Analysis of NiMnCo Li-ion Battery Material
An Atom Probe Application for Powder Specimens

Application Note #APT-24

In recent years, atom probe tomography (APT) has demonstrated great capability for analyzing lithium ion battery materials. Applications include detecting Li loss in cycled $LiCoO_2$ [1], impurity segregation to particle interfaces in spinel $LiMn_2O_4$ [2], and compositional heterogeneities in layered $Li(NiMn)O_2$ [3]. APT's ability to provide nanoscale composition and spatial quantification for Li atoms and other low concentration species provides unique complementary information to other analytical techniques.

APT sample preparation for powders is evolving. For particles larger than ~10 µm, the conventional focused ion beam (FIB) lift-out methods allow extraction of numerous APT specimens from single particles [4]. This approach enables comparisons both between particles and from different locations within the same particle.

In this example, APT was performed on two types of commercially available NiMnCo (NMC) cathode materials. The nominal compositions are $Li(Ni_xMn_yCo_z)O_2$ with X:Y:Z=622 and X:Y:Z=811. APT specimens were prepared from sub-surface particle regions, Figure 1. Multiple particles from each sample were examined to better understand particle to particle variation. APT analysis of NMC materials produces time-of-flight mass spectra where all the peaks may be clearly identified. Compositional analysis shows clear Ni-to-metal ratio distinction between NMC622 and NMC811 materials, Figure 2. Compositional variation within each material type is well below the ±2σ error, estimated from three 622 particles and two 811 particles, indicating statistical homogeneity from particle to particle.

APT has been shown to provide important spatial and compositional information for many types of Li-ion battery cathode materials. This offers outstanding capability for the characterization of light elements and/or low concentration dopants including fine-scale compositional variations. APT is an emerging technique for supporting the engineering of Li-ion battery materials with higher energy storage capacity and longer term cycling performance.

[1] D. R. Diercks, et al. Journal of the electrochemical society 161.11 (2014): F3039.

[2] J. Maier, et al. Energy Technology 4.12 (2016): 1565-1574.

[3] A. Devaraj, et al. Nature communications 6.1 (2015): 1-8.

[4] T. J. Prosa and D. J. Larson, Microscopy and Microanalysis 23.2 (2017): 194.

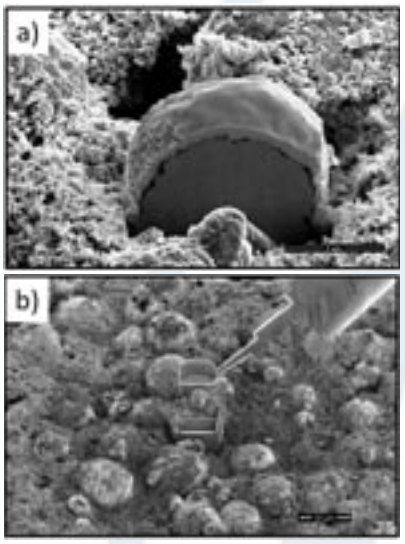


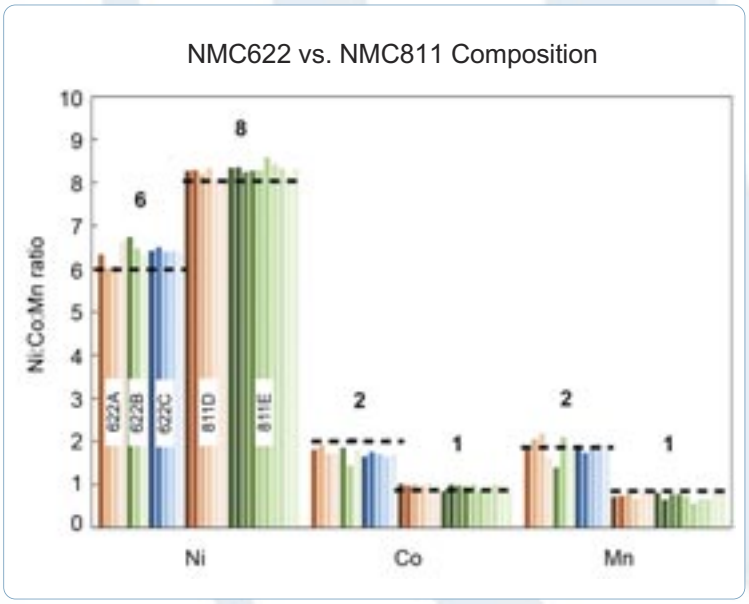
Figure 1:
NMC cathode tapes composed of 90% active particles (~10 µm), 5% binder and 5% conductive carbon.

a) Deposition of protective layer on a selected particle.

b) A ~10 µm long specimen extraction (lift-out) which can be used to make five or more APT specimens from a targeted particle.

Figure 2:
Measured compositions from NMC622 particles A, B and C along with NMC811 particles D and E (5, 3, 5, 6, and 10 measurements from each particle respectively).

The dashed lines indicate nominal compositional ratios, which are in good agreement with the measured APT ratios. The chemical variation is well below the statistic error within each population.



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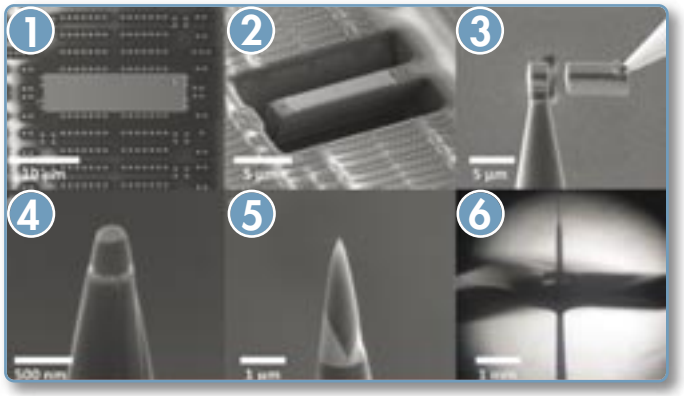
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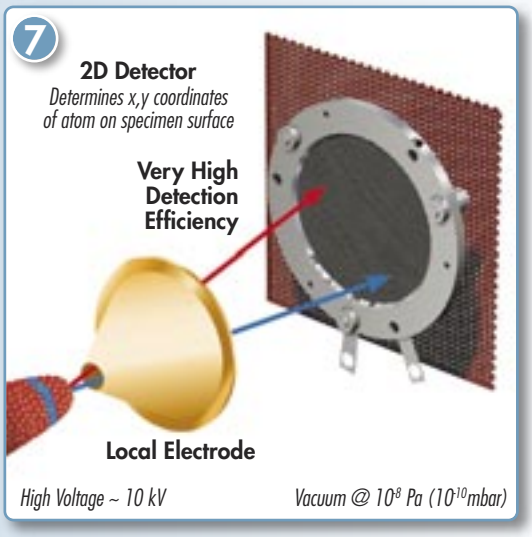
AMETEK® MATERIALS ANALYSIS DIVISION

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.

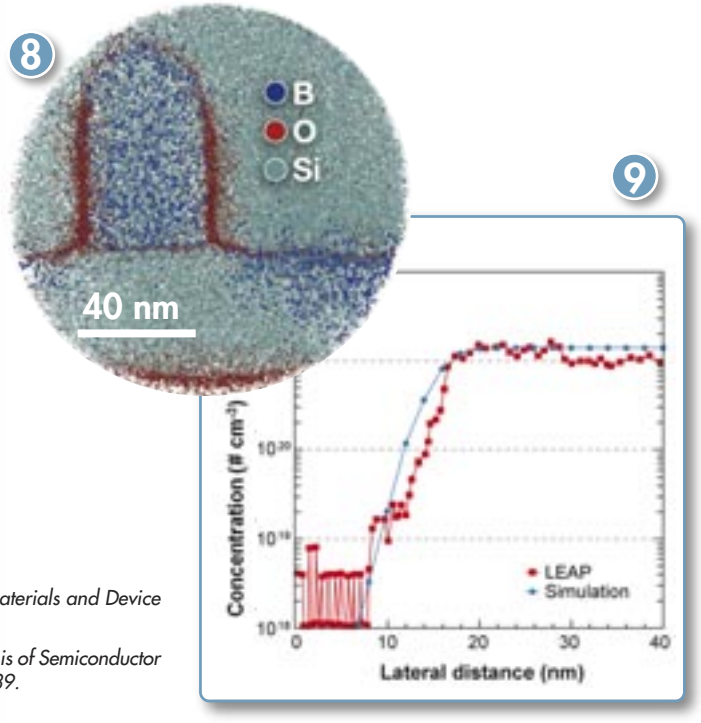
A high magnification results from the ~ 80nm tip being projected onto an 80mm detector resulting in a magnification of approximately 10^6.

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.*