the world's largest Li-ion battery – the Hornsdale Power Reserve in Australia – connected to a nearby wind farm, and is so far successfully managing demand.

The fabrication costs of Li-ion batteries, and the continuing technical challenges with alternative lithium-based battery technologies, mean they are not yet suitable for such high-capacity energy storage applications. But the steady reduction in manufacturing costs, and the discovery of solutions to the technical challenges with the help of characterization techniques such as AFM and nanoindentation, will certainly facilitate the use of lithium-based batteries in off-grid renewable energy in the not-so-distant future.

CASE STUDY 2. Chemo-mechanical coupling assessed by time-dependent nanoindentation

Graphite is currently the gold standard for the anode material in Li-ion batteries. However, scientists are actively searching for replacement materials to increase capacity and prevent the growth of lithium dendrites.

One potential alternative material for the anode is germanium (Ge), a semiconductor similar to silicon. Ge has a high Li-ion diffusivity, and can therefore achieve very high charge/discharge rates and is mechanically robust. But the use of Ge is complicated by the large volume changes that take place during cycling. Alongside diffusion of Li ions, this large mechanical deformation can cause irreversible chemical and structural changes that reduce capacity.

Researchers from Georgia Institute of Technology and Northwestern University in the US recently collaborated to investigate the interaction between the electrical, chemical and mechanical processes that occur inside lithiated Ge. Their approach involved using nanoindentation to assess the stress-diffusion coupling behavior of lithiated Ge (ie the way the diffusion of Li ions changes the volume of the solid electrode). These volume changes can induce mechanical stress, further affecting the diffusion process. It is important to understand how ion diffusion and mechanical stress interact in order to design more powerful batteries.

The researchers created thin films of lithiated Ge, which they subjected to nanoindentation in an inert environment to study the creep deformation induced by indentation at a range

of load levels (2500 μ N to 4500 μ N). At the same time, they used a continuum chemo-mechanical model of the nanoindentation test to further probe the mechanisms responsible for the stress gradient-driven creep deformation. By comparing their simulation of the nanoindentation response with the real measurements, they were able to calculate a stress-diffusion coupling coefficient and the diffusivity of lithium in Ge.

This revealed that a high value for the stress-diffusion coupling coefficient, which suggests mechanical stress, has a significant effect on diffusion in lithiated Ge. The researchers also demonstrated that combining experimental nanoindentation with computational approaches can produce powerful insights into the chemo-mechanical coupling at play in Li-ion battery electrodes. This finding could prove useful for future tests of other potential anode materials, such as silicon and tin.

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