Developing Next-Generation Multimodal Chemical Imaging Capability by Combining STEM/APT/STXM/HIM

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Key Collaborators: David Shuh (ALS), Tolek Tyliszczak (ALS), Francois Vurpillot (UR)

Pacific Northwest NATIONAL LABORATORY

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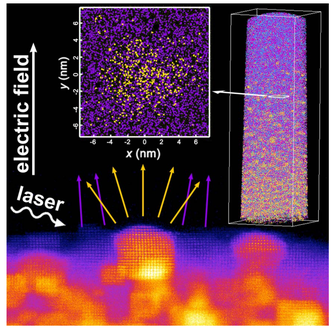
Purpose

- Better understanding of capacity degradation mechanisms in Li and Na ion battery cathode materials using multimodal chemical imaging
- Understanding factors influencing heterogeneous ice nucleation by mineral dust aerosols in clouds using multimodal chemical imaging and ice nucleation studies
- Multimodal chemical imaging using aberration-corrected TEM/STEM with APT, STXM, and XPS to provide full 3D analysis of structure and chemistry with sub-nanometer spatial, chemical resolution, and ppm-level mass sensitivity.

Key Successes

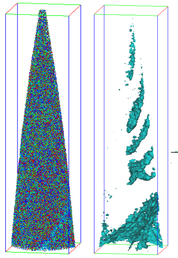
- Achieved the first sub-nanometer scale spatially resolved mapping of Lithium in Li ion battery cathodes.
- Performed directly coupled STXM-TEM-APT analysis of Li and Na ion battery cathode materials: Important for understanding capacity degradation mechanisms.
- 5 publications, 2 invited talks, 1 NSF proposal under review

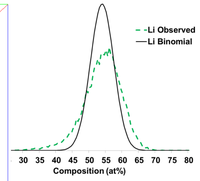
Research Accomplishments



Improving 3D characterization of metal-oxide composites (e.g., catalysts) by combining HRSTEM, APT, and computational simulations. Devaraj A et al. 2014. *JPC Letters* 5(8): 1361-1367. Collaborators: F Vurpillot, WP Hess

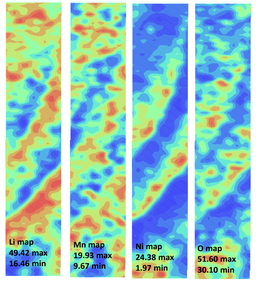
Li-ion Battery Cathodes

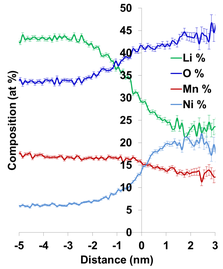




Li partitioning in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ particle

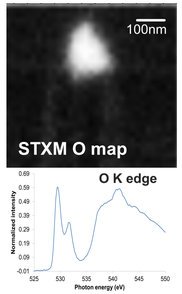
Li segregation to Mn rich regions in advanced Li-ion battery cathodes. Devaraj A et al. 2014 (*to be submitted to Nat. Comm.*)

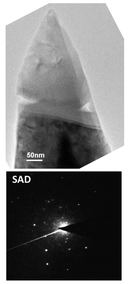


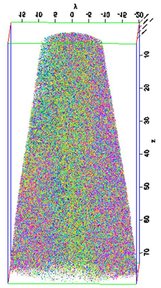


Collaborators: J Zhang (PNNL), G Chen (LBNL)

Li-ion Battery Cathodes: STXM-TEM-APT







Chemical state: STXM imaging and NEXAFS of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$

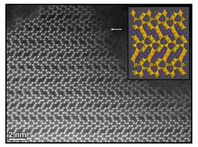
Structure: TEM imaging and diffraction of the same particle

Composition: APT analysis of the same particle

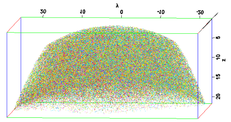
Multimodal chemical imaging of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode nanoparticles by STXM, TEM, and APT.

Na-ion Battery Cathodes

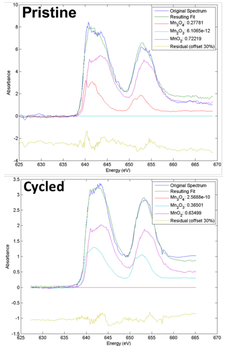
Study of $Na_{0.44}MnO_2$ cathode capacity degradation mechanisms using HRSTEM, NEXAFS, and APT



Tunnels of Na ion transport by HRSTEM

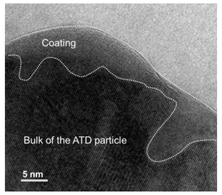


APT analysis showing nanoscale distribution of elements



STXM NEXAFS spectroscopy aids in understanding oxidation state changes as a function of cycling

Atmospheric Aerosols



Developing new parameterization for heterogeneous ice nucleation of mineral dust aerosols by correlating detailed characterization of acid-coated and bare aerosols with their ice nucleation properties.

HRTEM image of H_2SO_4-coated Arizona test dust (ATD)

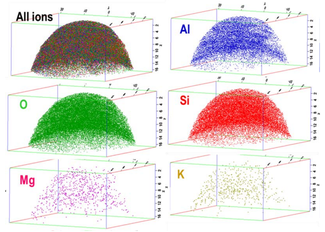
As Received ATD

	Si	Al
tilt- 0	74.1	25.9
tilt-25	74.54	25.46
tilt-45	74.67	25.33

Reacted ATD

	Si	Al
tilt- 0	79.15	20.85
tilt-25	84.43	15.57
tilt-45	100	0

Angle-resolved XPS of bare and H_2SO_4-coated ATD



APT analysis providing nanoscale distribution of major element and impurities

Publications

- Devaraj A et al. 2014. *JPC Letters* 5(8): 1361-1367
- Jiang X et al. 2014. *JAP* 115, 063902
- Kattakkam Set al. 2014. *JAP*, 114, 184901
- Vijaykumar M et al. 2014. *PCCP*, In Press
- Devaraj A et al. 2013. *Scripta Mat* 69, 513-516

Next Steps

- Extend and refine use of STXM-TEM-APT multimodal capability for analyzing Li and Na ion battery cathode materials to ultimately understand mechanism for capacity loss on cycling and cycling-induced phase transformations.
- Develop detailed understanding of structural, compositional, and chemical modification of atmospheric aerosols during cloud processing; understand their influence on heterogeneous ice nucleation properties.

Abbreviations: TEM: transmission electron microscopy, STEM: scanning TEM, APT: atom-probe tomography, STXM: scanning transmission X-ray microscope, XPS: X-ray photoelectron spectroscopy (XPS), HIM: helium ion microscope, HRSTEM: high-resolution scanning transmission electron microscopy

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