Diagnostic Studies – Argonne

Project Id: ES032

D.P. Abraham

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start date: FY09
- End date: On-going
- Percent complete:
  - project on-going

Budget

- Total project funding
  - 100% DOE
- FY09: $600K
- FY10: $600K

Barriers

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

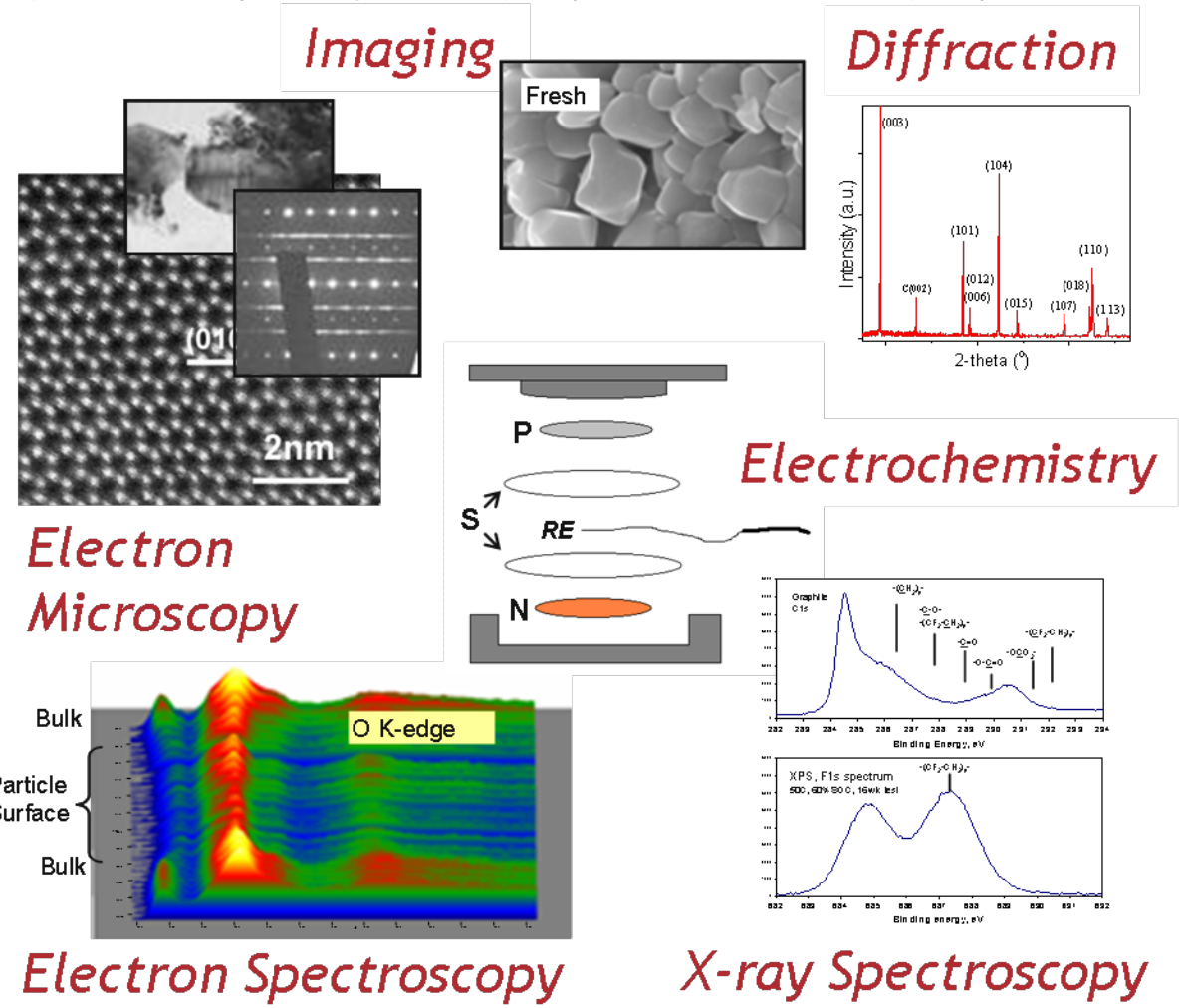
Targets

- Composition/Structure/Performance Correlations

Partners

- Argonne colleagues
- University of Illinois
- University of Rhode Island
- University of Puerto-Rico
- Idaho, Brookhaven, Sandia and Lawrence Berkeley National Labs

Diagnostics provides a fundamental understanding of materials and processes responsible for system performance and performance degradation



Identifying phenomenological mechanisms enables development of solutions to overcome performance limitations of each system

Technical Accomplishments

- Investigation of oxide structures and structural rearrangements during electrochemical cycling
  - Completed Microscopy/Spectroscopy of $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ *(met milestone)*
  - Completed Analytical Electron Microscopy of Li_2MnO_3 *(met milestone)*
  - Initiated Structural Study of $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ *(met milestone)*
- "Wrapped up" studies on Gen3 cells and cell constituents *(met milestone)*
  - Cell disassembly, electrochemical and physicochemical characterization of harvested cell components, determined sources of performance degradation
  - Documented data in an Argonne report
- Initiated characterization of PHEV baseline electrodes/cells *(met milestone)*
  - Electrochemical cycling and impedance (EIS and HPPC) data obtained on electrodes and full cells.
  - Data obtained in coin cells and reference electrode cells are similar to those obtained for cells with ATD-Gen2 chemistry

Technical Accomplishments - *continued*

- Completed characterization of SEI formed on graphite electrodes cycled in cells containing various electrolytes
  - SEI on binder-free graphite electrodes characterized by XPS, FTIR, and TGA
  - Formulated formation mechanisms based on the data
- Initiated study of positive electrode surface films on electrodes formed and aged in various electrolytes
  - Experiments on binder- and carbon-free $Li_{1.04}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.96}O_2$ electrodes
  - Electrochemical and physicochemical characterization of electrodes and surface films generated on the electrodes during cycling/aging
- Effect of Impurities and Moisture on LiBOB electrolyte performance in lithium-ion cells
  - Cycling, impedance, NMR, FTIR, and TGA data obtained to identify species responsible for inconsistency in salt performance
  - Formulated reaction mechanisms based on the data

Oxide Structure Investigations

Oxide Structure Investigations

- Lithium-bearing manganese-based layered oxides are being considered for PHEV applications because of their potential to achieve high energy densities
  - The structure and structural rearrangements in these oxides, which show anomalously high-capacities when cycled at high-voltages, have a significant effect on cell performance, calendar-life, and safety
  - Obtain a detailed structural understanding of $Li(Li_xMn_aNi_bM'_c)O_2$

$$\alpha\ Li_2MnO_3 + (1-\alpha)\ LiTMO_2$$

Li_2MnO_3

$Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$

$Li(Li_{0.2}Mn_{0.4}Cr_{0.4})O_2$

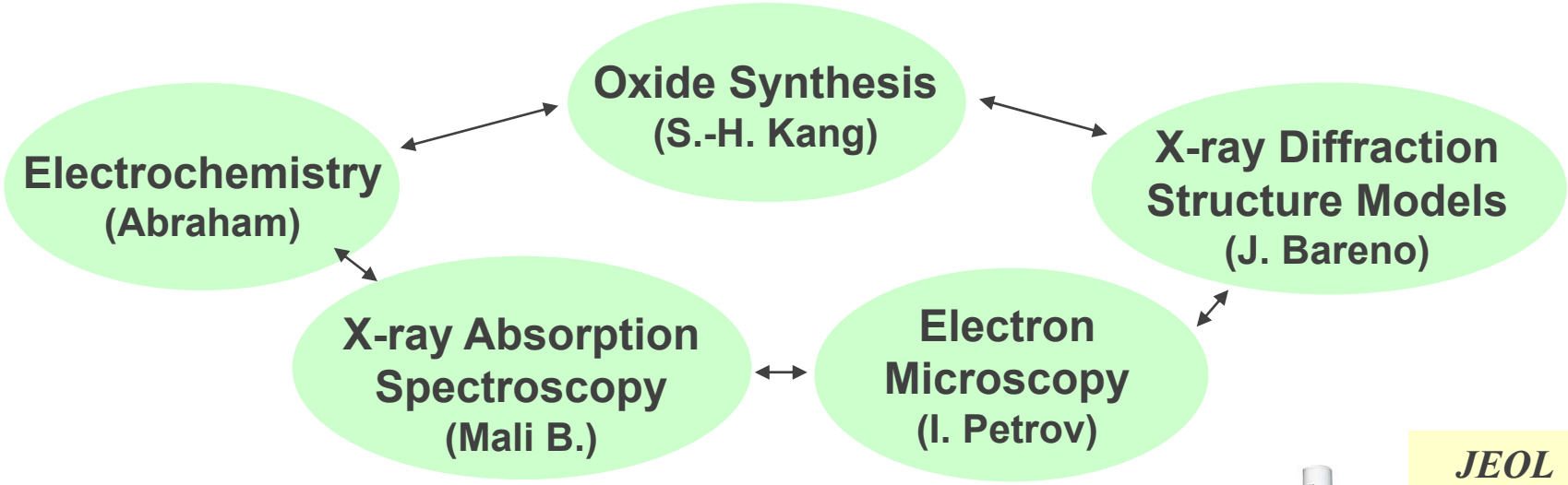
$Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$

$Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x})O_2$

$Li(Li_{0.04}Mn_{0.32}Ni_{0.32}Co_{0.32})O_2$

Approach

- **Multi-institution team assembled to synthesize, characterize, and model oxide structures.**



Argonne Advanced Photon Source

XANES - TM oxidation states
EXAFS – TM environments

JEOL 2200FS

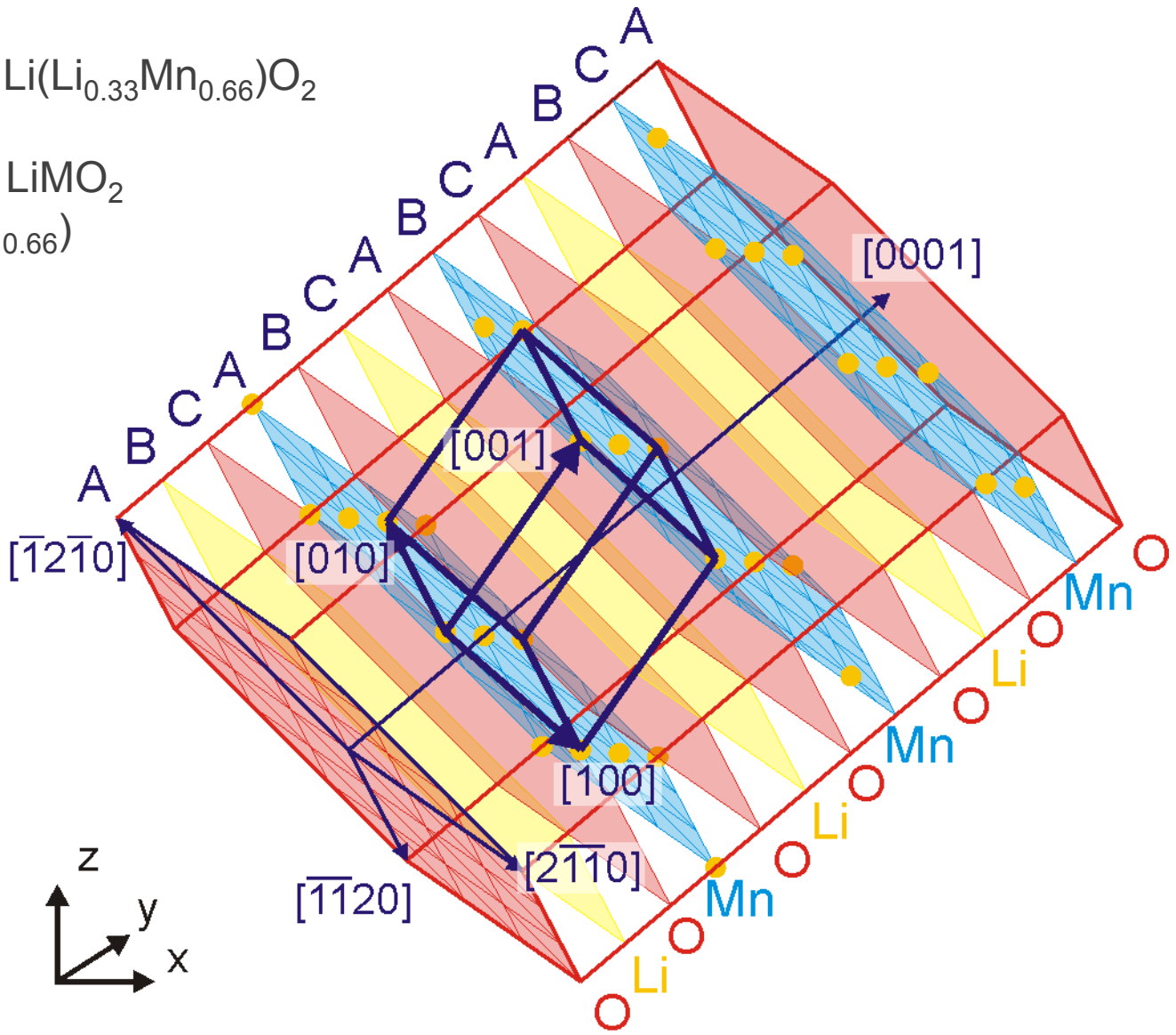
Resolution ~ 0.1 nm (HAADF STEM)

MICROSCOPY & SPECTROSCOPY
Local variations (< 2nm) in structure and composition

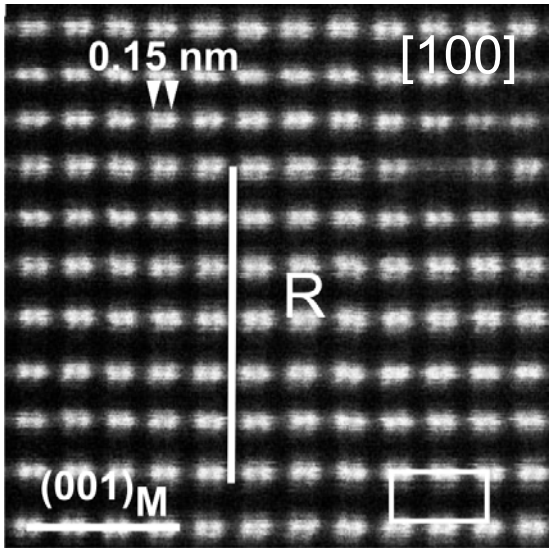
End member: Li_2MnO_3 - Structure

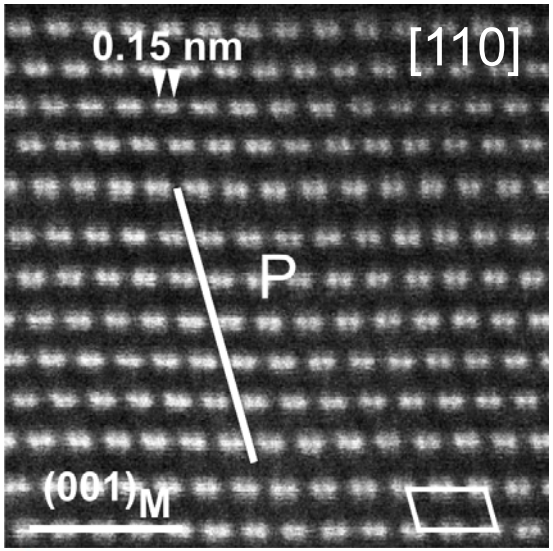
(C2/m) $Li_2MnO_3 = Li(Li_{0.33}Mn_{0.66})O_2$

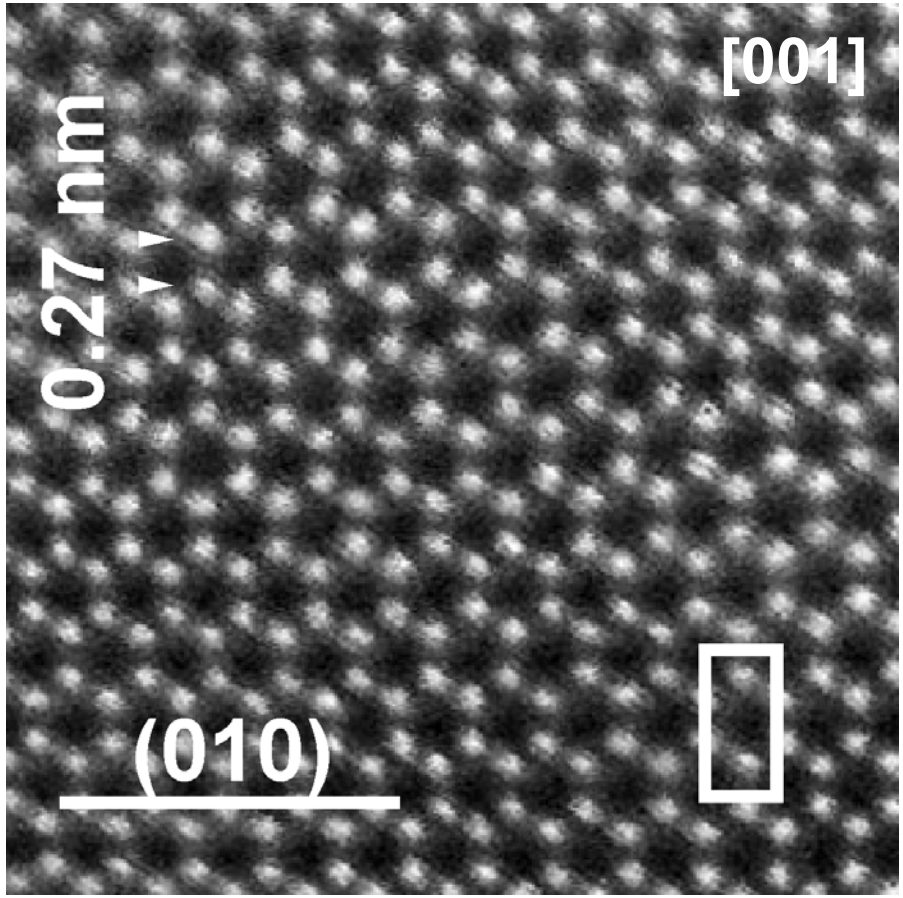
Related to (R-3m) $LiMO_2$
with TM =$(Li_{0.33}Mn_{0.66})$

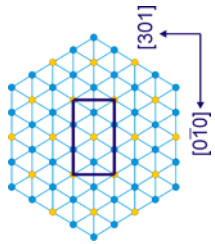


End member: Li_2MnO_3 - Z-contrast STEM



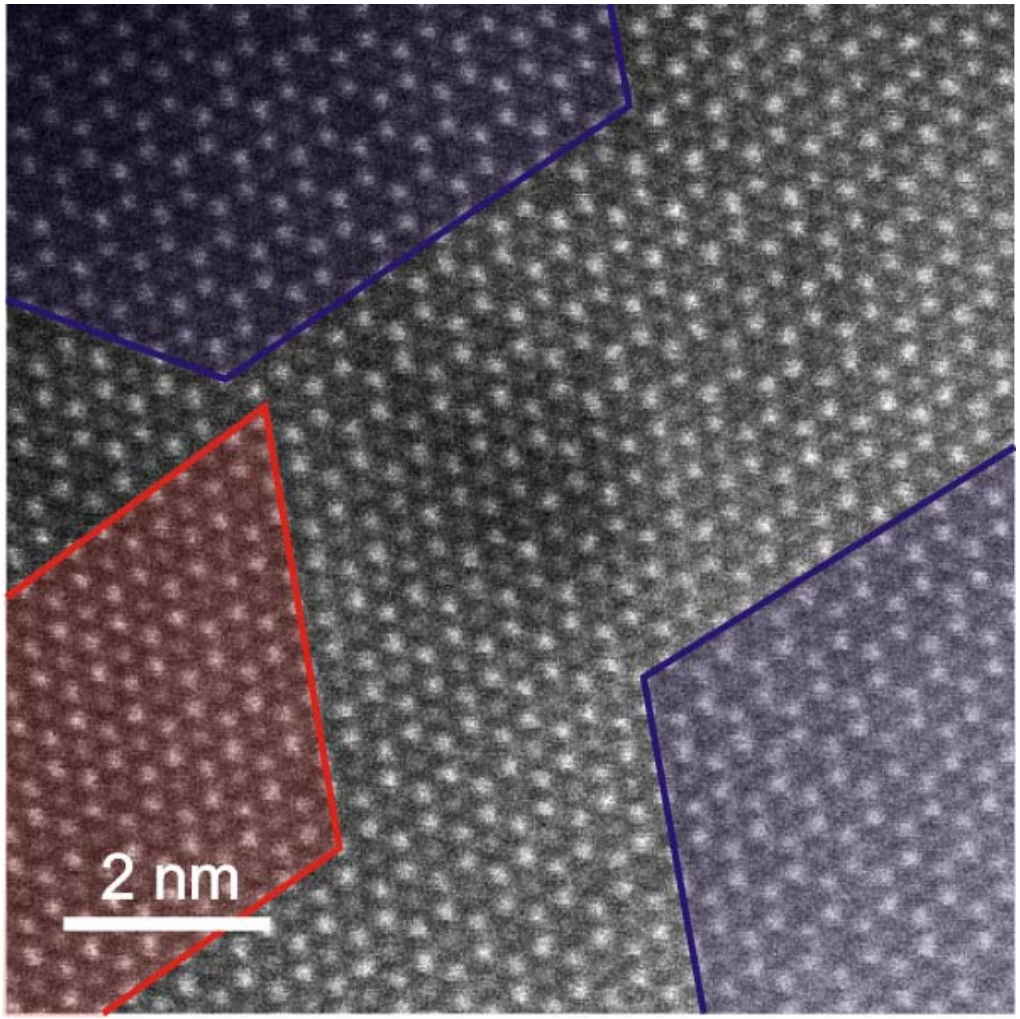






Bright-spots in images are TM columns and Li columns appear dark.
Images show Li ordering in TM planes.

$Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ - Z contrast STEM



View of transition metal planes along $[001]_M$

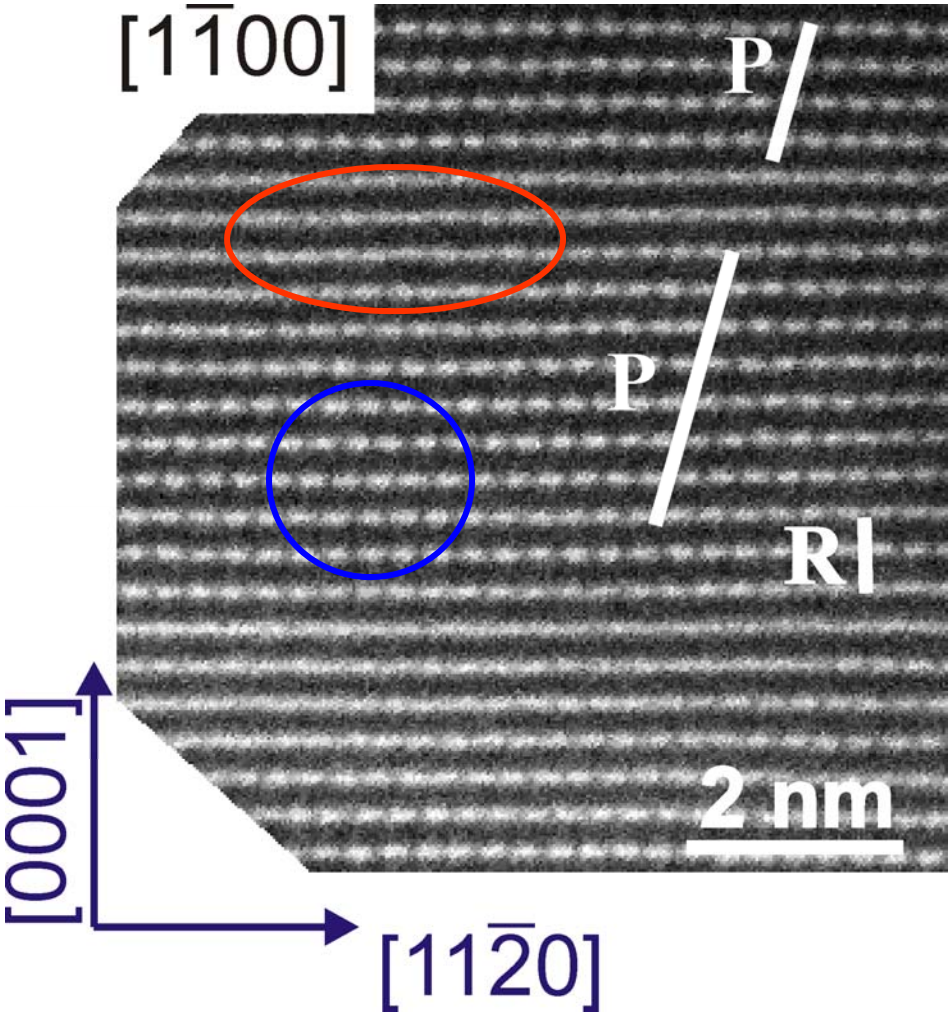
Bright-spots in images are TM columns and Li columns appear dark.

Honeycomb regions (hollow core = Li column) are Li_2MnO_3-like.
Hexagonal regions (filled core = TM column) are $LiCoO_2$-like.
No sharp boundaries between honeycomb and hexagonal areas.

Li_2MnO_3-like and $LiCoO_2$-like areas observed in TM-planes

$Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ - Z contrast STEM

$[100]_M$ // $[1\text{-}100]_R$



View of transition metal planes along $[100]_M$

Bright-spots in image are TM columns. Li columns appear dark.

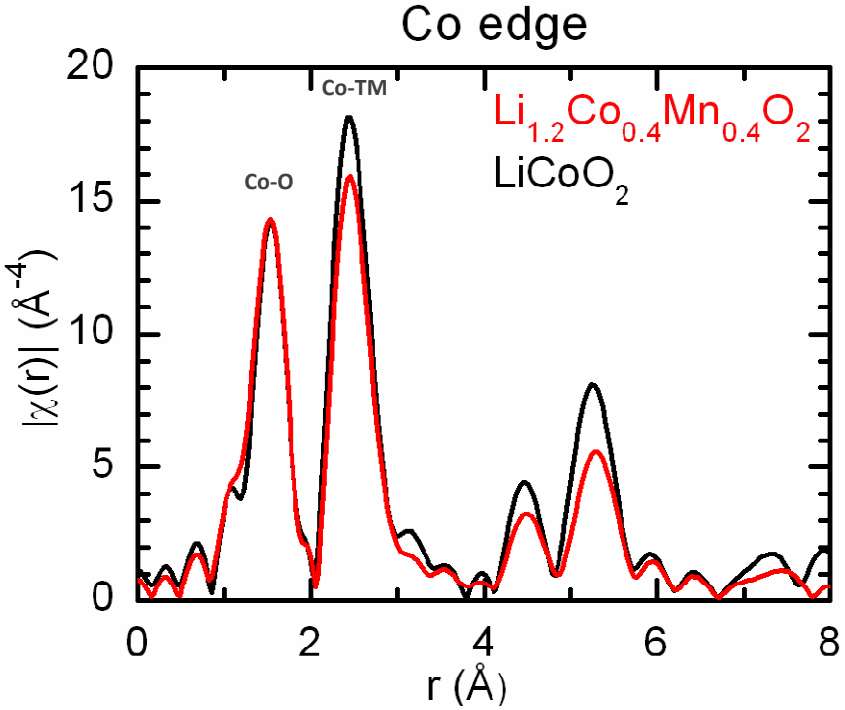
Li ordering in TM planes (Li_2MnO_3-like) are seen in some portions of image – P and R type meshes indicate local monoclinic character.

TM planes showing a fringe contrast do not have Li-ordering ($LiCoO_2$-like).

Li_2MnO_3-like and $LiCoO_2$-like areas observed in TM-planes

X-ray Absorption Spectroscopy - $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$

EXAFS data provides information on environment around TM atoms

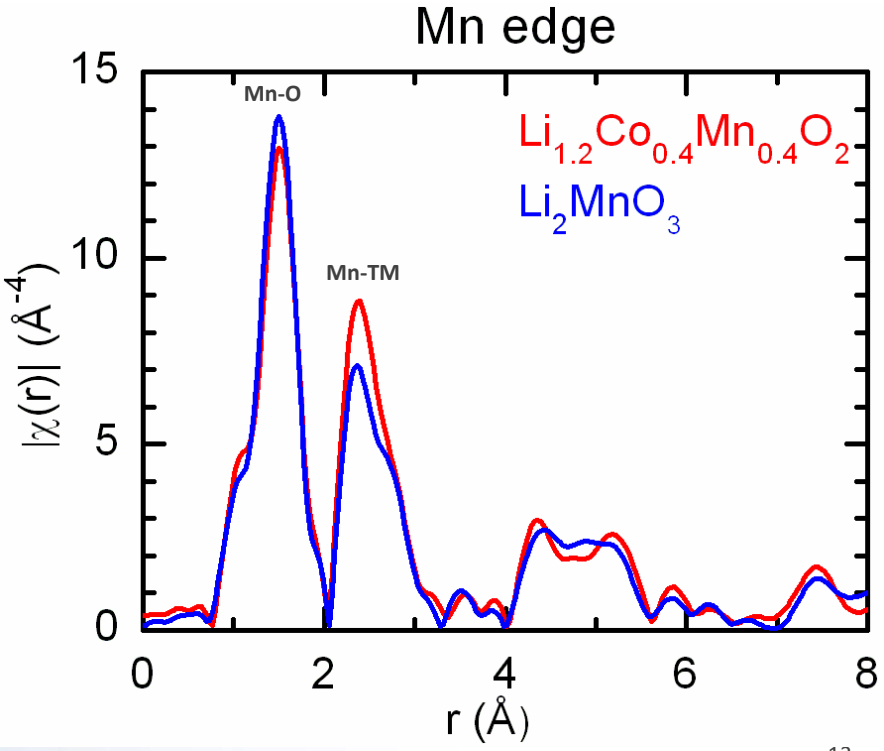


Co-O bond distance ~ 1.92 Å (same as in $LiCoO_2$)

Co-TM coordination is 5.5 +/- 0.7 (6 in $LiCoO_2$)

Exact phase matching of peaks in 4-6 Å range

Co environment in $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ appears very similar to $LiCoO_2$ environment up to 7 Å



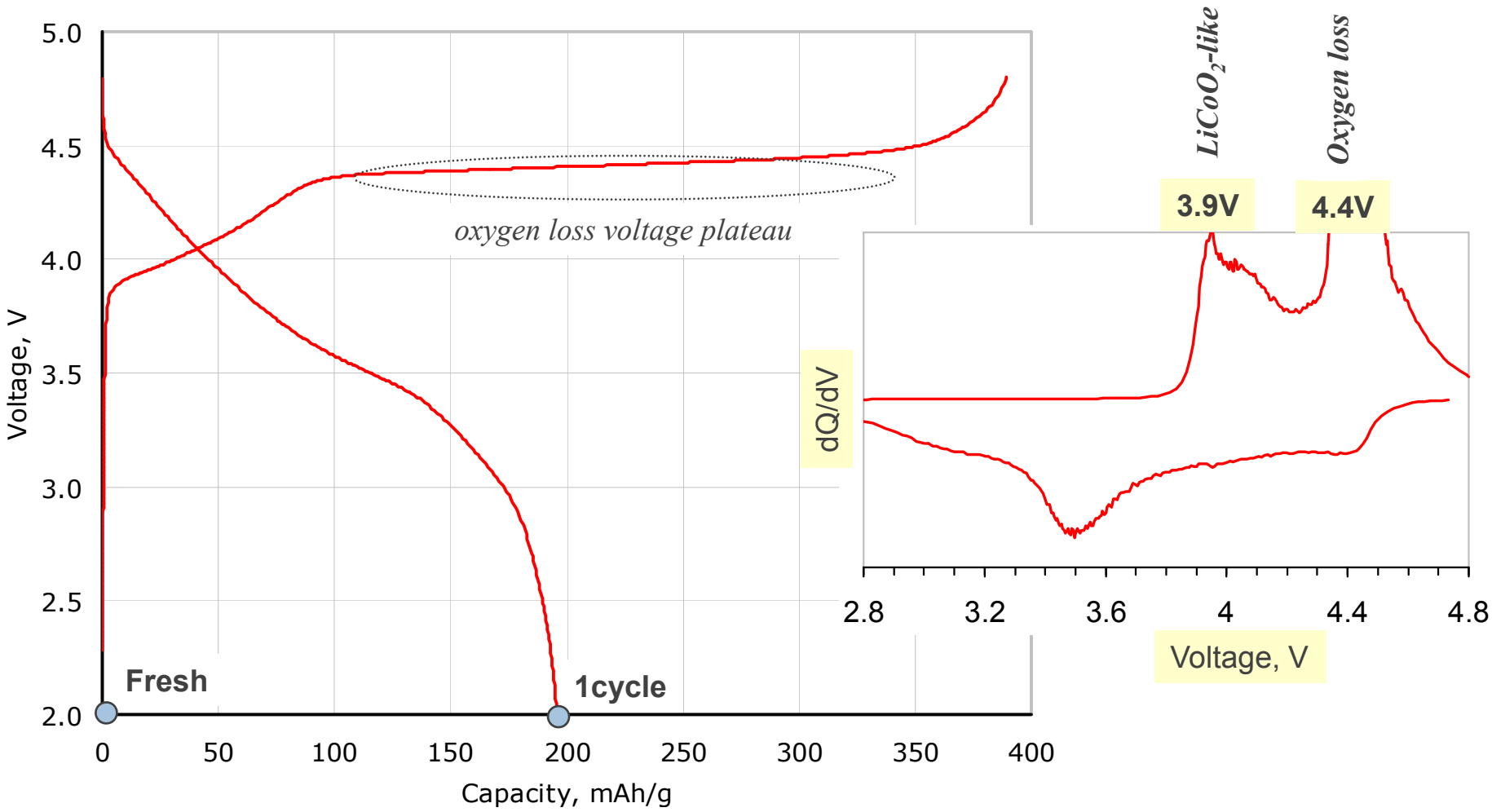
Mn-O bond distance ~ 1.90 Å (same as in Li_2MnO_3)

Mn-TM coordination is 3.7 +/- 1.5 (3 in Li_2MnO_3)

Exact phase matching of peaks in 4-6 Å range

Mn environment in $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ appears similar to Li_2MnO_3 environment to 7 Å

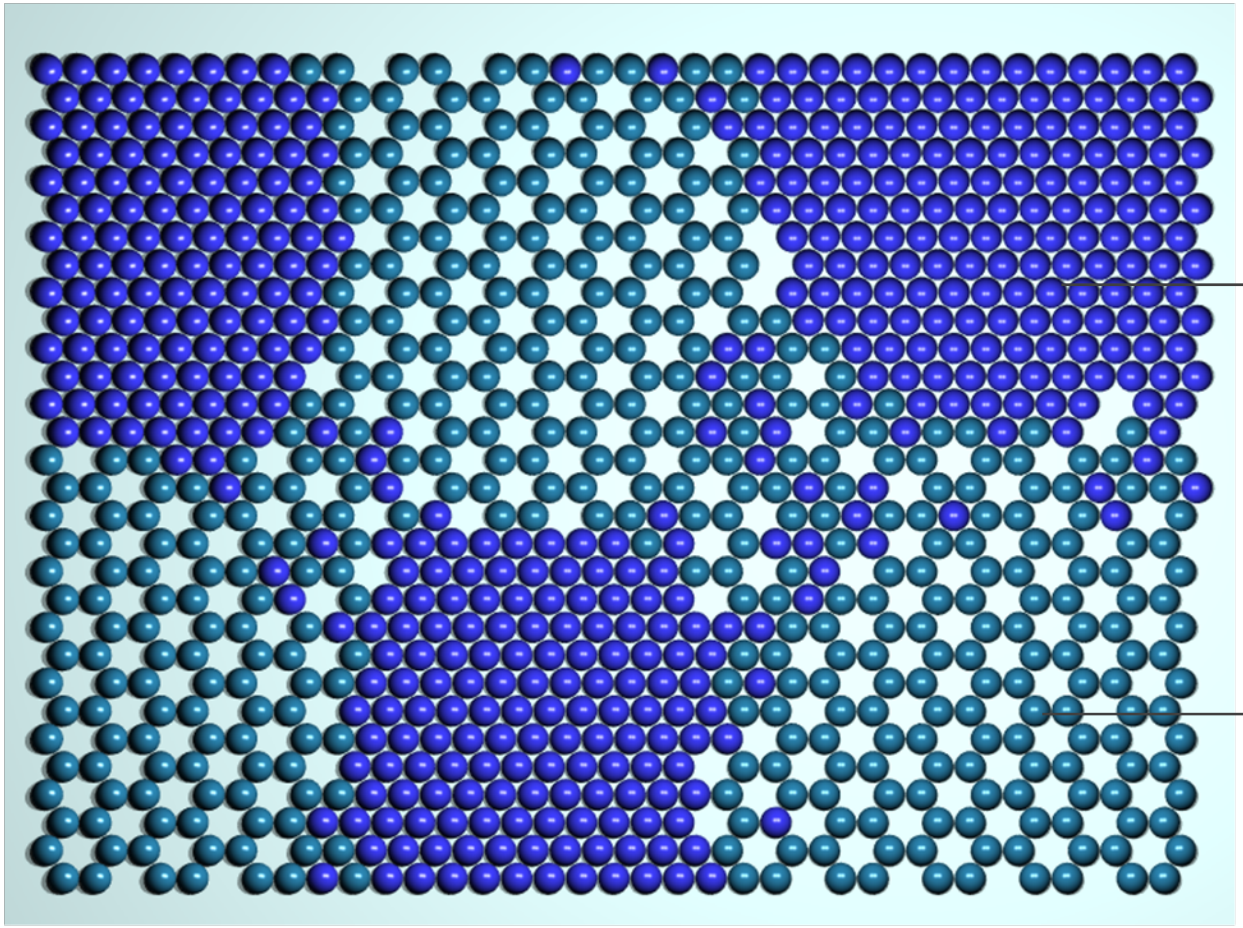
Electrochemistry - $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$



X-ray diffraction data from fresh and cycled samples are similar – unlike TEM and XAS, XRD is not sensitive to changes in local structure

TM plane - $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$

$Li_{1.2}Co_{0.4}Mn_{0.4}O_2$
(= $0.5LiCoO_2.0.5Li_2MnO_3$)



An intimate mixture of $LiCoO_2$-like and Li_2MnO_3-like areas (~1-3 nm size) are present in $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ sample.

Oxide Structures - Work in Progress

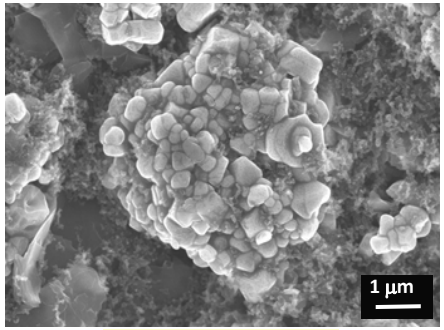
- **Structural investigations continue to answer questions that include the following:**
  - ✓ What are the local atomic arrangements in the as-prepared oxides and how are these arrangements influenced by composition?
  - ✓ What are the charge compensation mechanisms during oxide delithiation & lithiation, i.e., during electrochemical cycling?
  - ✓ What phase transformations result during cell cycling and aging? How does this affect the oxide's capacity and rate performance?

PHEV electrodes/cells characterization

PHEV baseline Electrode Characterization

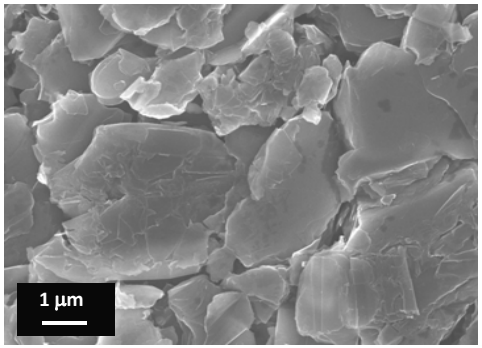
Single-sided electrodes

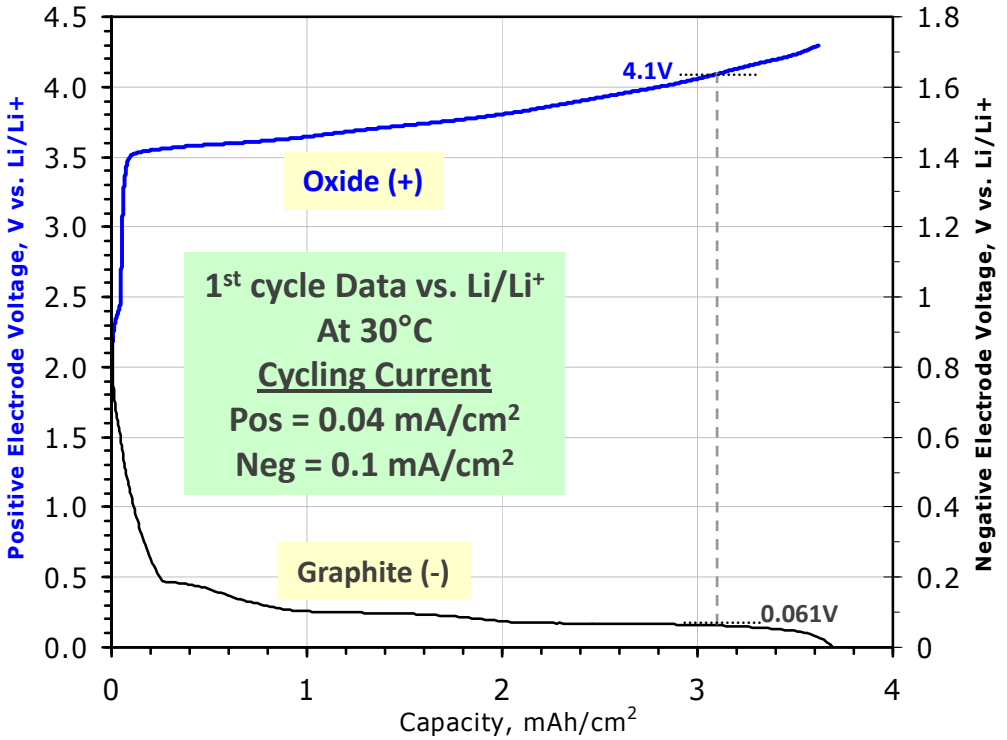
	Cathode (+)	Anode (-)
Composition		
Active	84% LiNi0.8Co0.15Al0.05O2	95% Mag-10 graphite
	4 wt% SFG-6 graphite	
	4 wt% Super P	
Binder	8% PVDF (KF1120)	5% Binder (SBR+CMC)
Loading Density		
Coating	18.8 mg/cm^2	10.8 mg/cm2
Active Material	**15.8 mg/cm2**	**10.3 mg/cm2**
Thickness		
Current Collector	**Al - 22 µm**	**Cu - 10 µm**
Electrode Coating	**65**	**79**
Total	**87**	**89**



Cathode(+)

Anode(-)





1st cycle capacity at 30°C

Pos (4.1V) = 3.1 mAh/cm^2 = 196 mAh/g

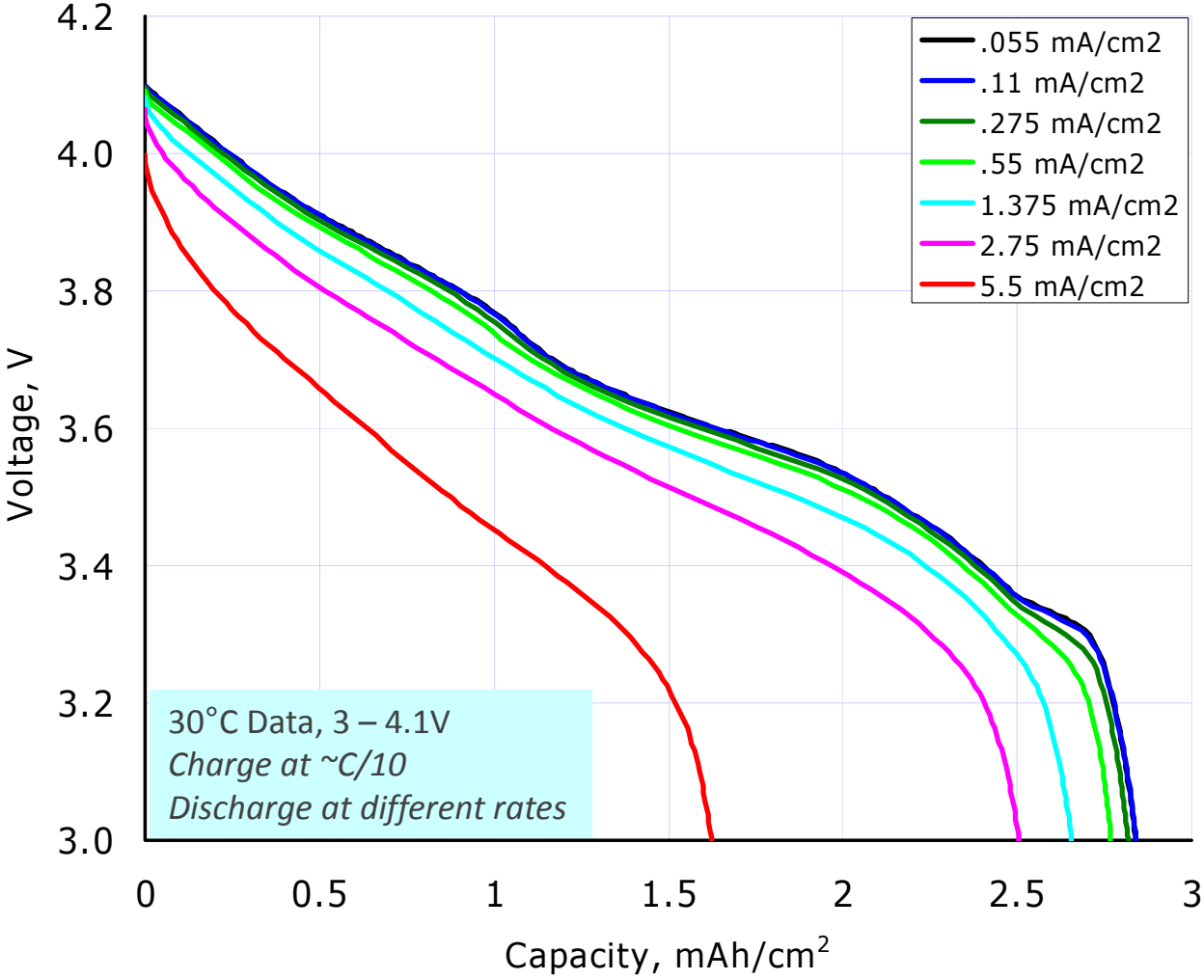
Pos (4.2V) = 3.4 mAh/cm^2 = 215 mAh/g

Neg = 3.7 mAh/cm^2 = 358 mAh/g

N/P (Full at 4V) ≈ 1.19

N/P (Full at 4.1V) ≈ 1.08

PHEV baseline single-sided electrodes
Full Cell - C/1 measurement



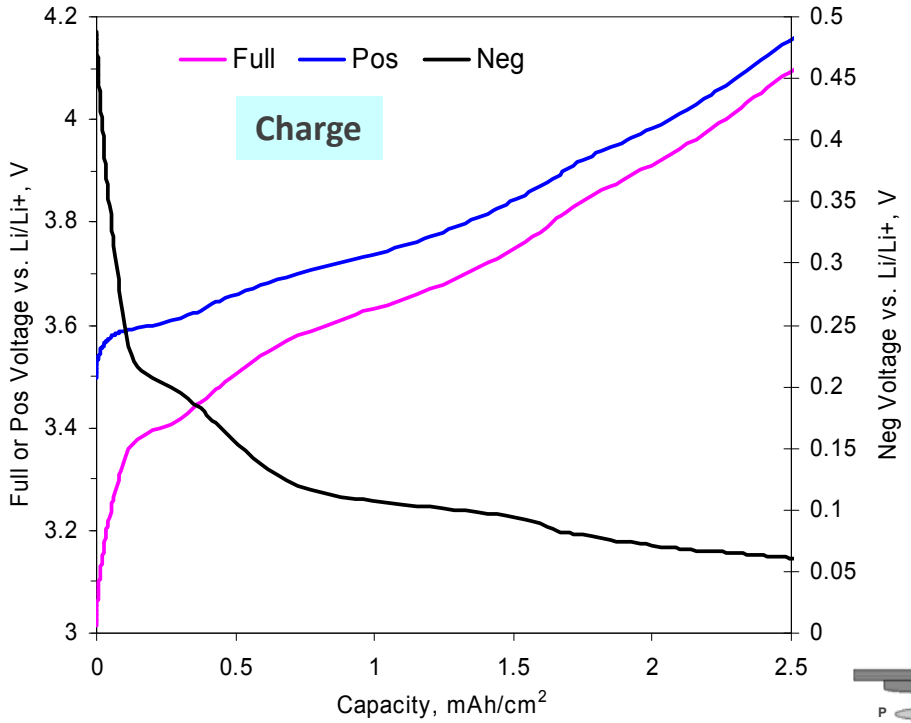
Current mA/cm^2	Time h	Capacity mAh/cm^2
0.055	51.65	2.84
0.11	25.83	2.84
0.275	10.25	2.82
0.55	5.03	2.77
1.375	1.93	2.66
2.75	0.91	2.51
5.5	0.30	1.63

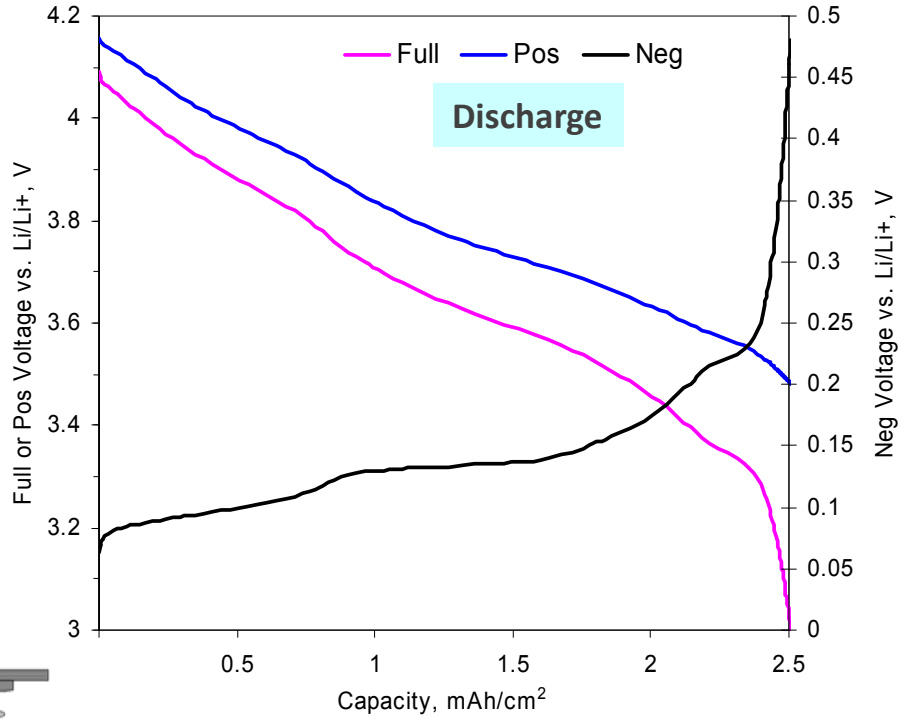
C/1 = 2.53 mAh/cm^2
= 160 mAh/g (+)

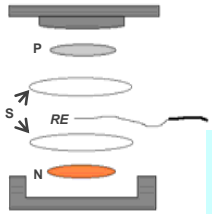
3.4 – 3.9V (1C)
≈ 1.7 mAh/cm^2
= 108 mAh/g (+)

Discharge capacities decrease rapidly at high rates

PHEV baseline single-sided electrodes
Reference Electrode Cell Data at 30°C





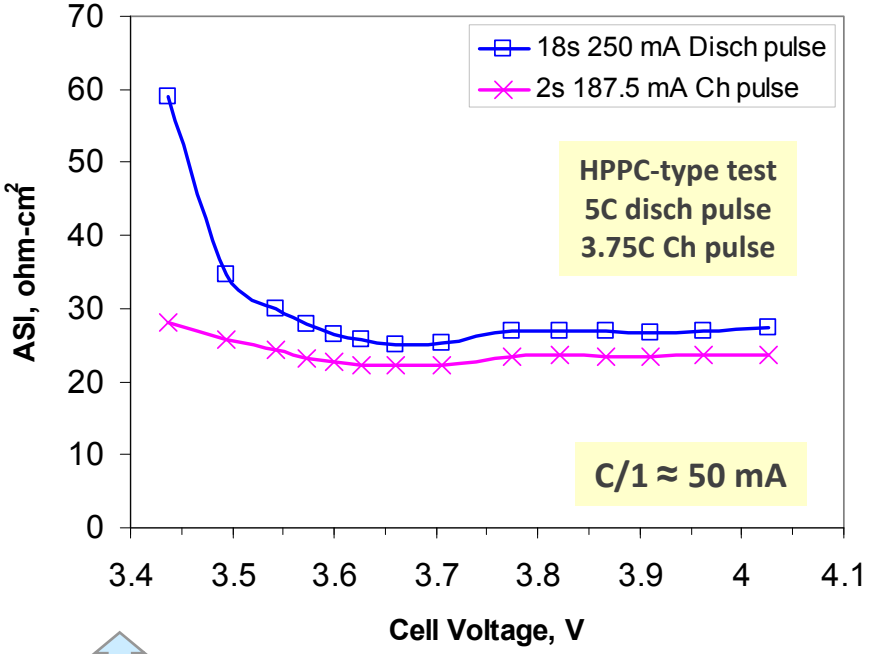


Charge cycle (after formation)
Full Cell Swing = 3 to 4.1V
Positive Electrode Swing ≈ 3.5 to 4.15 V
Negative Electrode Swing ≈ 0.5 to 0.05 V

Discharge cycle (after formation)
Full Cell Swing = 4.1 to 3V
Positive Electrode Swing ≈ 4.15 to 3.5 V
Negative Electrode Swing ≈ 0.05 to 0.5 V

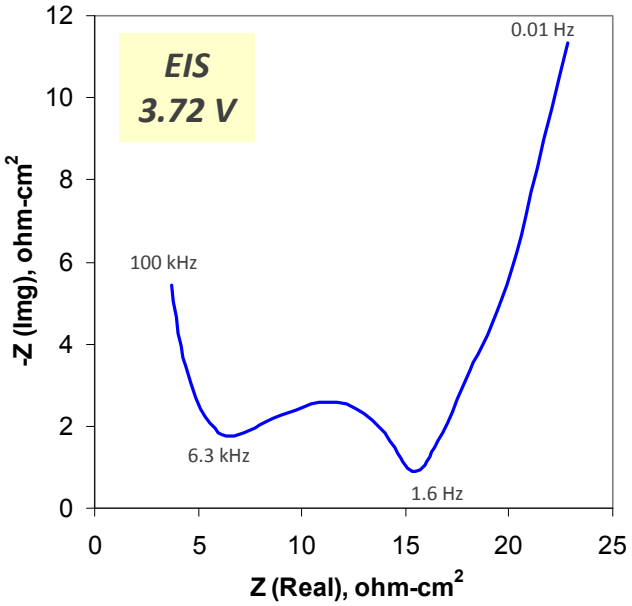
PHEV baseline single-sided electrodes - Full Cell Impedance

Data at 30°C



ASI (18s) ~ 27 ohm-cm² (3.6 to 4V)

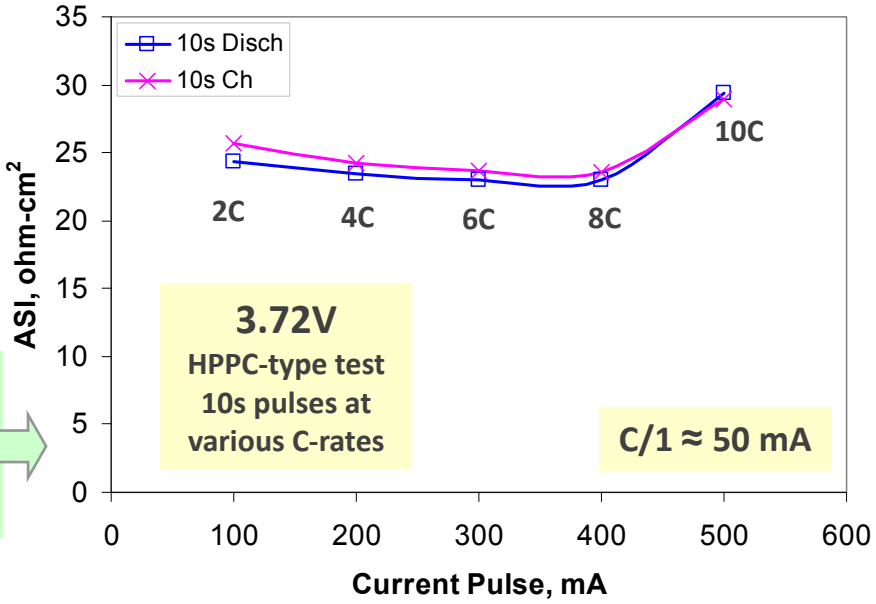
Impedance increases below 3.6V



ASI (2C – 8C) ~ 23 ohm-cm²

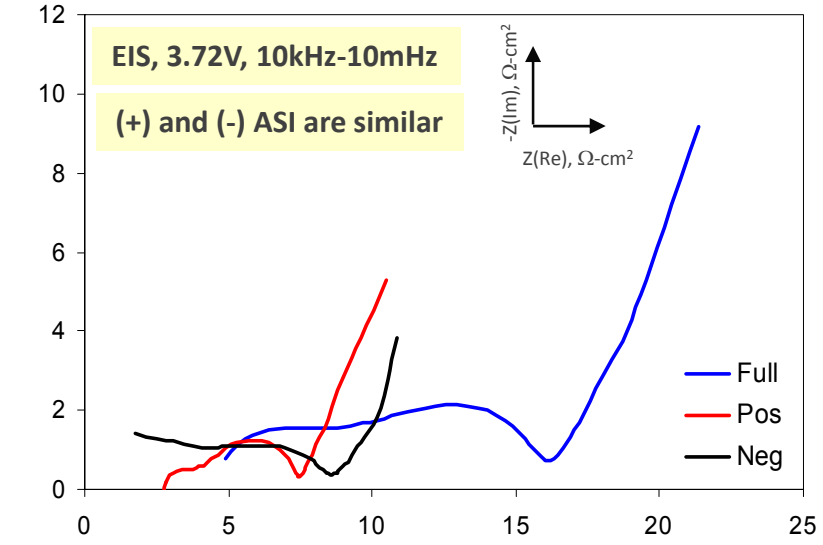
ASI (10C) ~ 29 ohm-cm²

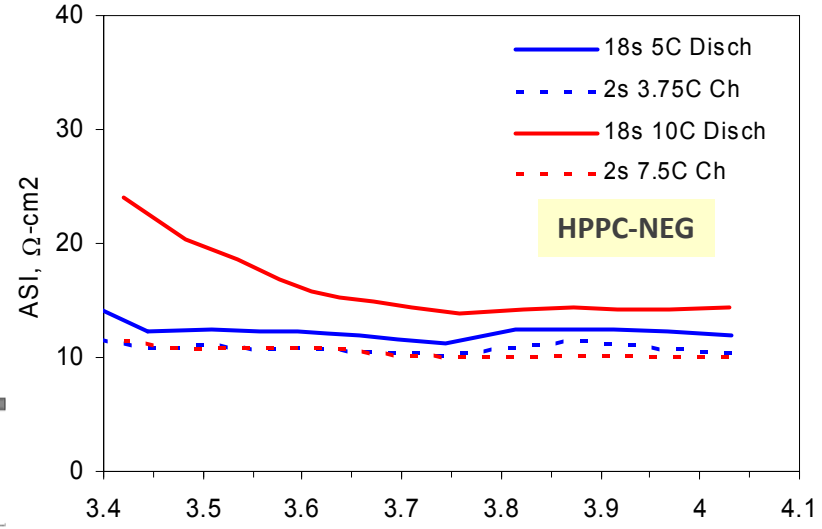
Impedance increases above 8C

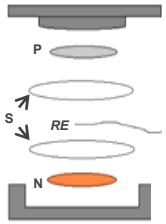


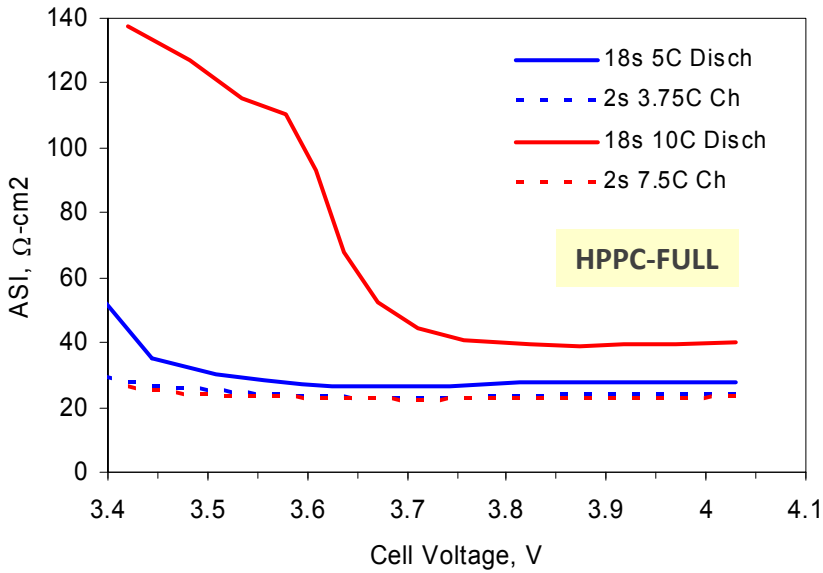
PHEV baseline single-sided electrodes RE Cell Data - EIS and HPPC at 30°C

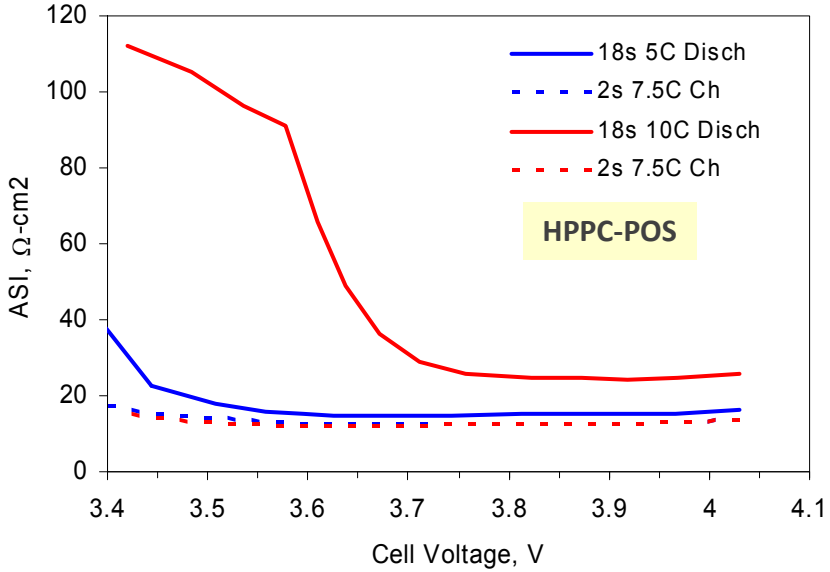
HPPC – Pulse discharge impedance at 10C is higher than at 5C – Arises mainly from the positive electrode











PHEV electrodes/cells - Work in Progress

- **Continue investigation of electrochemical couples (materials and cells) identified for PHEV cells**
  - Examine performance and performance degradation under PHEV test conditions, which include wider voltage windows and greater SOC swings
  - Identify sources and components responsible for performance degradation (capacity fade, impedance rise) and suggest solutions to improve cell life

Diagnostic studies – LiBOB electrolyte systems

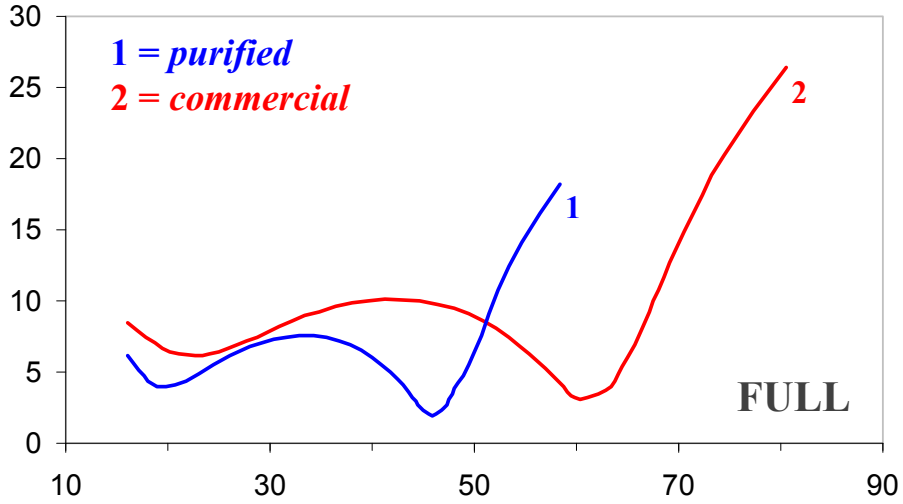
LiBOB salt purity can have a significant and often detrimental effect on cell performance.

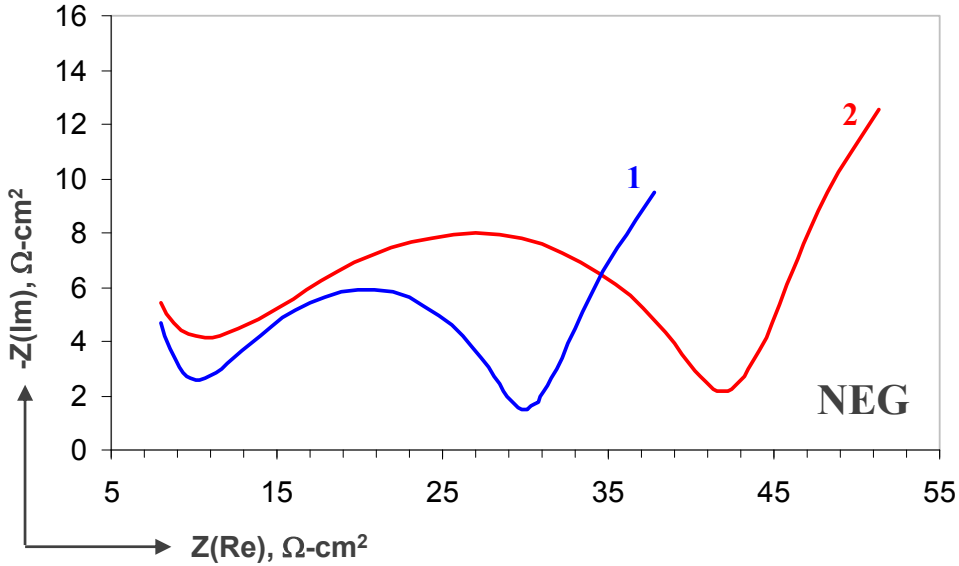
- In a recent article Xu et al.[1] showed that impurities in the LiBOB salt degrade the cycle life of $LiNi_{0.85}Co_{0.1}Al_{0.05}O_2$–bearing large-format (8Ah) cells, especially at elevated temperatures. Their ^{1}H, ^{13}C, and ^{11}B NMR data indicated the presence of oxalate and carboxylate impurities which apparently decompose and generate sufficient gas pressure to vent the cell.
  - **Cells containing purified (recrystallized) LiBOB display significantly improved cycling behavior and thermal stability characteristics.**
- Over the years, we've observed inconsistency in cell performance arising from batch to batch variations in LiBOB purity (all batches from same source)
  - We were unable to dissolve commercial LiBOB (0.7M) in EC:EMC (3:7 by wt.) solvent, but were able to dissolve it in EC:DEC (1:1 by wt) solvent.
  - **LiBOB purified by repeated recrystallization dissolves easily in EC:EMC (3:7 by wt.) solvent.**
  - The impurity apparently inhibits LiBOB dissociation in EC:EMC (3:7 by wt) solvent. **What is this impurity?**

[1]Xu et al., *JES* 155, 2008, p. 959

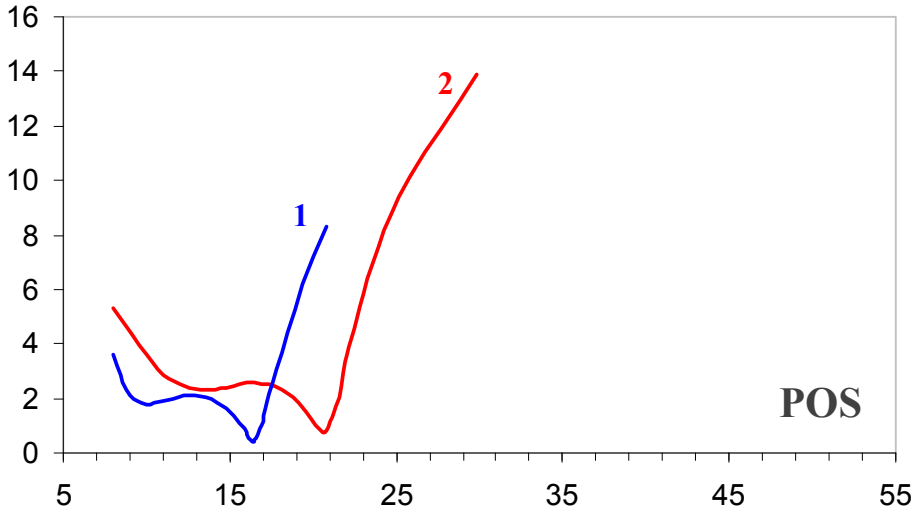
Effect of LiBOB impurity on Impedance

RE cell, Gen2+/- electrodes, 0.7M LiBOB in EC:DEC (1:1 by wt.), 3.72V, 30°C, 25 kHz-0.01Hz



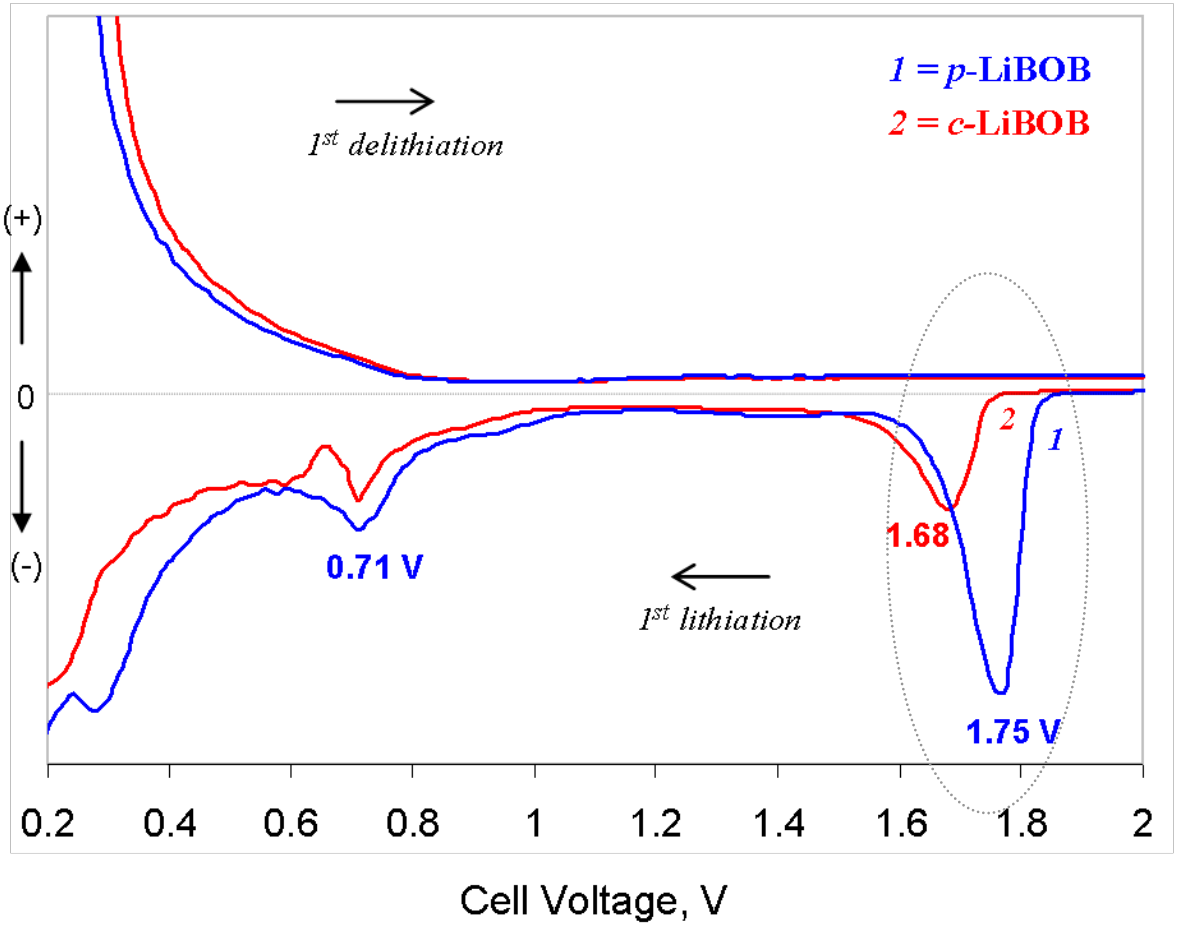


The *commercial* LiBOB cell shows higher impedance. The main effect is on the negative electrode, which suggests that the impurity affects SEI characteristics. There appears to be a small effect on the positive electrode.



Effect of LiBOB impurity

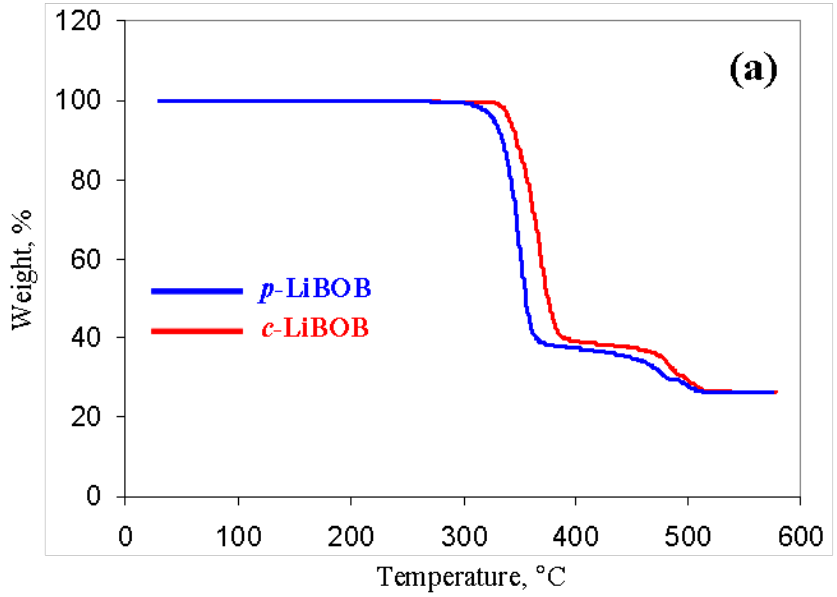
1st cycle differential capacity data – Gen2-//Li cell, Data at 30°C



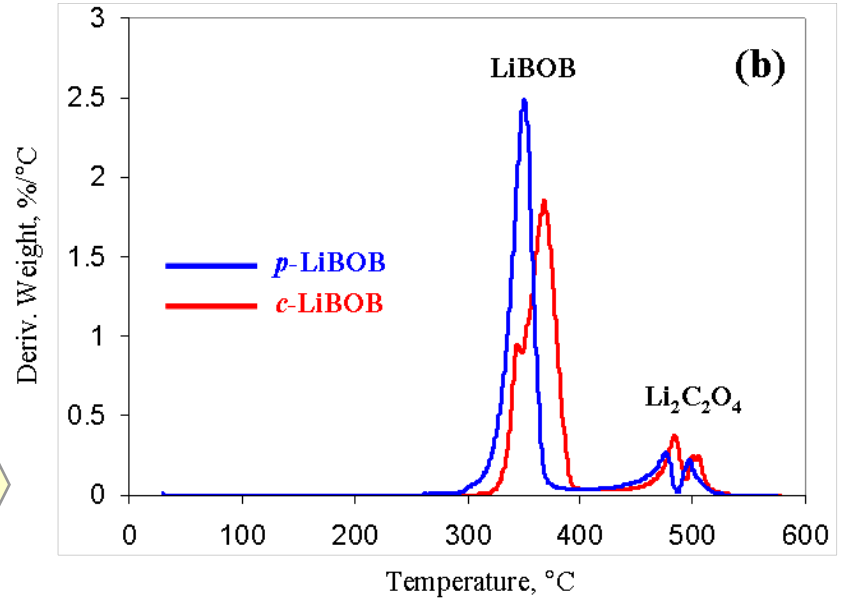
The commercial (c) - LiBOB shows a shorter peak and at a lower voltage than the purified (p) – LiBOB. Impurities inhibit reduction of LiBOB salt.

TGA data showing (a) weight change and (b) derivate of weight change on LiBOB salts

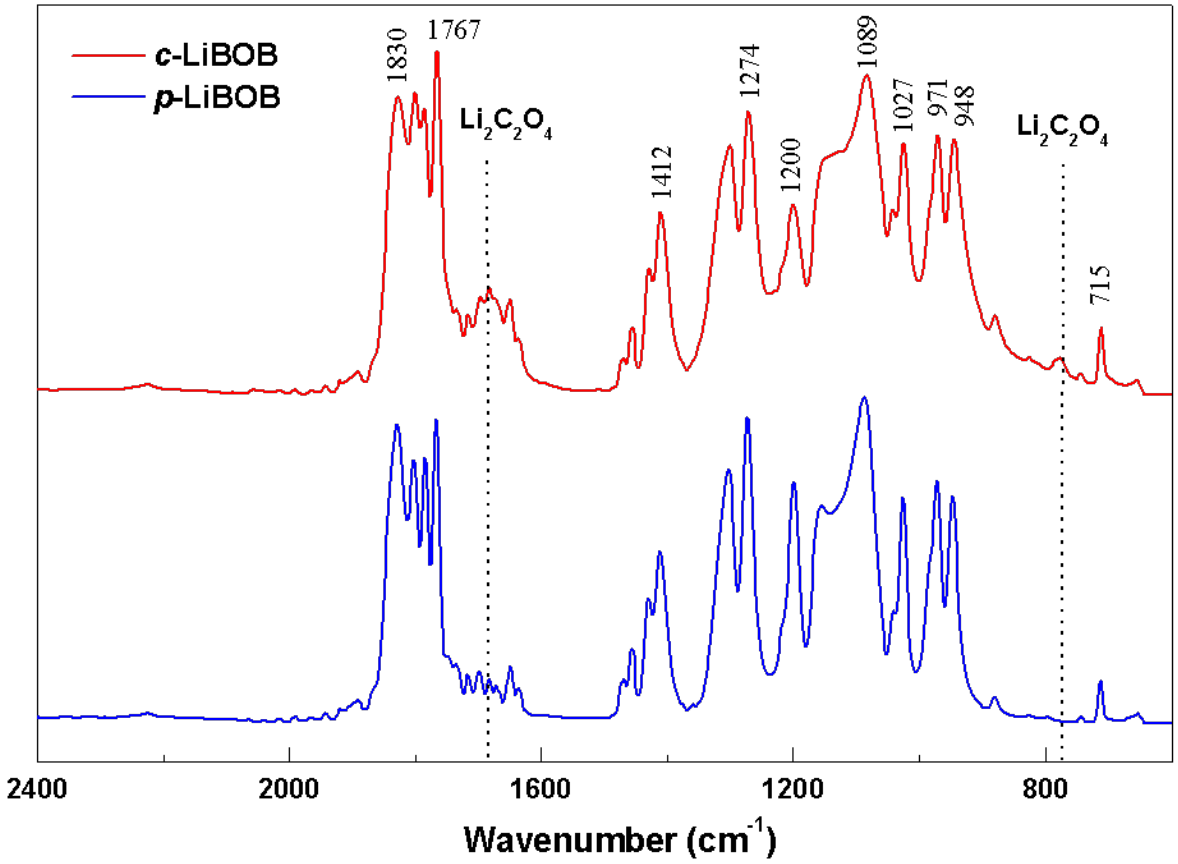
The weight change data shows that c-LiBOB has a higher onset-T for decomposition and lower weight loss in the 300 to 400 ° C range.



The weight change derivative shows a single low temperature peak for p-LiBOB, but two peaks for c-LiBOB. The lower peak (~ 350° C) in the c-LiBOB data corresponds to the pure LiBOB salt, whereas the higher peak (~ 370° C) is consistent with the presence of mixed aggregates or co-crystals of LiBOB with an impurity compound.

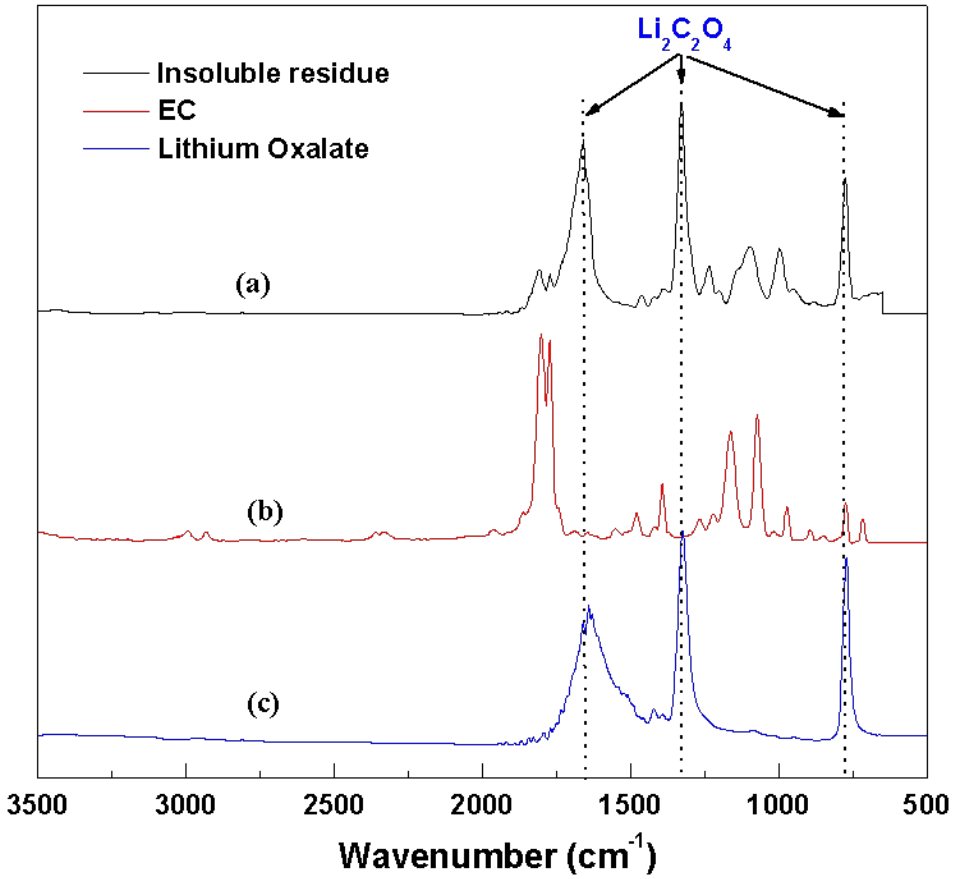


$^{1}H, ^{13}C, ^{11}B$ NMR spectra obtained from *c*-LiBOB and *p*-LiBOB salt were very similar. But differences observed in FTIR data



The *c*-LiBOB spectrum contains additional absorptions at 1658 and 778 cm^{-1} that suggest the presence of lithium oxalate in the sample.

FTIR spectra from *c*-LiBOB residue after attempted dissolution in 3EC:7EMC solvent. *EC and lithium oxalate spectra shown for comparison.*



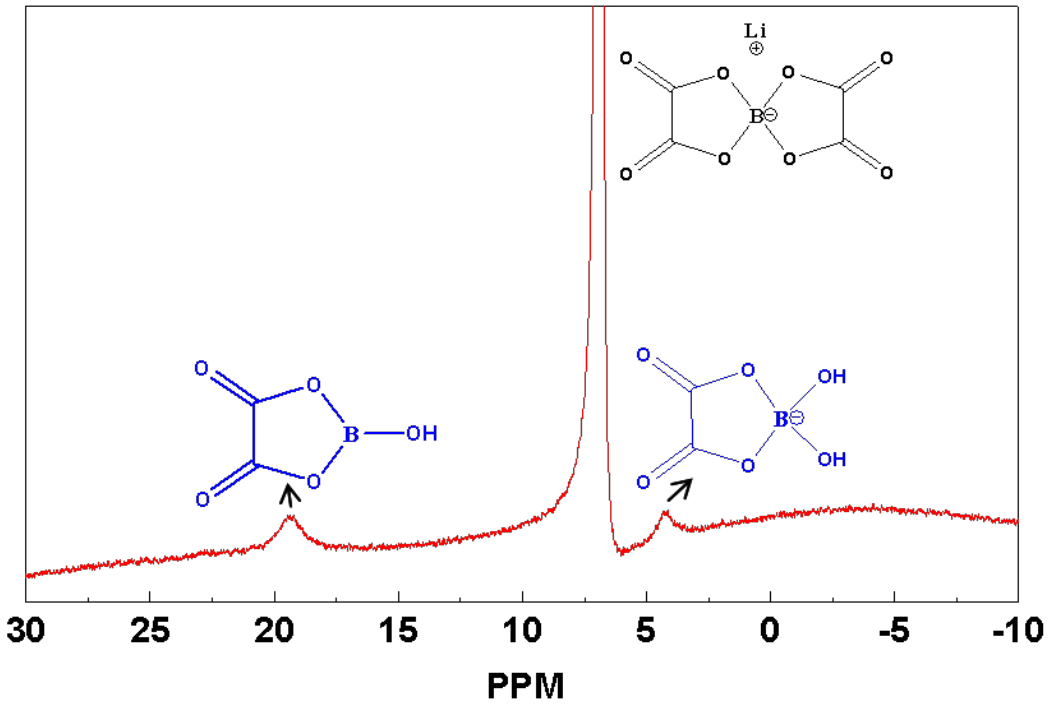
Insoluble residue spectrum contains significant absorptions at 1658, 1328, and 775 cm^{-1}, which are characteristic of $Li_2C_2O_4$

The *c*-LiBOB sample contained a lithium oxalate impurity probably as a co-crystal (or mixed aggregate) with the pure LiBOB salt.

LiBOB-bearing electrolytes containing trace amounts of water (~100 ppm) are known to be relatively stable.

What happens at higher moisture contents *(that may result from "improper" salt storage in high-humidity environments)*?

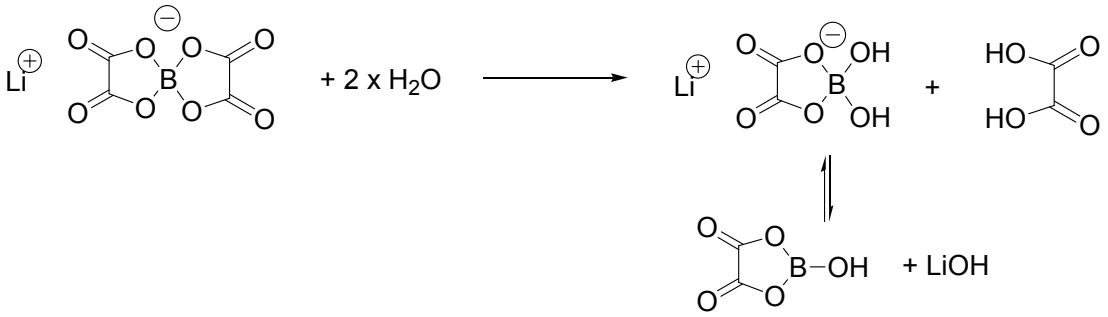
^{11}B NMR spectrum of *p*-LiBOB salt exposed to 100 % humidity at RT for 12 hours

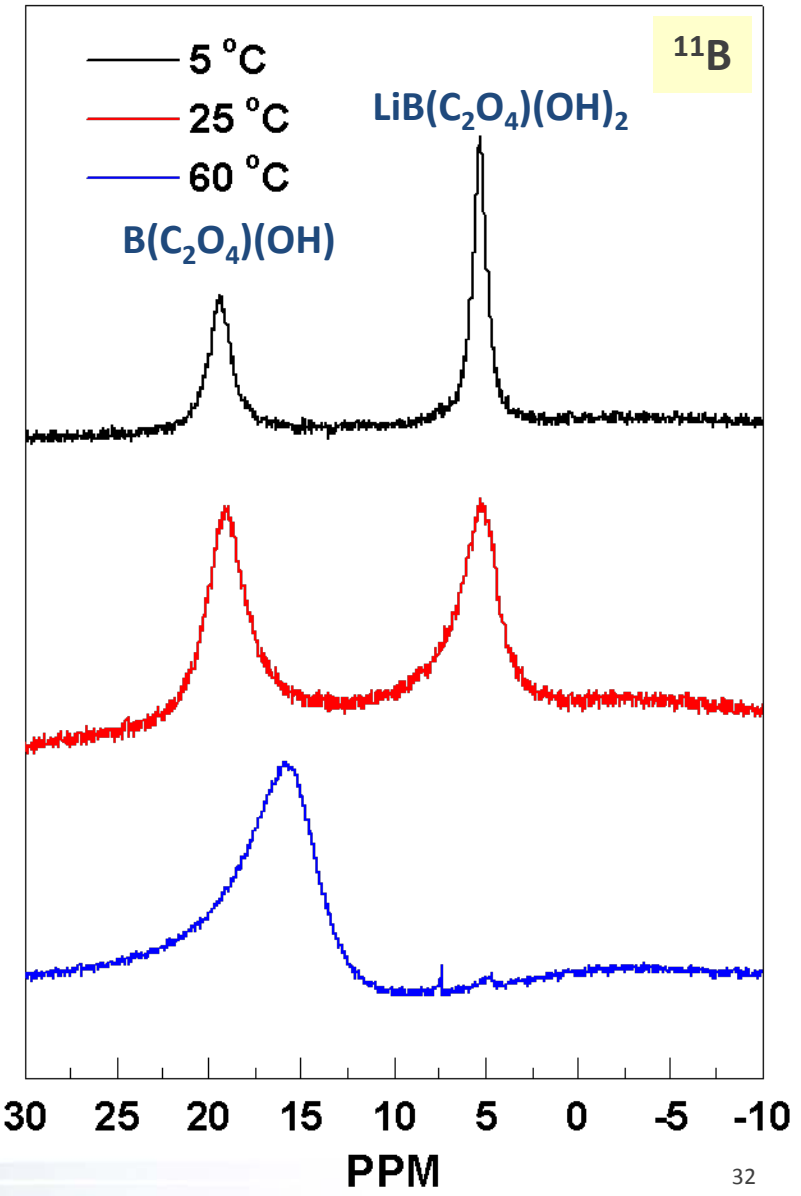


In addition to the main LiBOB peak at ≈7 ppm, peaks from $LiB(C_2O_4)(OH)_2$ (≈4.5 ppm) and $B(C_2O_4)(OH)$ (≈20 ppm) are observed. Peak identities confirmed by model experiments.

Variable temperature NMR spectroscopy of *p*-LiBOB soaked in water for 12h. *Data at 5 ° C, 25 ° C, and 60 ° C.*

Broadness of ^{11}B signals suggest a continuous exchange of $LiB(C_2O_4)(OH)_2$ and $B(C_2O_4)(OH)$. We propose the following scheme for the LiBOB-water reaction:





Summary

- The objective of our diagnostic studies is to obtain a fundamental understanding of materials and processes responsible for system performance and performance degradation. Our approach is to employ electrochemical- and physicochemical- diagnostic techniques, which include a combination of spectroscopy, microscopy, diffraction, and chemical analysis techniques.
- We've been studying the structure and structural rearrangements in Mn-based layered oxide materials that are relevant from a PHEV perspective. Our AEM data on defect-free Li_2MnO_3 show Li-ordering in the transition metal (Mn) planes. Microscopy and spectroscopy studies on as-prepared $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ indicate that the sample contains an intimate mixture of Li_2MnO_3–like and $LiCoO_2$–like areas. Studies on $Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$ show that Li atoms are ordered both in, and normal to, the transition metal planes in the as-prepared material. Studies on cycled electrodes indicate loss of Li_2MnO_3–like ordering in the TM planes after high-voltage cycling (> 4.5V). We're currently studying the phase transformations that result from high-voltage cycling/aging of these oxides and plan to correlate the phase transformation characteristics to oxide performance (capacity/impedance behavior).
- We've concluded studies on Gen3 cells and constituents and documented the data.
- We've initiated the characterization of PHEV baseline electrodes and cells. Microscopy, diffraction, and electrochemical data (cycling, impedance) have been obtained. Future plans include performance and performance degradation studies of other electrochemical couples identified for PHEV cells.
- We continue to (a) examine SEI formation on graphite electrodes in various electrolyte systems, (b) correlate surface film formation and electrochemical performance of positive electrode materials, and (c) correlate of electrolyte composition and electrolyte additives to cell performance and performance degradation (i.e., effect on calendar life).