# Off-the-shelf NMC Cathode Material Characterization by APT

## Nanoscale compositional quantification in Li-based materials

Li-ion based battery systems facilitate efficient energy storage and transfer, powering devices from smart phones to electric vehicles and are envisioned to be crucial components in a sustainable energy ecosystem. Microstructural optimization of all the components including cathodes, anodes, electrolytes and separators is essential for enhancing their performance, safety and longevity. In this regard, analyzing the nanoscale compositional distribution within the various components is of great importance. While X-ray based techniques that are readily available with electron microscopy are useful, quantitative compositional characterization of such light elements as Li, B, C and O with nanoscale spatial resolution remains a challenge. The capability of atom probe tomography to achieve this with *equal sensitivity* to all elements makes it ideally suited to help execute battery materials research and development.

To demonstrate this capability of APT, we have analyzed a class of commercially available Li-based oxide cathode materials known as 'NMCs'. NMC refers to nickel, manganese and cobalt, which are present in varying amounts in these Li-based oxides. The properties of the cathode, for example, ionic transport is controlled by the 'NMC' stoichiometry along with the addition of dopants such as Ti, Al, and Mg. As an illustrative example, Figure 1 depicts the nanoscale 3D elemental distribution within an NMC cathode that is doped with Al. Distinct compositional features including the segregation of the Al dopant to a grain boundary, and a faceted region of Li-enrichment adjacent to the grain boundary can be observed. The quantitative composition distribution across the grain boundary, plotted in Figure 1 also reveals the correct Li:O and Ni:Mn:Co stoichiometries expected for this material, which are difficult to obtain from X-ray based techniques.

Finally, the major improvement in data quality for these NMC materials, i.e., a ten-fold increase in mass resolving power (MRP), achieved in our latest generation 6000 LEAP systems in comparison to the 5000 LEAPs is shown in Figure 2. In the example shown, the MRP increase has revealed a Li-carbide peak (highlighted in Figure 2), allowing us to understand the interaction between the cathode and the organic binder phase in the microstructure.

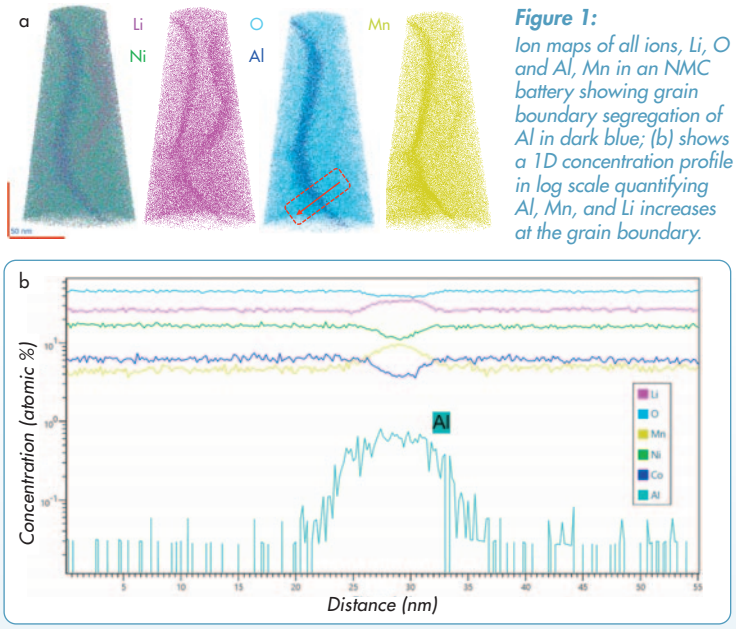



***Figure 1:***
*Ion maps of all ions, Li, O and Al, Mn in an NMC battery showing grain boundary segregation of Al in dark blue; (b) shows a 1D concentration profile in log scale quantifying Al, Mn, and Li increases at the grain boundary.*

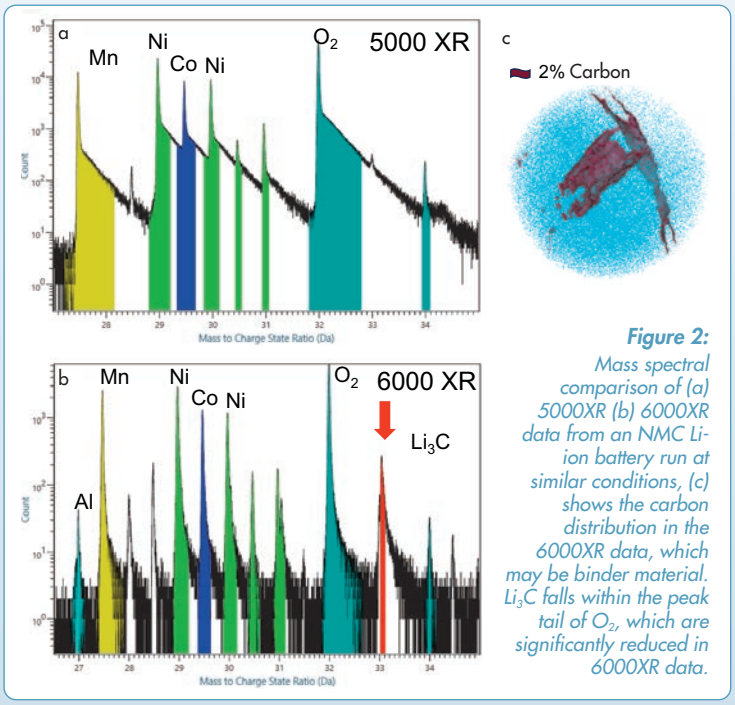



***Figure 2:***
*Mass spectral comparison of (a) 5000XR (b) 6000XR data from an NMC Li-ion battery run at similar conditions, (c) shows the carbon distribution in the 6000XR data, which may be binder material. $Li_3C$ falls within the peak tail of $O_2$, which are significantly reduced in 6000XR data.*

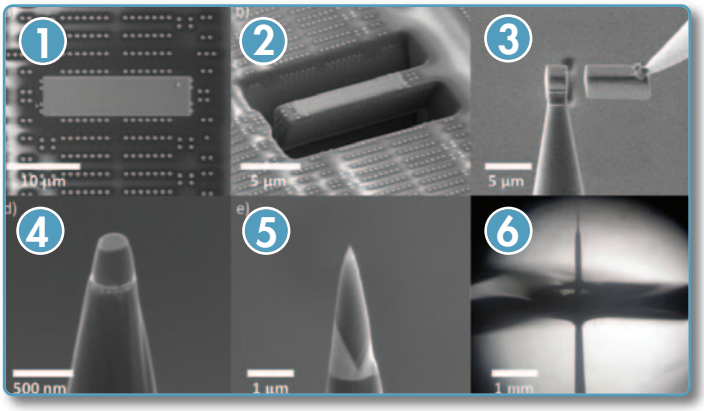
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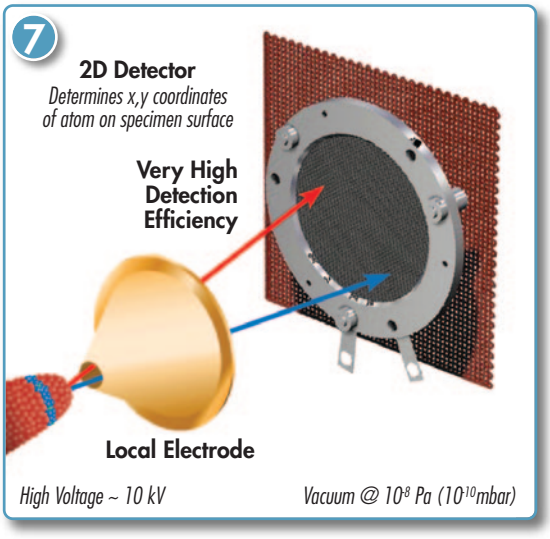
# Three Steps to 3D Nanoscale Analysis

## An Introduction to Atom Probe Tomography

### Step 1: Specimen Preparation

An atom probe specimen usually has a nanoscale region of interest (ROI) requiring both 3D compositional imaging and analysis. The sample is formed into a needle shape containing the ROI. Common APT specimen preparation methods using electropolishing or a Focused Ion Beam system (FIB) are very similar to TEM methods except instead of forming a thin sheet, a needle shaped sample is desired. At the right, standard FIB liftout and mounting of a specimen (figures 1 through 3) and then sharpening the sample with the ROI left at the very apex ( 4 and 5). In 6, a wire geometry sample is being electropolished.




### Step 2: Data Collection

An atom probe produces images by field evaporating atoms from a needle-shaped specimen and projecting the resultant ions onto a detector 7.

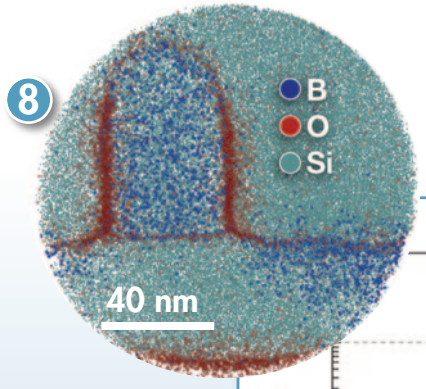
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately $10^6$.

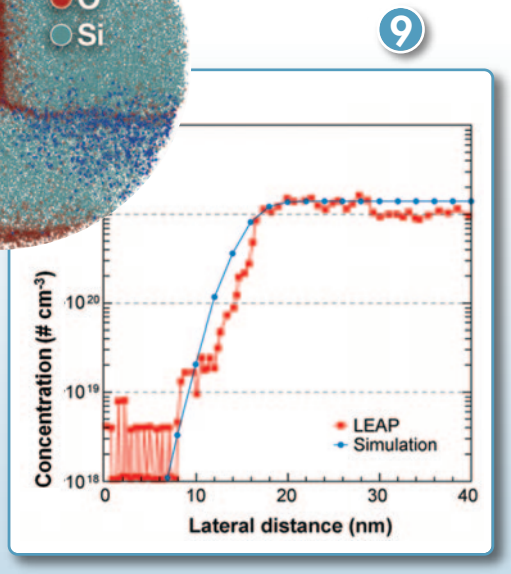
An atom probe identifies atoms by their mass-to-charge-state ratio *(m/n)* using time-of-flight mass spectrometry. Charge state, *n*, is typically 1 to 3.

The specimen is held at approximately 50K to reduce surface diffusion during the experiment. The high electric field results in 100% ionization and the high speed detector is capable of measuring up to 80% of the collected ions, independent of ion mass.

### Step 3: Data Visualization and Analysis

Examples of data output are illustrated by a slice of a 3D atom map of a transistor† 8, and a dopant composition profile‡ 9. The image shows the positions of individual atoms (oxygen is red and boron is blue) in the transistor with subnanometer resolution. From the reconstructed data set many types of useful analyses are possible. These include 3D visualization, 2D atom mapping 8, 1D depth profiling and line scanning 9, as well as mass spectra and compositional analysis from user-selected volumes.




† *Lauhon, L. J. et al, MRS Bulletin "Atom Probe Tomography of Semiconductor Materials and Device Structures" 34(10) (2009) 738.*

‡ *Moore, J. S.; Jones, K. S.; Kennel, H.; Corcoran, S., Ultramicroscopy "3-D Analysis of Semiconductor Dopant Distributions in a Patterned Structure using LEAP" (2008), 108, 536–539.*

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