

Perspective

In situ, operando characterization of materials for electrochemical devicesGerald Gourdin^{1,*} and Vicky Doan-Nguyen^{1,*}

SUMMARY

For the development of advanced batteries, it is essential to correlate information obtained from the characterization of materials to properties critical to the battery's performance. *In situ/operando* characterization and cells specifically designed to conduct such analyses have proven to be the best means of accomplishing that objective. However, complimentary analytical techniques are required to obtain a comprehensive understanding of those changes, pointing to a need for devices that allow for multimodal, *in situ/operando* characterization of materials and interfaces. This perspective briefly examines the evolution of *in situ* and *operando* devices and highlights important considerations in designing such devices. From that discussion arises a clear opportunity regarding the evolution of these devices: magnify their usefulness through incorporating near-simultaneous, multimodal capabilities to advance the development of electrochemical energy storage materials.

INTRODUCTION

To determine the suitability of materials for advanced energy-storage technologies, it is essential to employ analytical techniques that characterize the structure of materials and the changes they undergo. That structural evolution can then be correlated with pertinent properties, such as internal impedance, chemical stability, voltage window, cycling rate, storage capacity, and cycle life. To aid that determination, an abundance of analytical techniques employed in the field of battery research provide invaluable information via both direct means, such as, characterization of the structure or surface of the material, and indirect means, such as impedance spectroscopy, differential electrochemical mass spectroscopy, or thermogravimetric analyses. Although the standalone results of these analyses track the physical and chemical changes that occur, it has only been through the application of *in situ/operando* analyses that has led to key insights relevant to the development of novel materials with enhanced properties.

There are key advantages to materials characterization using *in situ* analyses, including studying the development/progression of the solid electrolyte interphase (SEI) layer,^{1–3} determining failure mechanisms (Li filament formation, etc.),^{3,4} and elucidating the evolution and degradation of active materials and electrolytes.^{5–7} Recent reviews have ably covered these particular topics in depth: general battery^{3,8} and Li battery diagnostics^{9–11} as well as interfacial stability in solid-state batteries.¹² In general, interfacial and structural characterization are the targets of *in situ/operando* analyses and an in-depth understanding of how to correlate the collected information to the performance of the materials is the main goal.^{3,9}

Effective employment of *in situ* or *operando* modes has required cell designs that allow for the analysis to be conducted while the environment of the battery is

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maintained. This need has manifested in two approaches: (1) modification of existing cell geometries to accommodate *in situ* measurements, or (2) development of specialized cells that allow for either strictly *in situ* analyses of the materials or for characterization using a single *operando* technique. This Perspective will serve as a progress report, briefly examining the state of devices that have been developed for *in situ* and *operando* analyses and highlighting challenges to the next step in this technological evolution.

POST-MORTEM STUDIES

The simplest approach to analyzing battery materials is to perform an *ex situ* analysis, in which the material is removed from the testing environment for characterization of any changes that occurred using optical microscopy,¹³ infrared and Raman spectroscopies,^{14–16} electron microscopies,^{15,16} X-ray spectroscopies,^{15,16} and nuclear magnetic resonance spectroscopy (NMR).^{15–17} Although this approach continues to provide useful information, the temporal evolution of the region of interest is a missing crucial aspect. However, to evaluate the structural or chemical evolution using *ex situ* approaches requires the fabrication of multiple cells to study transformations during electrochemical measurements. Implicit is the assumption that the characterization of each sample at a specific time point represents the general evolution of the material along a timeline of continual changes.

However, *ex situ* analyses interrupt the material's evolution, possibly introducing interphases and phase transformations that may not form under operating conditions. Rather, analyses of a material or its interfaces conducted when the material is still within the testing environment (*in situ*) or is actively undergoing testing at the time of the analysis (*operando*), are the best means of correlating changes in a material's properties in a near real-time manner. The design and development of cells that allows for conducting analytical measurements under *in situ* or *operando* conditions has eliminated the need for post-*operando* correlation of electrochemical measurements and materials characterization.

CONSIDERATIONS FOR IN SITU/OPERANDO CELLS

Two key aspects that allow results from *in situ/operando* analyses to be effectively extrapolated to commercializable cells are sample conformation and cell geometry. Sample conformation may superficially be thought of as the minimum sample dimensions required to perform the desired analyses. However, considerations also include the spatial resolution of the analytical techniques, knowledge of the desired specific information and how it will be collected, and whether the sample size can be considered statistically representative. [Figure 1](#) depicts analytical techniques frequently used in materials analysis correlated by spatial resolution and the information generated.

Electrochemical cell geometry can be broadly classified into two configurations, as illustrated in [Figure 2](#): (1) a stack of the battery components with the analysis conducted from a position facing the surface of one of the electrodes ([Figure 2A](#)), or (2) by creating a cross-sectional view of the interfacial regions in the cell stack ([Figure 2B](#)). The caveat with the first configuration is that, if the interest is in the interface, then either the analytical technique must be capable of penetrating the electrode/current collector material or a hole is created in the material through which the analysis can be conducted. The second configuration affords opportunities to acquire more interesting information because *operando* characterization would be able to collect information from both the bulk and the interface regions. However, the

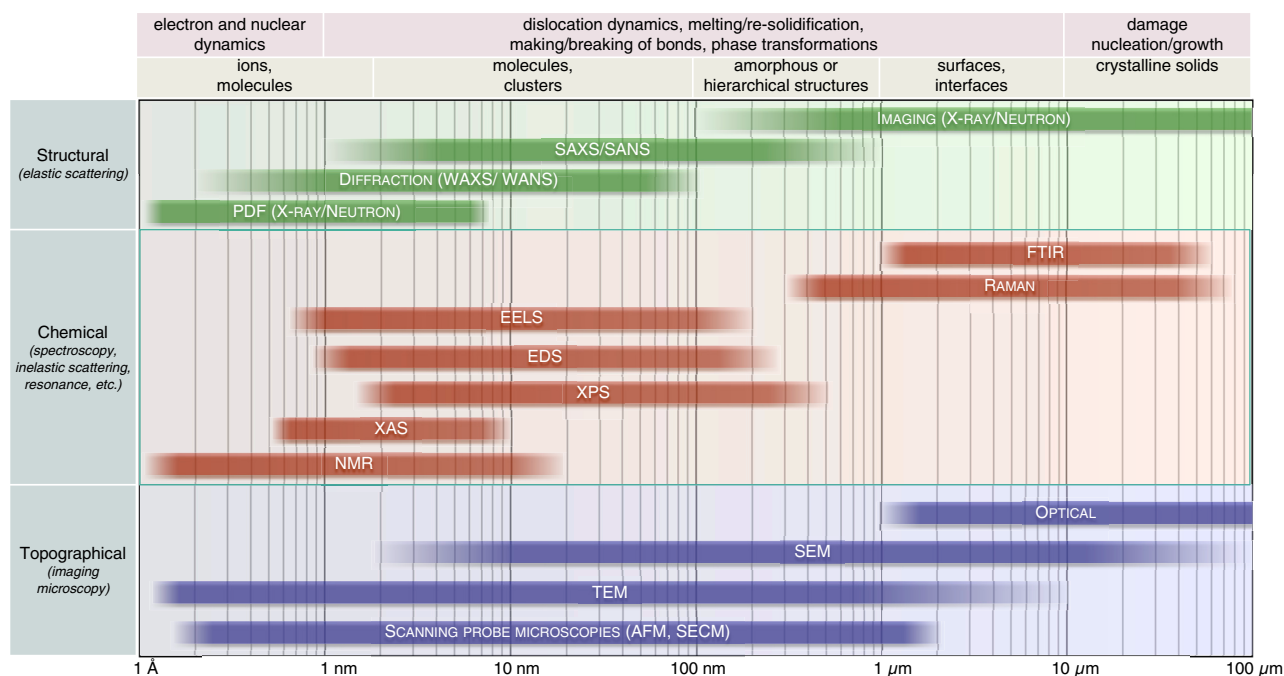


Figure 1. Spatial resolution of analytical techniques

Comparison of analytical techniques used in the characterization of materials correlated by length scales or spatial resolution, mode of analysis, and information obtained.

second method presumes that creating the cross-section is benign, which is not necessarily true because another interface is created.

Early approaches to *in situ/operando* analyses employed non-standard geometries, such as modified electrochemical beaker cells. These approaches provided useful insight into the processes involved with the formation and evolution of the passivating SEI layer.^{1,18,19} However, none could be considered a representative cell geometry, even though the materials do remain in the cell environment during analysis in those examples. A more-reliable approach to *in situ/operando* measurements that maintains a representative cell configuration has been to modify commercially available cell cases.^{5,20–24} Although the original cell geometry is maintained, modifications are more improvised which makes a comparison between reports more difficult. Regardless, significant progress has been made with specialized cells to not only take advantage of advancements in characterization techniques but also to adapt to their restrictions. It is the balancing of these competing aims that has engendered considerable evolution in the fabrication of novel cells.

This evolution in design can be illustrated with a few examples. As reported in 1978, a single transparent window limited X-ray analyses to reflection mode only,²⁵ whereas Argonne's multi-purpose *in situ* X-ray (AMPIX) cell (2012)²⁶ employs dual windows, allowing for analyses in either reflection or transmission mode. A tubular design²⁷ composed of an X-ray transparent material, allowed for combined synchrotron X-ray microcomputed tomography (μ CT)/X-ray diffraction (XRD) *in situ* analyses. Similarly, *in situ* Raman analyses have progressed to the analysis of a full cell with a Swagelok-type design.²⁸ Furthermore, other notable examples include pouch-type cells modified to incorporate different transparent windows suitable for either XRD

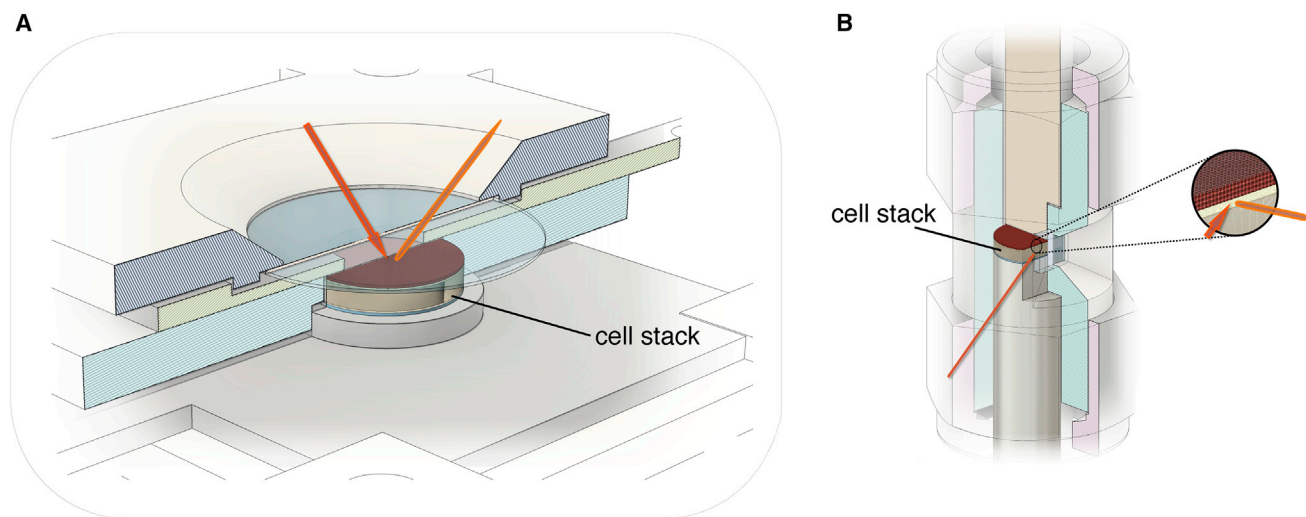


Figure 2. Representative cell geometries

Representations of two configurations employed in *in situ* characterization: (A) analysis of a surface or bulk region of a component in a cell stack, and (B) cross-sectional analysis of the interfacial region between two components within a cell stack.

or Raman spectroscopy studies.²² Lastly, the availability of neutron-transparent materials, such as Al, Ti–Zr alloy,^{29,30} or quartz³¹ has allowed neutron-based techniques to be successfully employed.

However, certain analytical techniques impose more restrictions on cell design. With infrared (IR) analyses, the penetration depth is only a few microns, which typically requires the material to be in direct contact.^{1,19} This approach was employed in the work by Rikka et al.³², who used a combination of *in situ* Fourier transform IR (FTIR) and electrochemical impedance spectroscopy (EIS) with *ex situ* transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses to confirm the structure and composition of the SEI layer. Similarly, scanning probe microscopy techniques require access to the surface of the material, so designs place counter electrodes well away from the region of interest to maximize the analysis area.^{33–35} Although *in situ* NMR has become widely used in studying battery materials, it is performed under static conditions which imposes experimental challenges for both detection and analysis. The approaches have been to either incorporate toroid probe heads into electrochemical cells, acting as a “battery imager” or to use static NMR probes, where the electrochemical cell is placed inside the coil of a static NMR probe. This latter approach results in greater sensitivity and flexibility.^{36,37}

Analyses that require high-vacuum conditions (XPS, scanning electron microscopy [SEM], and TEM, among others) pose the additional challenge for characterizing liquid-electrolyte-based cells: evaporation of the solvent components. One tactic has been to replace a portion of the electrolyte with low-vapor pressure solvents or to use solid electrolytes. This has been employed for both XPS^{38,39} and in an open *in situ* TEM cell designed to examine the lithiation of silicon nanomaterials.^{40,41} The other approach is to use an enclosed cell, as was done by Zeng et al.⁴² for use in TEM analysis. The entire battery stack was enclosed within a thin film of silicon nitride—an electron-transparent material—to visualize the electrode-electrolyte interface and to study the inhomogeneous lithiation of a gold electrode.

MULTIMODE OPERANDO CHARACTERIZATION

As discussed, different analytical techniques are needed to address the same questions regarding, for example, the development of the SEI layer, battery failure mechanisms, and degradation of battery materials. However, the advances that have arisen to accommodate the increased range of cell geometries has emphasized the need for a stronger correlation between electrochemical measurements and materials characterization. Initial attempts to accomplish this have been by separately monitoring the similar regions of interest using a combination of complementary *in situ* or *operando* techniques. Examples of this include neutron-depth profiling and SEM,⁴³ atomic force microscopy-scanning electrochemical microscopy (AFM-SECM) and Raman,³⁴ X-ray tomography and diffraction,²⁷ X-ray tomography and energy-dispersive diffraction,⁴⁴ and XRD and Raman spectroscopy.²² However, obtaining the desired information in this manner requires that the characterizations be conducted independently but under the same conditions. There is an implicit assumption that changes quantified during either analysis are universal and apply throughout the entire material under study. The employment of a *single* cell for multiple analyses provides the impetus for more innovation with *in situ/operando* characterization and is an opportunity that the research community has begun to address.

There are common challenges with combining multiple, disparate characterization techniques for *in situ/operando* characterization, two of which have already been discussed: optimal sample conformation and determining the appropriate cell geometry. However, if there is a conflict between the requirements for one technique that differs from those of the other technique, the considerations for those common challenges become much more demanding. For example, AFM/SECM requires an open cell to allow access to the region of interest (e.g., interfaces). An FTIR or Raman analysis would be useful for mapping compositional information across that same region. This combination of techniques would work well for all solid-state materials but would only work well for liquid-electrolyte-based cells if the exposed layer of the electrolyte is thin enough ($\approx 1 \mu\text{m}$) to not significantly interfere with the FTIR or Raman signal. There has to be sufficient confidence that the information that is obtained is both reliable and *translatable* to real-world operating conditions.

With respect to liquid-electrolyte-based cells, a closed-cell geometry is necessary for the analyses to still be considered statistically representative of a commercializable cell. Single-mode characterization is not a significant challenge for Raman, FTIR, X-ray, or neutron techniques because suitable transparent materials are readily available. However, because multimode analyses depend on balancing disparate requirements, the issue becomes determining a *compatible* transparent material that possesses sufficient transparency to be acceptable for multiple techniques. Specific to X-ray or neutron diffraction, a material that gives either a broad indistinct background or a limited number of well-defined peaks that can be clearly discerned or removed. Examples include silicon, which is suitable for IR spectroscopy, X-ray, and neutron scattering; diamond and sapphire for use in Raman and X-ray analyses; or silicon nitride for SEM/TEM and X-ray analyses.^{42,45} It should be noted that aluminum has a small neutron cross-section, and it is feasible to employ as the cell case material.^{29,30} However, if a single compatible material is not readily available, then it will be necessary to have multiple windows, in which the foremost consideration would be ensuring the *same* region of interest is accessible for both analytical techniques. Of course, one of the benefits of a closed-cell geometry is that the device can be designed to be *representative* of a commercializable cell.

Certain characterization techniques, such as XPS, SEM/TEM, or scanning probe microscopies (AFM, SECM, and others), interact with the surface of the sample and, therefore, require an open cell geometry. When mapping a surface to obtain topographical, structural, and/or chemical information is desired, combining AFM/SECM with IR/Raman spectroscopies, or X-ray diffraction is clearly feasible. Although low-vapor pressure or solid electrolytes sensitive to atmospheric conditions require the analysis to be conducted in an inert environment or under vacuum, the considerations are more complex for liquid-electrolyte-based cells. As noted above, the electrolyte layer has to be thin enough to minimally affect the collected signal, while allowing for losses from evaporation. One notable approach employed in single-mode analysis entailed creating a microscopic hole in a thin (<100 nm) metal current collector using a focused high-energy beam. Although the hole is small enough (<5 μm) to impede the loss of electrolyte through capillary forces, it is still sufficient to probe the electrode/electrolyte interface during cycling.^{46,47}

For characterization techniques that require high vacuum conditions (XPS, SEM, TEM, among others), low-vapor pressure or solid electrolytes are a necessity. A glovebox antechamber with high-vacuum capabilities to directly transfer the cell into the ultra-high vacuum (UHV) chamber may be required. Combinations with techniques that allow correlation to chemical (FTIR or Raman) or reactivity (SECM) information would provide valuable information and are technically feasible, but it would require adapting current instrument designs to accommodate the other analytical method. However, FTIR and Raman non-contact, fiber optic probes have been extensively used in the field of conservation,^{48,49} so one can foresee how those devices could open up new possibilities for *in situ/operando* cells, including the collection of that information under high-vacuum conditions.

In addition, an effective integration of complementary techniques in a multimode *operando* cell has to contend with resolving disparities in their temporal and spatial resolutions. For some techniques, the mechanism by which it generates information is temporally independent, in the sense that the time required for the probe to interact with the material is nearly instantaneous. Examples of this include elastic scattering (X-ray and neutron), imaging (X-ray, neutron, and NMR), contact AFM, for example. For other techniques, a physical process has to take place, such as absorption, inelastic scattering, electron ejection, among other, which requires a transfer of energy as the means by which information is generated. It is this other physical process that will set the absolute minimum time required (i.e., temporal resolution) for techniques such as FTIR, UV, Raman, XPS, energy-dispersive spectroscopy (EDS). If a process of interest within a system occurs at a faster timescale than that physical process, then the associated analytical technique may not be capable of generating the desired information. In all cases, however, it is the acquisition time for the analytical technique, in other words, the minimum time required to obtain *useful* information, which will set the practical limit on the temporal resolution. Much of that will depend on the system under study.

Using the same example as above, scanning probe microscopy techniques (AFM and SECM) have demonstrated spatial and temporal resolutions that are on the order of nanometers and milliseconds, which far exceeds those for FTIR or Raman (microns and seconds).^{34,35,50} It has to be accepted that the compositional information obtained from spectroscopic analyses can only be broadly correlated with the more-detailed topographical information obtained from a scanning probe analysis. Because different analytical methods operate at different spatial and temporal resolutions, interpretation and integration of the results obtained from those

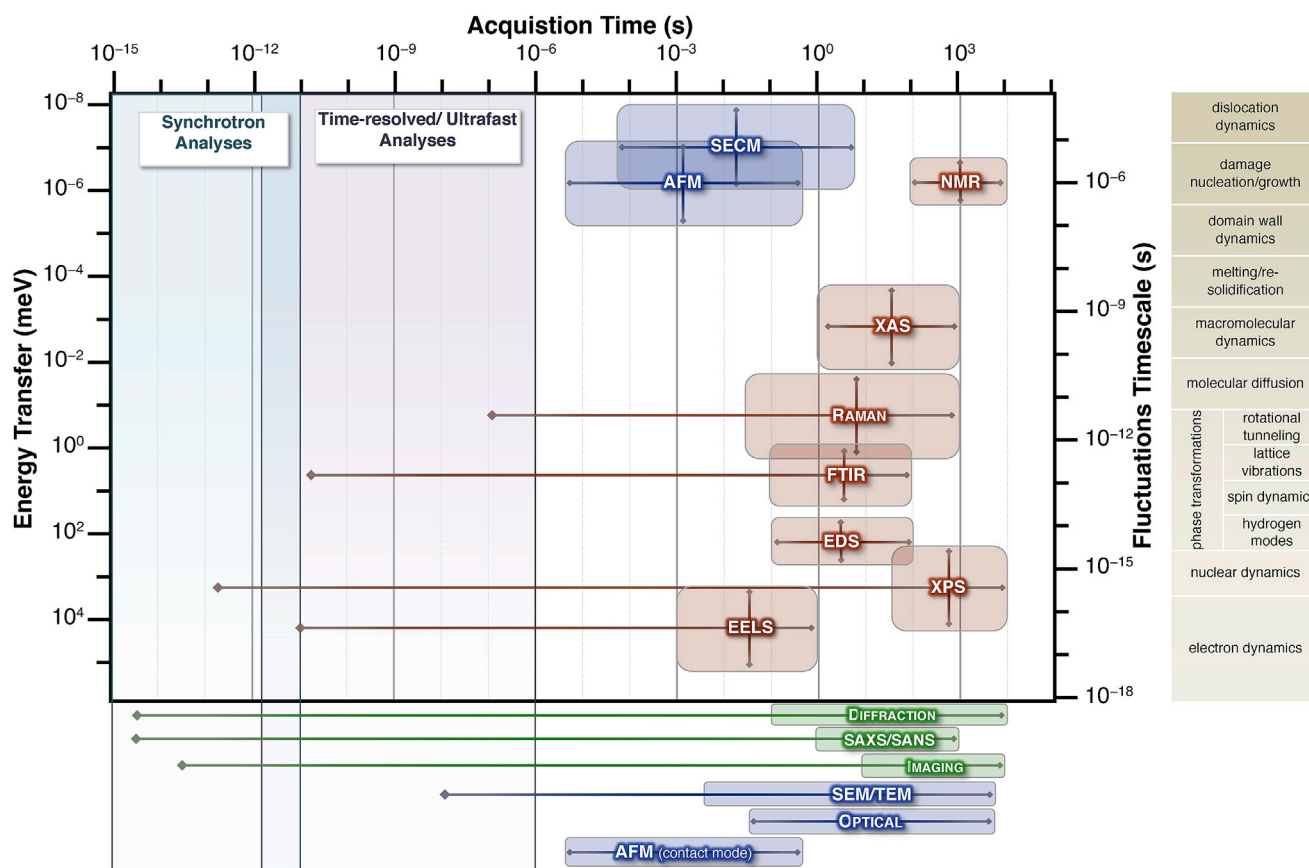


Figure 3. Temporal resolutions of analytical techniques

Comparison of analytical techniques used in the characterization of materials correlated by the mechanism timescale and typical acquisition time. Analytical techniques that have been adapted to ultrafast/time-resolved methodologies and synchrotron are noted by an extension of their temporal ranges into those timescales.

techniques is a critical challenge. The researcher needs to understand the length and timescales of the phenomenon of interest and then determine an appropriate, but *feasible*, combination of techniques to employ. Figure 3 depicts analytical techniques frequently used in materials characterization correlated by the timescale of fluctuations (i.e., temporal resolution) and acquisition time.

There are distinct advantages to explicitly designed electrochemical cells that accommodate different analytical modes simultaneously. Furthermore, there are numerous analytical techniques that provide complementary information, which would make them ideal for incorporating into multimode testing cells, if the corresponding challenges can be addressed. This would thereby allow for the collection of information that is either at different length scales, or both physical (structural and topographical) and chemical in nature, or obtained from both superficial and bulk penetration depths. Examples of these include AFM-SECM combined with Raman or FTIR,^{9,34} which would collect physical and chemical information; XRD and Raman,^{9,22} that provides complementary information at different length scales; X-ray and neutron diffraction, which probes bulk structural properties,⁹ and X-ray diffraction and tomography, which provide structural and imaging information.⁵¹ Analytical techniques that require either a completely enclosed environment (e.g., NMR) or high-vacuum conditions (XPS, SEM, and TEM) pose more-significant

Table 1. Selected complementary techniques

Technique 1	Technique 2	Challenges
XRD	Raman	Compatible transparent materials, temporal disparities (mechanistic)
XRD	FTIR	Compatible transparent materials, temporal disparities (mechanistic)
XRD	Neutron Diffraction	Cell materials, separate windows
AFM	XRD	Open cell, inert atmosphere, temporal disparities (acquisition)
AFM (SECM)	FTIR	Open cell, inert atmosphere, spatial and temporal disparities (acquisition)
AFM (SECM)	Raman	Open cell, inert atmosphere, spatial and temporal disparities (acquisition)
XPS	Raman	Instrument modification, transfer, spatial disparities
NMR	Raman	Instrument modification, transfer
SEM/TEM	FTIR	Instrument modification, transfer, spatial disparities
XRD	XTM	Spatial and temporal disparities (acquisition)

challenges. A selected list of complementary analytical techniques that have the potential to be incorporated into multimode cells, along with the associated challenges as discussed above, is provided in [Table 1](#).

Because the combination of disparate techniques will always impose certain restrictions on their capabilities, what is necessary for a successful implementation is a *determination* of what might be specifically limited and how to *minimize* that effect.

SYNCHROTRON RADIATION ANALYSES

As discussed above, focusing on the time required to *generate* information via a technique's fundamental mechanism is distracting, given the limitations of a technique's acquisition time. From the perspective of a realistic laboratory setting, the practical temporal resolution will be determined by both the response time of the detector and the speed of the digitizer (i.e., the acquisition time). Fortunately, the development and successful implementation of pump-probe methods to certain analytical techniques, such as Raman, IR, electron-energy-loss spectroscopy (EELS), and SEM, has allowed for "femtosecond" and time-resolved analyses to offer a 10-fold or greater decrease in the acquisition time. The basics of the pump-probe method consist of the sample being brought into an excited state, either directly or indirectly, via an ultra-short laser pulse (the "pump"), followed by a second light source (the "probe") to measure the response as a function of wavelength and time. Ultra-short laser pulses, by nature, have a broad-band optical spectrum, which have been employed as the pump in the Raman spectroscopy derivative or as the probe in the IR spectroscopy version.

However, it is synchrotron radiation and the associated techniques that developed around it that alleviates the tradeoff between acquisition time and a technique's mechanistic temporal resolution. Synchrotron light sources enable rapid acquisition of data at greater resolution than what is typically accessible in laboratory settings because the high-flux beams are integrated with systems that can apply the energy in very short bursts as well as *process* the generated information over very short timescales. In essence, allowing for faster acquisition times for a particular analysis. Electrochemical cells, such as the AMPIX cell, have enabled *operando* characterization for small-angle X-ray scattering (SAXS), total X-ray scattering, and X-ray absorption spectroscopy (XAS). Although these techniques have been carried out sequentially, there is potential for simultaneous dual acquisition of data. Although SAXS and total X-ray scattering require strategic placement of detectors to access a wider q range, both techniques can use the same set of cell windows. Combinations with XAS and total X-ray scattering could use the same set of cell windows, but the temporal mismatch between XAS (minutes) and X-ray scattering (potentially <1 minute) would limit the frequency of data acquisition. For combination measurements with

X-ray transmission microscopy,⁵² such as X-ray scattering,⁵³ the cell geometry can be modified to accommodate the required rotation of the cell during measurement.

X-ray free-electron lasers (XFEL) offer measurement capabilities at ultrafast timescales capable of detecting electronic motion. As such, XFELs such as the linac coherent light source (LCLS) can enable acquisition of X-ray scattering with pulses at the subfemtosecond timescale to probe surface chemical reactions at femtosecond timescales.⁵⁴ These capabilities can answer open questions regarding dynamic electrode/electrolyte interfacial reconstruction. To implement Li metal in Li-ion batteries, solid electrolytes, such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, have been investigated for their chemical stability against Li metal. Both metal/solid electrolyte and electrode/liquid electrolyte interfaces undergo significant structural reconstructions during charge transfer. In addition, self-healing polymers have been used at interfaces to arrest thermal runaway. For studying those processes, the intensity of the XFEL beam, which could be approximately 10^6 J cm^{-2} , can be cleverly used to induce interfacial reconstruction. With rapid detectors, structural evolution can be detected nearly simultaneously.

EXAMPLE COMBINATIONS

Disparate techniques that have been previously used to provide working examples of complementary techniques that could be incorporated into a multimode electrochemical cell. The use of an *in situ* electrochemical cell to perform AFM-SECM and Raman analyses to map interfaces in a Li-sulfur battery by Mahankali et al.³⁴ provides an example of simultaneous analyses. By necessity, the cell designed for SECM measurements was an open cell, which allowed for simultaneous *in situ* Raman measurements to be conducted. Another illustrative example of an advantageous design by Vanpeene et al.²⁷ involved the use of XRD and tomography to study lithiation of a silicon/graphene nanoplatelets electrode. The tubular design employed was constructed of an X-ray-transparent material, in which the detector for each mode could be moved into position to collect the relevant information.

In the case study of combining scattering and spectroscopy, XRD and Raman spectroscopy are frequently used to evaluate the structural evolution of battery materials.^{3,8,9,12,16,55,56} Multi-mode, *operando* analyses in which both chemical and structural information are obtained near-simultaneously would be of significant research interest. Shown in Figure 4 is an illustration of an *operando* cell design that could accommodate simultaneous XRD and Raman spectroscopic characterization. It should be expected that combining multiple complementary, but disparate, techniques will come with some compromises. In this particular example, the need for a material that is transparent to both X-rays and visible/near IR (NIR) light will impose limitations on the capabilities of both techniques because one single material will not be ideal for both.

FINAL WORDS

The real-time analysis of the interfaces and bulk properties of battery materials provided by *in situ* and *operando* cells has allowed for the unprecedented direct monitoring of the physical and chemical changes that materials undergo during the operation of an electrochemical device.^{3,6,9–12,33,55–60} Given the breadth of progress that has been made in the development of *in situ* and *operando* cells, it is clear that the research community values the insights that these approaches has afforded them. Furthermore, there are numerous instances in which complementary techniques have been separately employed to provide an in-depth understanding of those physical and chemical changes. Although specific challenges within the field of energy research are currently being

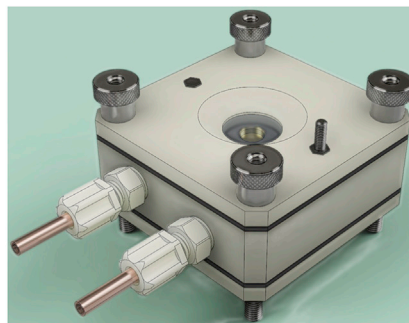
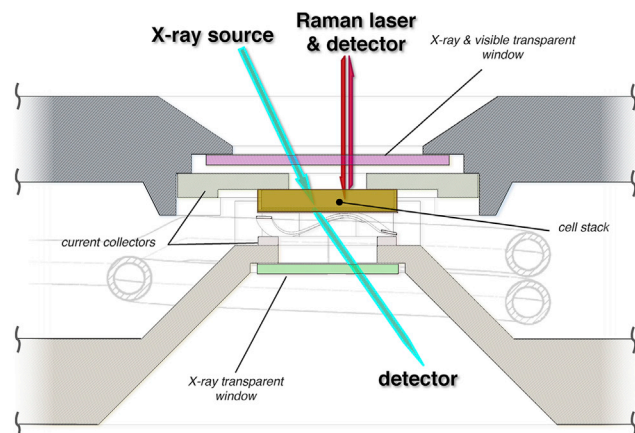


Figure 4. Operando cell design

A mockup of a cell design that illustrates the considerations necessary for conducting simultaneous XRD/Raman analyses under *operando* conditions.

addressed through the use of *in situ* and *operando* characterization, near-simultaneous analyses under the same conditions are desired.

Given that necessity, there is a need for continued development of testing cells that allow for multi-mode, *in situ/operando* characterization of materials and interfaces. Table 1 provides a matched list of selected characterization techniques that provide complementary information and have the potential to be conducted in a multimodal manner. The tasks and challenges that await are multiple:

- (1) The continued evolution of existing *in situ/operando* cell designs that lends themselves to multimodal applications
- (2) The development of new cells that can bridge those disparate, but complementary, characterization techniques
- (3) Opportunities presented by femtosecond techniques that bridge the time-scale gap between laboratory-scale and synchrotron facilities should be exploited
- (4) Researchers should address any complications from discrepancies that arise when analyses are performed under conditions required to perform the analyses, but which may not be representative of the physical/chemical environment of a commercializable cell
- (5) Questions should be noted and addressed when low-vapor pressure or solid electrolytes are employed in an analysis to meet high-vacuum requirements and the results from which are then extrapolated to liquid electrolyte-based systems

The information that would be obtained from these combined techniques could then be correlated with the electrochemical measurements (e.g., EIS) of the battery as it undergoes testing. When multiple datasets are linked to the measured electrochemical data, a more complete picture of the evolution of the battery materials can be obtained, allowing for a clearer path in the development of novel materials.

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AUTHOR CONTRIBUTIONS

G.G. and V.D.-N. contributed equally to the conception, writing, and revision of this perspective.

DECLARATIONS OF INTERESTS

The authors declare no competing interests.

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