

Multimodal and *In-Situ* Chemical Imaging of Critical Surfaces and Interfaces in Li Batteries

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Abstract: This article describes ways that a range of microscopy, spectroscopy, and spectrometry tools are being used to address important challenges associated with energy storage science and technology, in particular the development of advanced batteries for transportation, consumer use, and renewable storage. In this article *in-situ* transmission electron microscopy, *in-situ* secondary ion mass spectrometry, and x-ray photoelectron spectrometry (XPS) have been used to examine the formation and properties of the solid-electrolyte interphase (SEI) layer. Also transmission electron microscopy (TEM), atom probe tomography (APT), and high spatial resolution SIMS (nanoSIMS) have been used to optimize the structure and processing of a lithium transition metal oxide cathode.

Introduction

The development of longer-lasting, higher-capacity, lighter-weight, and/or lower-cost batteries relevant to consumer electronics, electric transportation, and sustainable energy storage presents a variety of scientific and technological challenges [1–2]. Many of these challenges concern the performance and stability of electrodes, the electrolyte that connects them, and the solid-electrolyte interphase (SEI) layer that forms between them [3–5]. Enhancement of the properties of current-generation Li-ion batteries and developing next-generation batteries (beyond lithium) is the subject of considerable private and public research.

An increasing variety of analytical tools is used to address the complex issues associated with electrode design, performance, and aging. These tools facilitate research focused on understanding the formation and operating properties of the SEI layer. Significant advances are being achieved through the use of tools that can examine batteries during operation (*in situ* or *operando*), although there remain roles for conventional and *ex-situ* methods that can provide complementary information not yet available using

in-situ methods. Because of the environmental sensitivity of battery material, both *in-situ* and *ex-situ* analysis methods benefit from specialized probes and sample handling adapted to controlled environments.

In this article we focus attention on two related but distinct battery issues that demonstrate how a range of tools, *in-situ* and *ex-situ*, are used in battery research. The first issue (A) concerns SEI layers: how they form, their properties, and how they change as a function of time or charge/discharge cycles. The work we describe involves analysis of Li-ion and Li-air batteries. The second topic (B) focuses on the development and optimization of lithium-transition-metal-oxide-based cathode materials.

Materials and Methods

Analytical tools are continuously improving in sensitivity as well as spatial and temporal resolution, and they are being extended to operation in increasingly relevant environments (*in-situ* and *operando* studies) [6–8]. However, it is increasingly recognized that a single analytical tool, even if highly versatile, can provide only limited information. Most often full understanding of a material's behavior requires complementary information captured with multiple types of instrumentation, sometimes with significantly different spatial and temporal resolution. Consequently, the significant challenge for the scientific community is to find ways to apply multiple types of instrumentation to analyze a specific site or region of the sample without damage to the desired information. The techniques used in this article are *in-situ* and *ex-situ* scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), x-ray photoelectron spectrometry (XPS), *in-situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS), atom probe tomography (APT), and high spatial resolution SIMS (NanoSIMS). The latter three techniques can provide isotope distributions and trace element detection in addition to element identification and quantification.

Results

(A) Structure and Chemical Composition of the Solid-Electrolyte Interphase (SEI).

***In-situ* TEM study of SEI layer formed on Pt in model Li-ion battery** The electrodes of alkali batteries of various types (Li-ion, Li-air, Li-S, Na-ion, and Mg-ion) undergo a variety of structural changes during charge and discharge cycles. The phases that form in the SEI layer may capture working ions as well as form dead layers or diffusion barriers, all of which can inhibit cycling and degrade battery performance. A wide variety of electrode designs have been

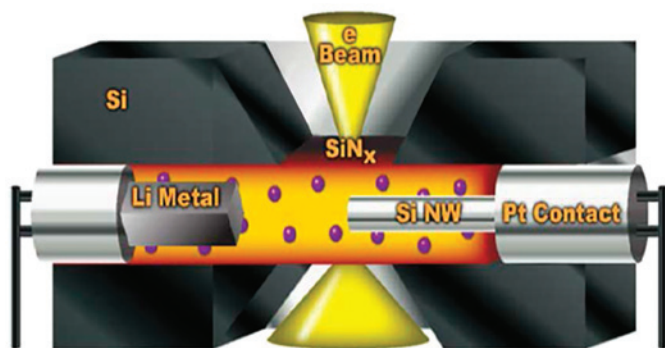


Figure 1: Schematic drawing illustrating the fundamental concept of a closed-cell *in-situ* STEM probe for the study of Li-ion batteries. Reproduced with permission from [11]. Copyright 2013, American Chemical Society.

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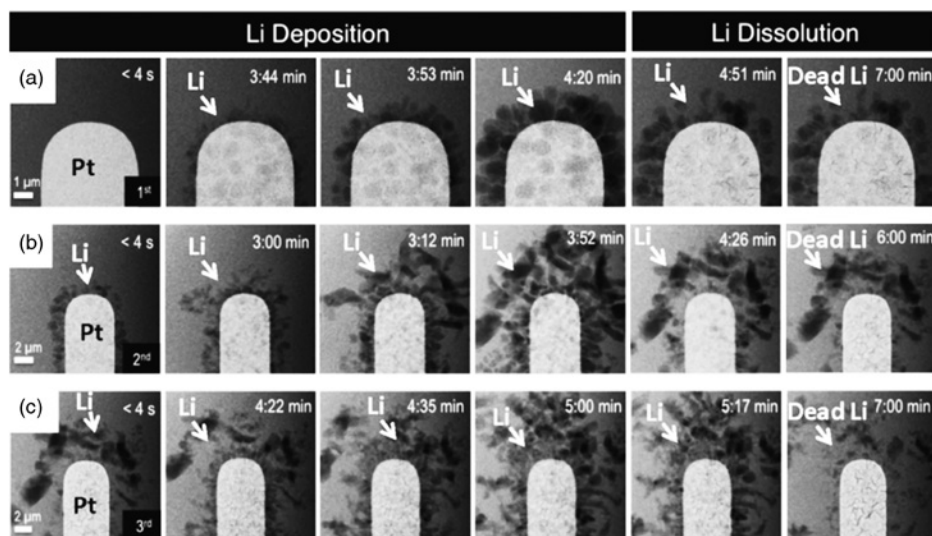


Figure 2: High-angle annular dark-field (HAADF) images of Li deposition and dissolution at the Pt working electrode using LiPF₆/PC electrolyte during the (a) first, (b) second, and (c) third charge/discharge cycles of the *operando* cell. The formation of the “dead Li” on the electrode can be seen in the images at the end of the Li dissolution cycle (the far right column of images), thereby demonstrating the degree of irreversibility associated with the battery cycling. Reproduced with permission from [12]. Copyright 2015, American Chemical Society.

conceptualized and synthesized in the effort to minimize both electrode changes and growth of deleterious SEI layers. *In-situ* probes, that are in essence model batteries, provide a way to actually observe how the material behaves during charge and discharge cycles. *In-situ* tools based on TEMs and SEMs employing open cells [9, 10] or closed cells [7, 11] have developed rapidly in the last five years. Figure 1 shows a schematic drawing to illustrate the general concept of the closed cell *in-situ* TEM “battery,” enabling the observation of electrode evolution in a model battery with realistic liquid electrolytes [11]. As an example, this *in-situ* TEM cell was used to observe lithium dendrite growth in STEM mode. The deposition of Li on a Pt electrode in LiPF₆/PC electrolyte is shown in Figure 2 [12].

With reversal of the voltage, the Li gets stripped off. Figure 2 provides direct morphological information of the deposited lithium related species and simultaneously reveals that the deposition and stripping off of the Li is not fully reversible. The non-reversibility of the Li deposition provides important information regarding the loss of accessible Li during battery operation. Although highly informative, a significant limitation of *in-situ* TEM/STEM measurements is the difficulty of obtaining chemical information of the deposited lithium-related species. When operating in a transmission liquid cell, the image and X-ray spectroscopic information obtained will inevitably include signals from the liquid electrolyte as well as the region of interest. Even electron energy loss spectroscopy (EELS) from *in-situ* liquid cells will yield a chemical composition that integrates multiple regions of the model battery. Deconvolution of the molecular structure in the SEI layer would be very difficult, if not impossible. Therefore, it is important to identify ways to obtain complementary information, especially about the molecular processes occurring at electrode surfaces.

***In-situ* SIMS of electrolyte-electrode interactions and SEI development.** During charge and discharge cycles of a battery, migration and reaction of mobile ionic species in the electrolyte cause structural and chemical modification of both electrode surfaces and the electrolyte. These chemical modifications are not well understood, and it is highly challenging to directly probe the liquid electrolyte-solid interface. A newly designed *in-situ* cell (Figure 3a) makes it possible to use SIMS to directly observe the structural evolution on the electrode and within the liquid electrolyte for a model lithium ion battery under dynamic operating conditions [13]. Similar to the *in-situ* TEM battery cell, the model battery used for SIMS measurements contains a thin

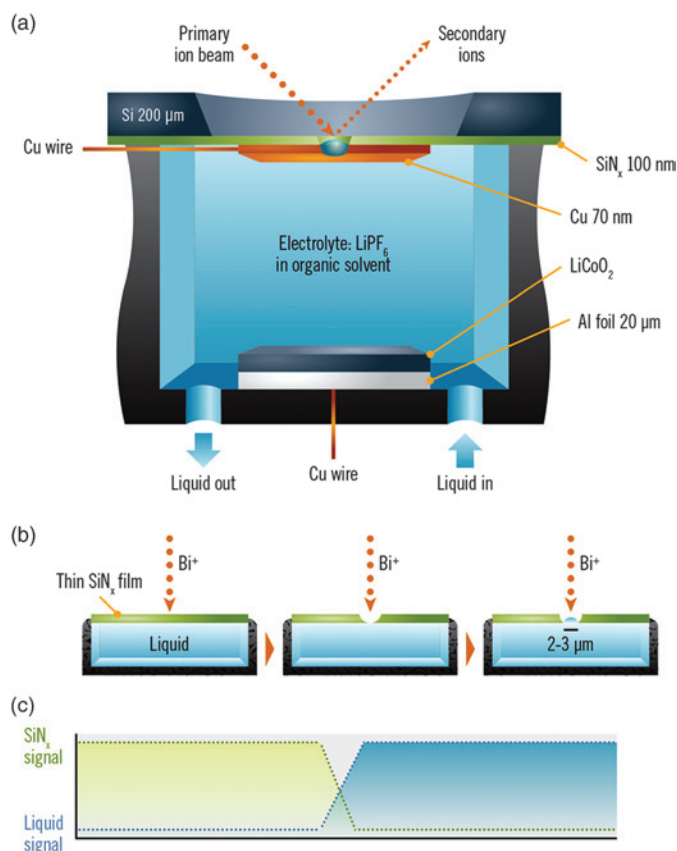


Figure 3: Conceptual drawing of a battery that can be examined in a SIMS system. (a) The assembled battery showing the thin SiN_x layer upon which a Cu anode is deposited. The LiCoO₂ layer is the cathode. (b) Schematic drawing showing the principle of *in-situ* liquid SIMS for which Bi⁺ ions were used as the primary ion for sputtering toward the solid-liquid interface. (c) SIMS signal as a functional of sputtering time (or depth) as the primary ion beam sputters through the thin SiN_x film. When the primary ion beam just sputters through the SiN_x film, the elemental, isotopic, and molecular information at the solid-liquid interface can be detected.

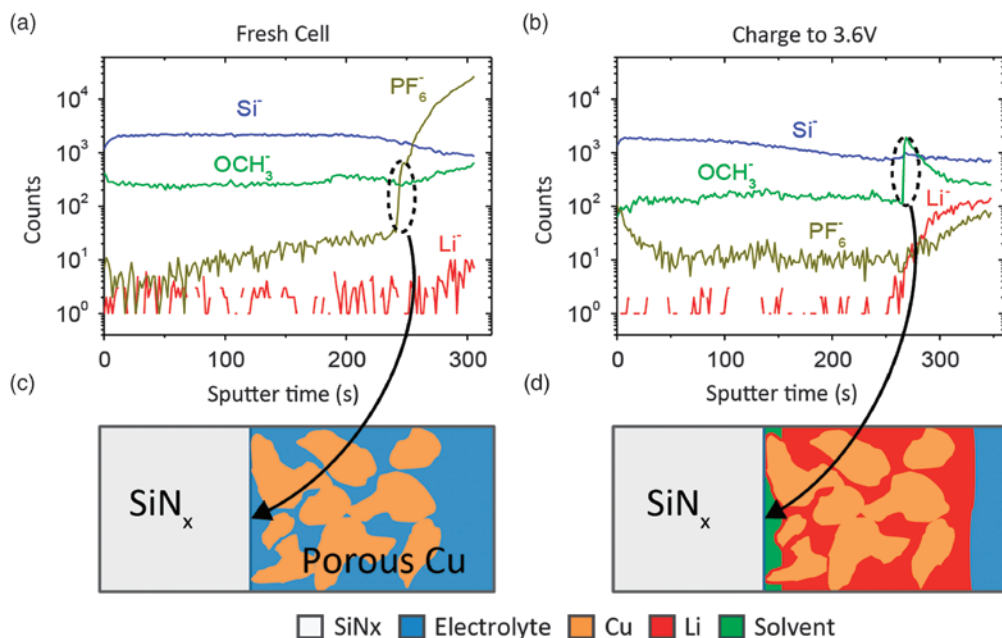


Figure 4: ToF-SIMS depth profiles of several representative negative ion species. (a) In a fresh cell, the PF_6^- signal dramatically increases after punching through the SiN_x film, indicating that electrolyte can diffuse to the SiN_x -Cu interface, which is supported by the SEM observation that the Cu film is porous. This situation is schematically illustrated in (c). (b) After charging, a jump of solvation signals (OCH_3^- as an example) appears at the SiN_x -Cu interface, but the PF_6^- signal greatly decreases, indicating a solvent layer depleted in LiPF_6 forms at the interface. Also, the Li^- signal significantly increases after charging, suggesting that metal Li forms after charging. This situation is schematically illustrated in (d).

SiN_x layer. In this case a copper layer is deposited onto the window to serve as the battery anode. In contrast to the thin window used for *in-situ* TEM, which needs to remain intact for the duration of the experiment, for SIMS an ion beam is used to create a $2\ \mu\text{m}$ hole large enough so that SIMS spectra can be collected, but small enough for capillary forces to minimize the loss of the electrolyte into the vacuum. Figure 3b shows the process of using an ion beam to create a hole in the SiN_x window to allow SIMS spectra to be collected

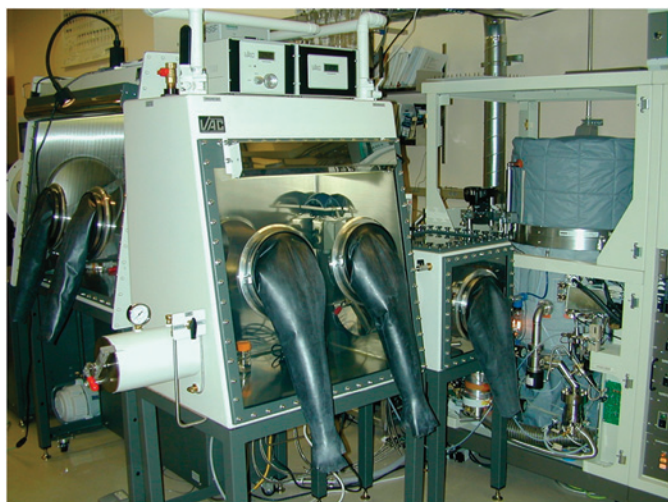


Figure 5: Glove box for anaerobic handling of battery components during and after disassembly in controlled environments in preparation for XPS measurements.

at the solid-liquid interface. For the data discussed below, the battery was held at the desired potentials, and a new examination hole was created by sputtering for each analysis at each potential.

The SIMS profiles of emitted negative ions obtained by sputtering through the SiN_x layer into the model battery are shown in Figure 4 for the as-assembled battery and when charged to 3.6 V. One key to understanding the profiles is to realize that there is an important difference between sputtering a solid and a liquid. Specifically, a liquid surface can be refreshed by diffusion to it, and some degree of evaporation of material takes place at the sputtered area. In contrast, during sputtering of a solid, material is removed and, in most circumstances, is not refreshed. The SIMS data for the fresh cell are consistent with the porous Cu electrode surrounded by

liquid electrolyte. Evidence for this includes the significant jump of the PF_6^- (m/z 145) peak when the SiN_x layer is penetrated. The presence of the liquid layer makes it impossible to sputter through the porous Cu electrode as evidenced by the Cu^+ depth profile (not shown in Figure 4) [13]. Upon charging, Li metal was found deposited on Cu electrode, and condensation of solvent molecules was observed around the electrode. Chemically, this layer of solvent condensate is depleted of both Li^+ and PF_6^- ions, forms an ionic insulating layer, and therefore contributes to the over-potential of the cell. Evidence for these effects include: the increase in the Li^- (peak at $m/z=7$) at the interface in comparison to the fresh battery, a significant drop of the PF_6^- ($m/z=145$) at the interface in comparison to the fresh battery, and the dramatic jump of the OCH_3^- ($m/z=31$) when the SiN_x layer is penetrated.

During charge and discharge cycles, insoluble Li salts gradually form and accumulate on the Cu electrode surface [13] (similar to the TEM observations above). The *in-situ* liquid SIMS measurements provide a new way to directly obtain molecular information at the electrode surface. This information complements that available by electron microscopy and has the potential to significantly impact other research work dealing with liquid-solid interfaces under dynamic operating conditions.

XPS study of SEI development as a function of charge. While there are efforts to mitigate the limitations of Li-ion batteries, there is also an aggressive search for other types of cost-effective and safe rechargeable batteries with higher-energy densities and

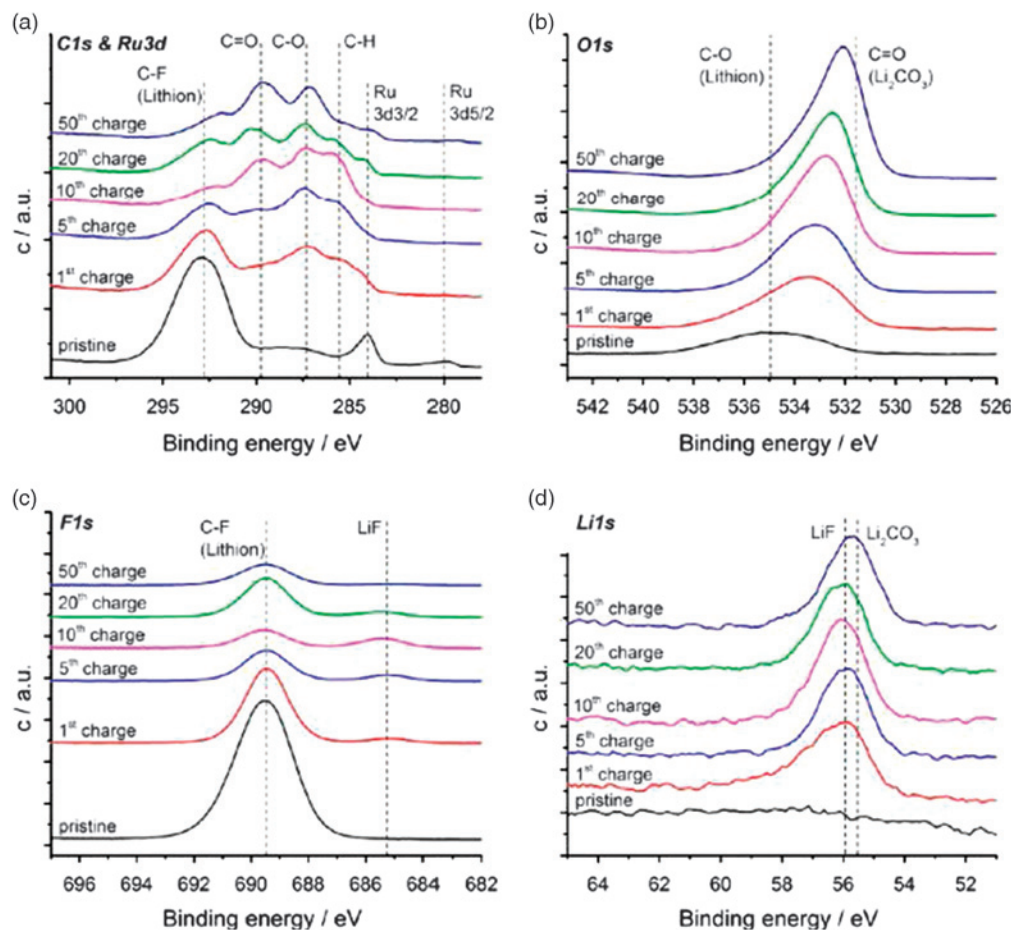


Figure 6: XPS results for pristine and charged CNTs/Ru electrodes scanned in (a) C 1s and Ru 3d, (b) O 1s, (c) F 1s, and (d) Li 1s regions. Changes in these spectra after charge and discharge cycles highlight the decomposition of the electrolyte and breakdown of CNTs. Reproduced with permission from [14]. Copyright 2014, American Chemical Society.

longer lifetimes. Among all sustainable rechargeable Li-batteries, Li-O₂ and Li-S batteries appear most promising with very high specific energy densities.

XPS is increasingly used to analyze the components and compositions of surface layers (0.1 nm to a few nm) on battery electrodes. In order to extract materials exposed to relevant conditions, battery cells were opened in a controlled atmosphere after being cycled to the desired potentials. A glovebox (Figure 5), or other controlled-atmosphere transfer system, is required to avoid or minimize oxidation and contamination of the exposed electrodes.

As one example, XPS has been used to analyze the changes in the chemistry of RuO₂-incorporated carbon nanotube (CNT) air electrodes after long-term operation of Li-O₂ batteries under full discharge/charge conditions in a glyme-based electrolyte (Figure 6) [14]. Spectra including the Ru 3d_{5/2}, C 1s, O 1s, F 1s, and Li 1s photoelectron peaks were examined as a function of charging cycles. The evolution of the spectra with the cycling of the battery as shown in Figure 6 clearly indicates the chemical evolution of the surface of the electrode, signifying the formation of side products generated from decomposition of the electrolyte, an increase in oxidized carbon (C=O-containing species), and the breakdown of the

CNTs. The surface sensitivity of XPS results provided important information about the nature of the interface and electrode changes during cycling that impact electrode stability and battery lifetime.

XPS measurements under controlled atmospheres as a function of time and at different potentials have been useful during battery development, testing, and failure analysis. However, even “routine” XPS measurements of electrodes and battery materials as they are assembled have been helpful in identifying “unintended” surface species (too small to be routinely identified by many other measurements) that occasionally appear during routine production and handling of materials. When XPS was conducted routinely, these problems were identified before battery testing experiments. Often XPS can help identify causes of experimental failure or lack of reproducibility.

(B) Effects of Elemental Distributions on Battery Performance.

Ni segregation in individual Li_{1.2}Ni_{0.2}Mn_{0.6}O₂ cathode particles. One approach to improve battery performance has been the incorporation of multivalence transition-metal ions

into metal oxide cathodes [15]. One system getting particular attention has been lithium-nickel-manganese-oxide cathodes for which the addition of nickel has been found to significantly improve battery performance. The biggest challenge limiting use of these layer-structured cathodes in lithium-ion batteries has been capacity and voltage fading. The power rate of a battery strongly depends on the lithium ion drift speed in the cathode. The classic wisdom regarding layer-structured materials is that lithium ion travels swiftly between the layers, moving out/in of the cathode during the charge/discharge cycles. The STEM-EDS analysis of as-synthesized electrode material (Figures 7a–7f) provided the unexpected discovery of a thermodynamically driven, yet kinetically controlled, segregation of Ni to surface facets of fresh electrode particles. This segregation served as a barrier to lithium diffusion near the surface of a particle [3, 16]. Therefore, the transition-metal dopant that helps provide high capacity and/or high voltage can be located in a “wrong” location and may inhibit lithium diffusion, limiting battery performance [17].

Although STEM-EDS can readily examine the relatively heavy elements, it is difficult to determine the location of Li or quantitatively provide the composition of different

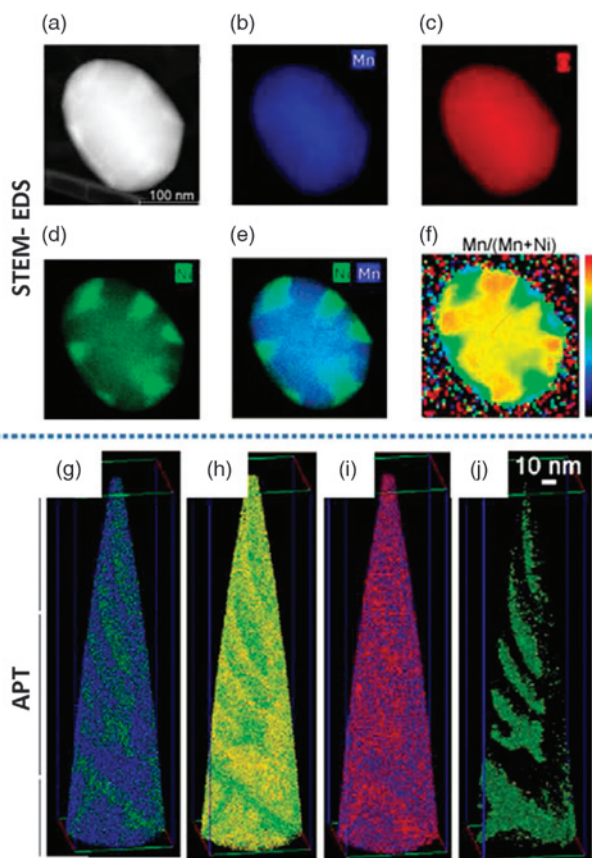


Figure 7: Comparison of STEM EDS mapping with APT results of the layered $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. (a) STEM image and EDS maps of (b) Mn (blue), (c) O (red), (d) Ni (green), (e) Ni and Mn composite map, and (f) ratio of Mn/(Mn+Ni). The intensity key, from bottom to top, represents increasing ratio. Because this is a ratio map, the low count outside of the particle gives large errors in dividing and causes the reddish background. APT: two-element composite maps of APT reconstructions are shown from (g) to (j) where each dot corresponds to an atom in the reconstruction. (g) Mn (blue) and Ni (green), (h) Li (yellow) and Ni (green), (i) O (red) and Mn (blue), and (j) 13 at% Ni isocomposition surface highlighting the Ni-rich regions in the reconstruction [18].

compositional regions within a battery cathode in three dimensions. With careful sample preparation, APT has been found to be a very successful tool for associating concentrations of Li to the relative segregation of other elements as a function of battery charging and discharging [18]. The APT data of Figure 7 (g–j) show the distributions of Ni, Mn, O, and Li, revealing that Li is concentrated in the Mn-rich part of the electrode. By comparing the APT-measured distribution of all elements in cathode materials before and after cycling, a detailed understanding of cycling-induced nanoscale compositional changes can be obtained: for example, Ni alters the Li distribution and likely impacts battery performance.

Optimizing electrode structure for performance

Having learned that component segregation occurs during cathode synthesis and operation, it is useful to explore the options of using different synthesis approaches to minimize or avoid such segregation and to correlate such changes to battery properties. The performance of batteries made of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode materials processed by different methods is shown in Figure 8a. Note that the hydrothermal-produced material shows significantly less

degradation in performance upon cycling compared to material produced in other ways. The STEM/EDS images in Figures 8b, 8c, and 8d indicate minimum Ni segregation for the hydrothermal processed material while both sol-gel processed material and co-precipitation processed material have significant Ni segregation to the surface. Upon correlating the Ni segregation to battery performance, it shows that material without initial Ni segregation retains a high level of battery performance after more than 150 charge/discharge cycles [19].

NanoSIMS was also used to confirm the change in surface Ni/Mn distribution because it provides information about chemical composition with good depth resolution. The NanoSIMS-determined elemental distributions in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ cathode materials fabricated by hydrothermal and sol-gel methods are shown in Figure 9, confirming the significant decrease in surface-segregated Ni for the hydrothermal process [19].

Discussion

In the past decade we have witnessed significant progress toward high sensitivity, high spatial resolution, and increased temporal resolution for many microscopy and surface-analysis instruments. The *in-situ* or operando operation of certain instruments can accelerate understanding, but usually data from such studies still need to be correlated with complementary methods employing conventional or *ex-situ* analysis and/or system modeling.

The need for multiple methods suggests several challenges and opportunities:

1. Integration of different instrument or analytical concepts on the same platform such that data may be acquired at the same site from several methods under *in-situ* or *operando* conditions. New combinations of such methods need to be designed without degrading the capabilities of the different methods involved. For example, microfabrication techniques and manipulations should make possible the integration of SIMS and STEM [20].
2. For some tools the integration of capabilities in a single instrument is not (yet) possible and may not be desirable. The creation of methods to enable easy and “spatially registered” transfers of samples in a controlled manner to different instruments is critical for some studies.
3. Application of multiple methods for different types of research may require expertise beyond that available in one research group or even one institution. The need for such expertise favors instrument centers and national user facilities and has implications for training of the next generation of researchers.
4. Multiple data streams and real-time data acquisition place increased demands on methods of data collection, storage, processing, and integration; further development in these areas would be helpful.

Conclusion

A combination of tools provided complementary information at a variety of spatial resolutions for addressing issues related to improvements in advanced batteries. No single method provided

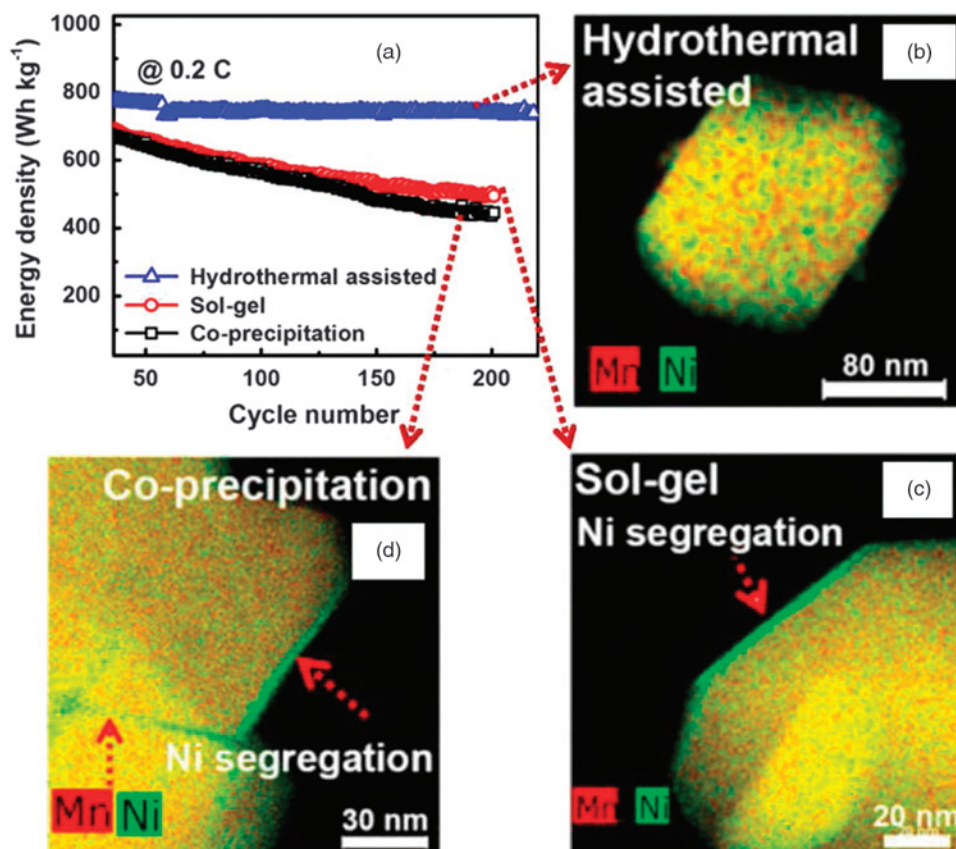


Figure 8: Correlation of structure and battery capacity retention for using $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ as cathode for lithium battery. Note the Ni segregation is directly related to the processing route of the material, which directly affects the battery performance. (a) Energy density as a function of cycling number of the battery. (b) Hydrothermal-processed material showing minimum Ni segregation. (c) Sol-gel processed material shows Ni segregation. (d) Co-precipitation processed material shows Ni segregation.

provide important information often difficult to obtain by other methods.

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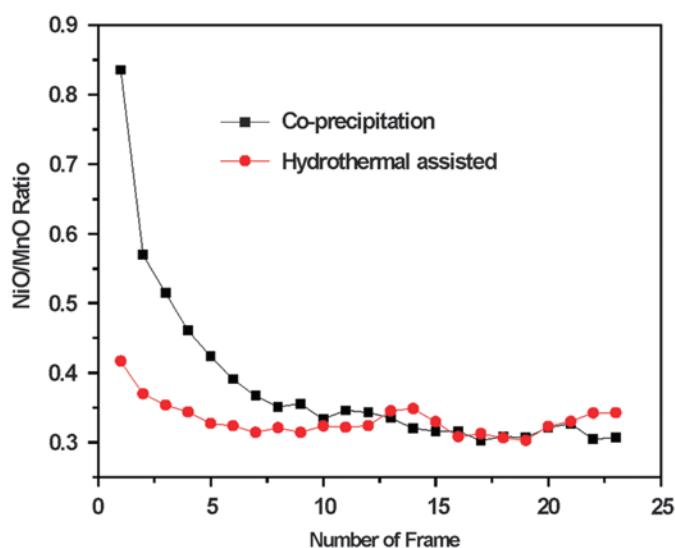


Figure 9: NanoSIMS depth profiles showing an enrichment of NiO at the surface of electrode material produced by co-precipitation and little or no NiO enrichment at the surface of hydrothermal grown materials. Each frame corresponds to 2 to 3 nm.

the required range of information about elemental distributions, chemical states, and the evolution of structure and composition during charge/discharge cycles. The surface and interface sensitivity of XPS, different versions of SIMS, APT, and STEM

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