Diagnostic Studies on Li-Battery Cells and Cell Components

Project Id: ES032

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Overview

Timeline

- Start date: FY10
- End date: On-going
- Percent complete:
  - project on-going

Budget

- Total project funding
  - 100% DOE
- FY10: $600K
- FY11: $600K

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners

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

Project Objectives - Relevance

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

- To identify constituents and mechanisms responsible for cell performance and performance degradation through the use of advanced characterization tools

- To recommend solutions that improve performance and minimize performance degradation of materials, electrodes, and cells

- To enable a safe, 40-mile range PHEV battery that will last 10y and thereby reduce petroleum consumption in vehicular applications

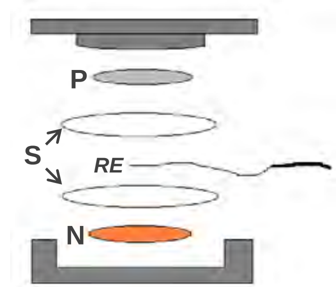
Approach

- **Multi-institution effort to identify factors that contribute to cell performance and performance degradation (capacity fade, impedance rise)**
  - *Includes development of novel diagnostic tools*

Electrochemistry
(ANL, INL)
Coin, pouch, prismatic, cylindrical cells

Electrochemical Couples

Electrochemistry (ANL)
Reference Electrode cells – identify cell components responsible for impedance rise

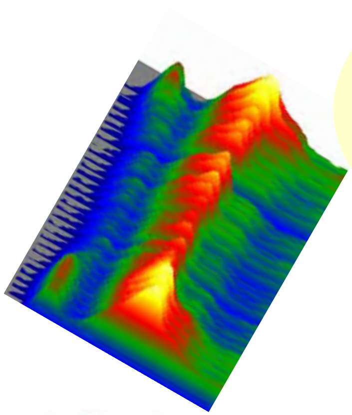


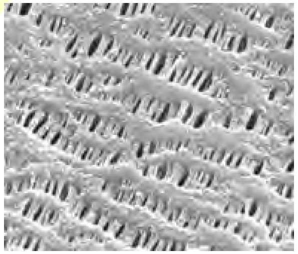
Disassembly of New and Aged Cells

Electrode Surface & Bulk Analyses (ANL, BNL, LBNL)

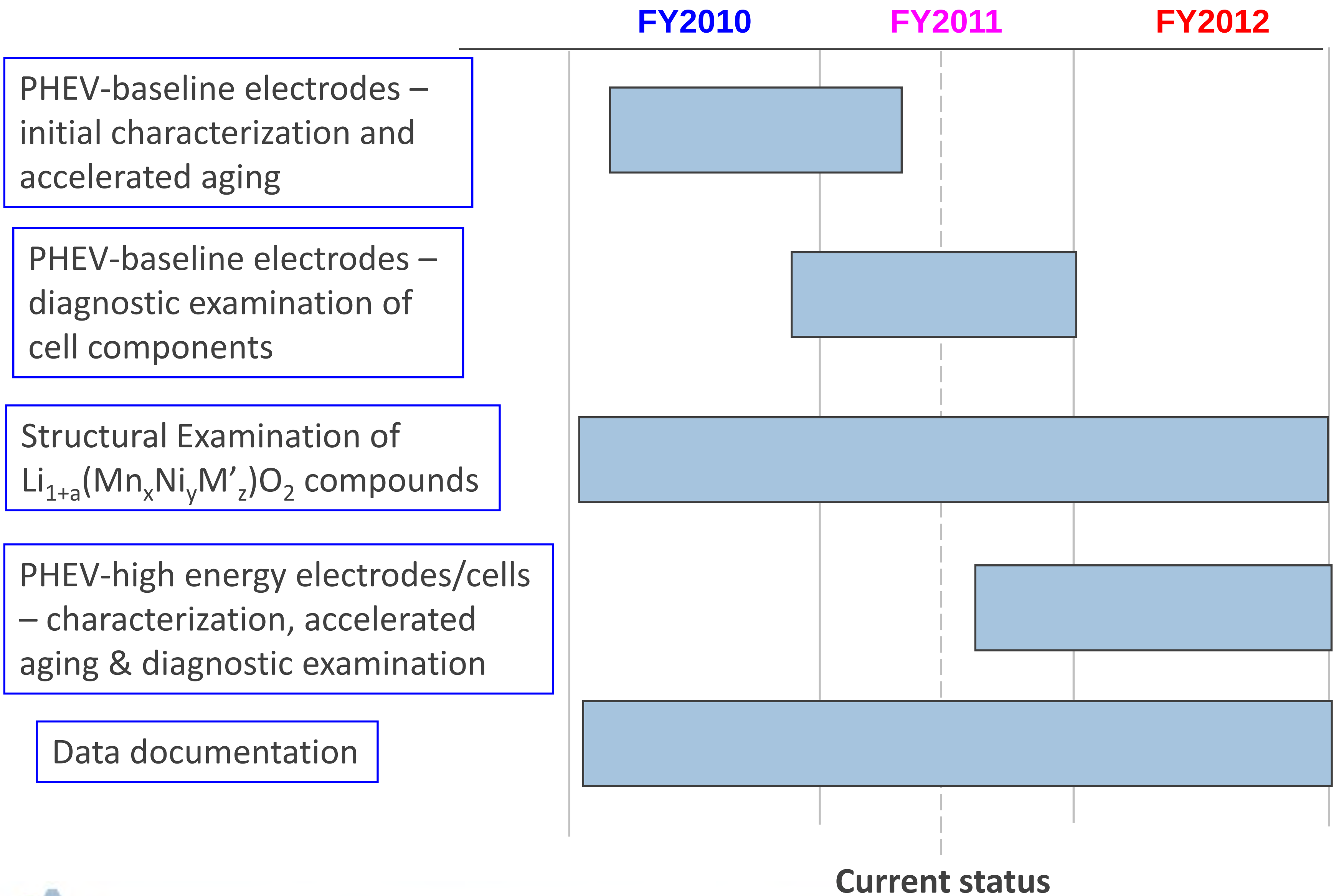
Electrolyte & Separator study (ANL, LBNL)

(UIUC, URI)





Milestones

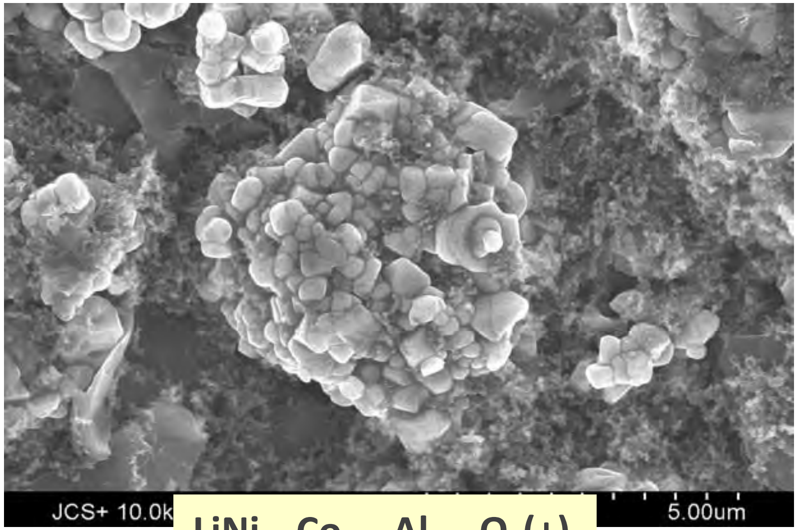

FY2010
FY2011
FY2012
PHEV-baseline electrodes – initial characterization and accelerated aging
PHEV-baseline electrodes – diagnostic examination of cell components
Structural Examination of $Li_{1+a}(Mn_xNi_yM'_z)O_2$ compounds
PHEV-high energy electrodes/cells – characterization, accelerated aging & diagnostic examination
Data documentation
Current status

Technical Accomplishments and Progress

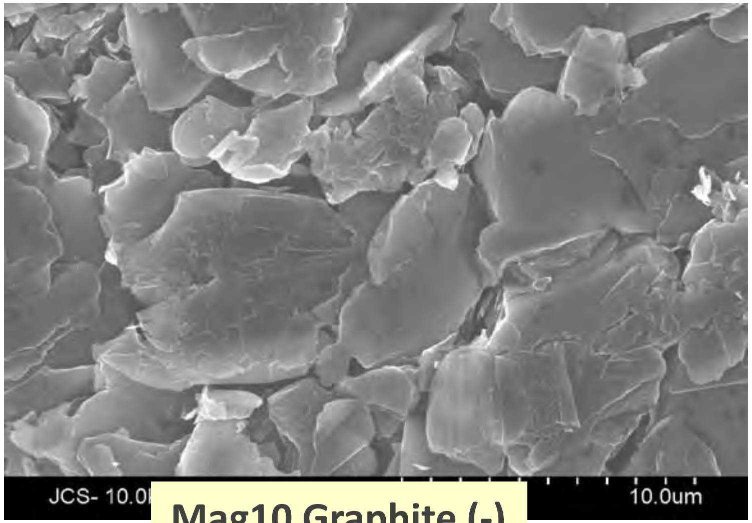
- Completed accelerated aging of PHEV baseline cells *(met milestone)*
  - Obtained capacity and impedance (EIS and HPPC) data on full cells with and without a reference electrode
- Initiated diagnostic examination of PHEV baseline cells and cell constituents *(met milestone)*
  - Conducted electrochemical measurements on electrodes harvested from disassembled cells
  - Examination of harvested cell components using diffraction, microscopy, and spectroscopy techniques is in progress
- Continued Investigation of Long Range and Local Structure of $Li(Li_xMn_aNi_bM'_c)O_2$ compounds
  - Completed structural study of as-prepared $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ *(met milestone).* Determined that the oxide contains a mixture of Li_2MnO_3-like and $LiCoO_2$-like areas, which are integrated and interconnected at the atomic scale
  - Initiated structural study of cycled $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ samples *(met milestone)* Observed differences in local atom arrangements between as-prepared and cycled samples may be responsible for changes in the oxides' voltage profile

PHEV baseline electrode chemistry

	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**



$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$(+)

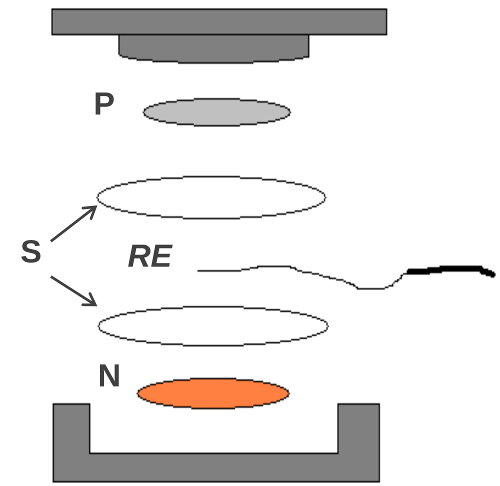


Mag10 Graphite (-)

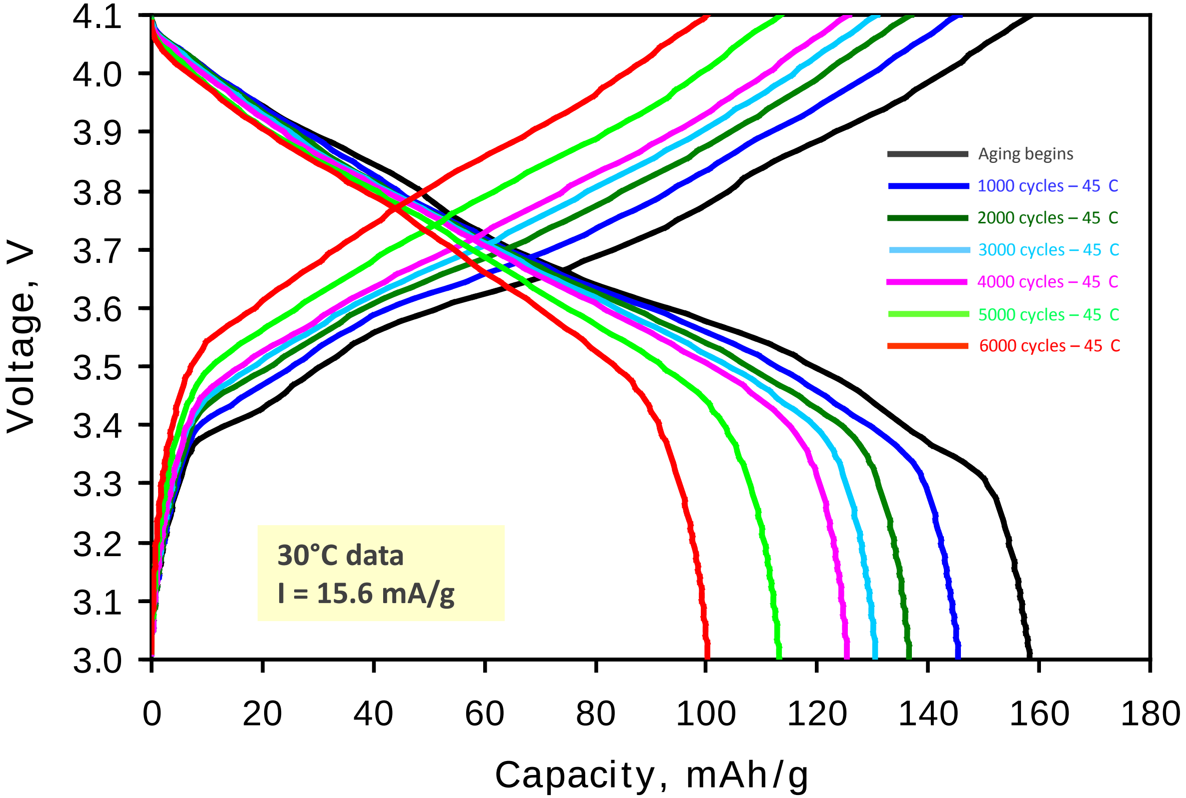
*with S. McLaren, UIUC

Excellent data obtained on cells with and without a Reference Electrode

Cells contain
Single-sided electrodes (20.3 cm^2), Celgard 2325 separator
Gen2 electrolyte (1.2M $LiPF_6$ in 3EC:7EMC)



Representative Capacity-Voltage plots

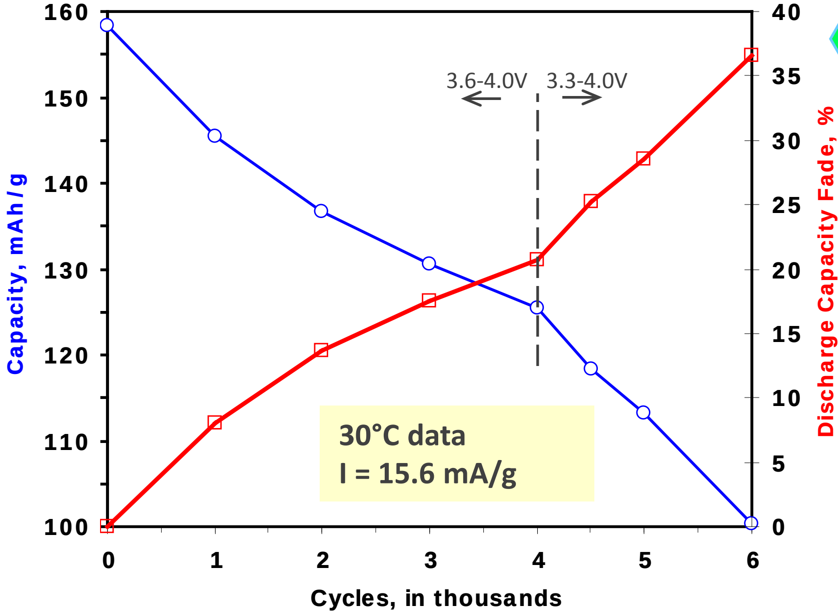


Representative Example

Cell was on test for > 1y
Cell cycling/aging at 45°C
Cell capacity and impedance measured periodically at 30°C

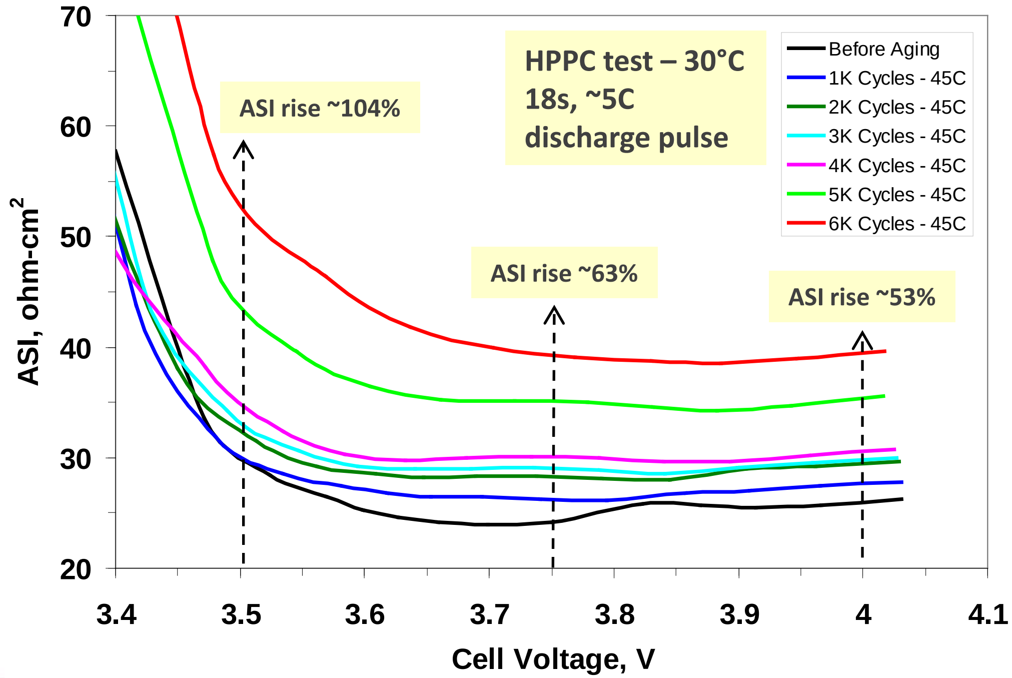
Cells show capacity loss and impedance rise on aging

Aging Protocol: C/1 cycling at 45°C; 4000 cycles (3.6 – 4.0V), 2000 cycles (3.3 - 4.0V)



Rate of capacity fade greater for wider voltage window

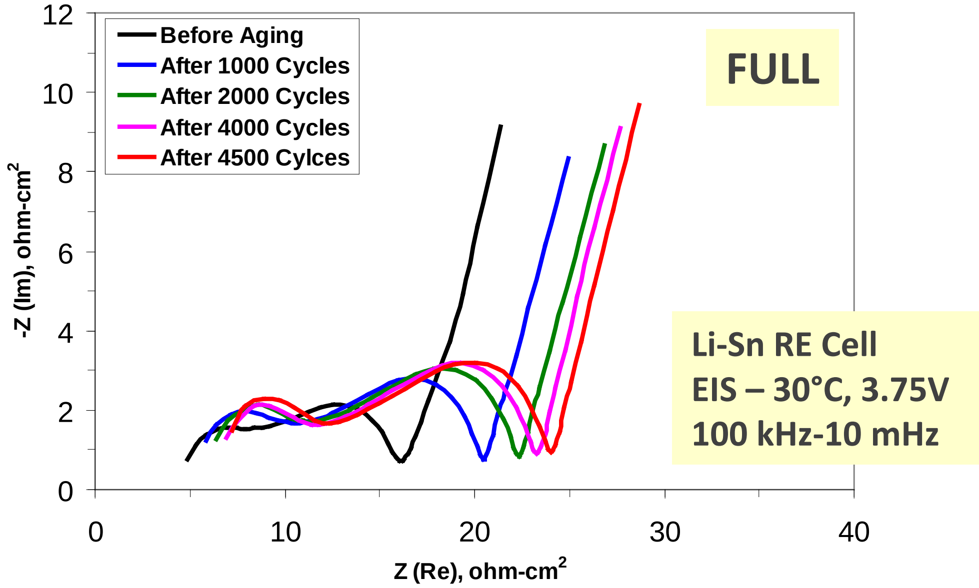
Impedance rise greater for wider voltage window. Impedance rise is non-uniform across voltage range – rise greater at voltages < 3.6 V

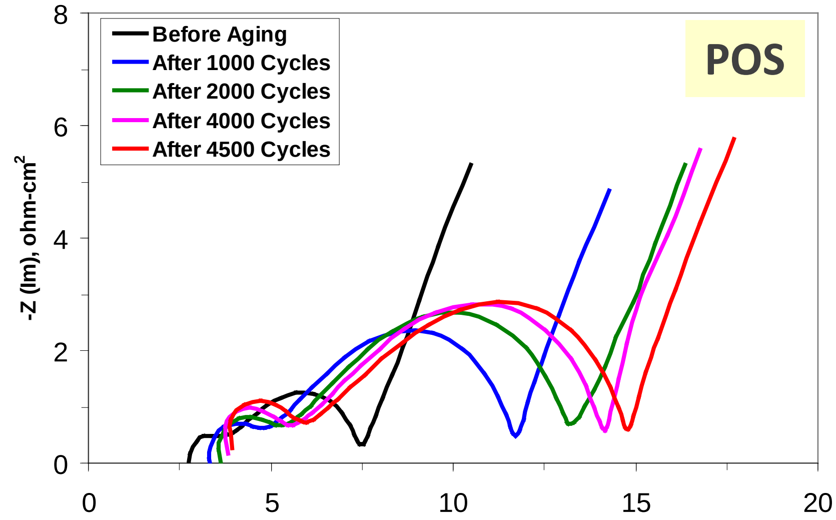


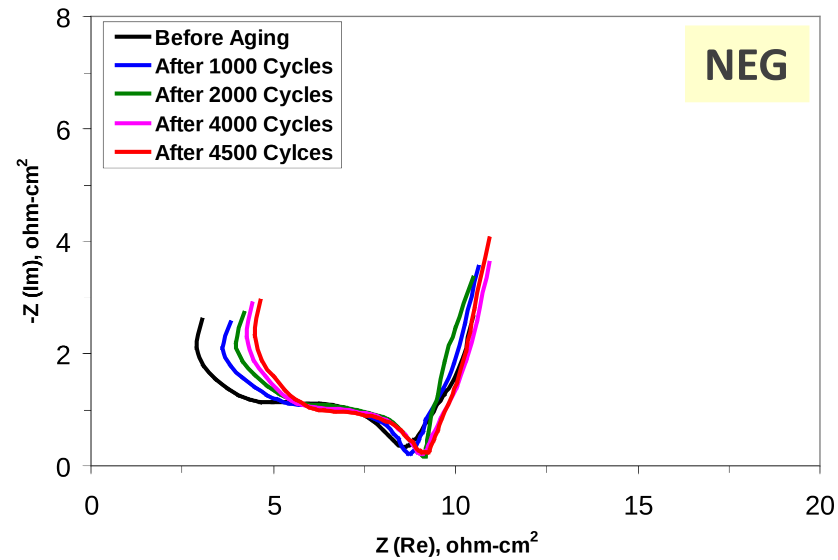
Performance degradation is greater for wider voltage cycling windows. That is, when a larger proportion of the Li^+ inventory is shuttled between the electrodes. Wider windows are typical of PHEV and EV profiles.

AC impedance data is consistent with HPPC data

Aging Protocol: C/1 cycling at 45°C; 4000 cycles (3.6 – 4.0V), 500 cycles (3.3 - 4.0V)





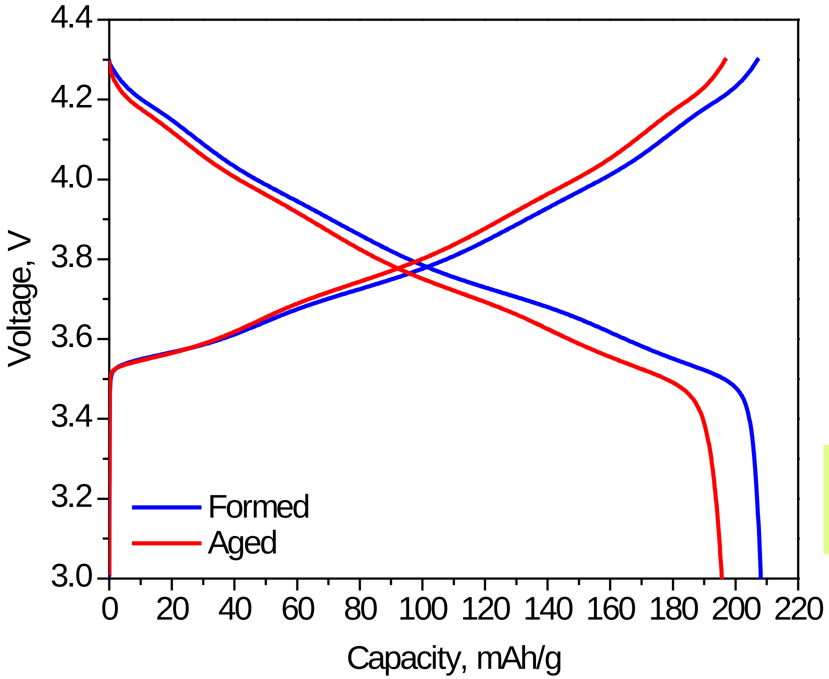


Full cell impedance increases on aging

Data from cells with a Li-Sn reference electrode show that negative electrode contribution is minimal. The impedance rise arises mainly at the positive electrode, and can be attributed to processes (i) at the electrode-electrolyte interface (mid-frequency arc) and (ii) within oxide bulk (Warburg diffusion tail – *data not shown*).

Electrochemistry on harvested electrodes shows that positive electrode contribution to "true" capacity fade is small

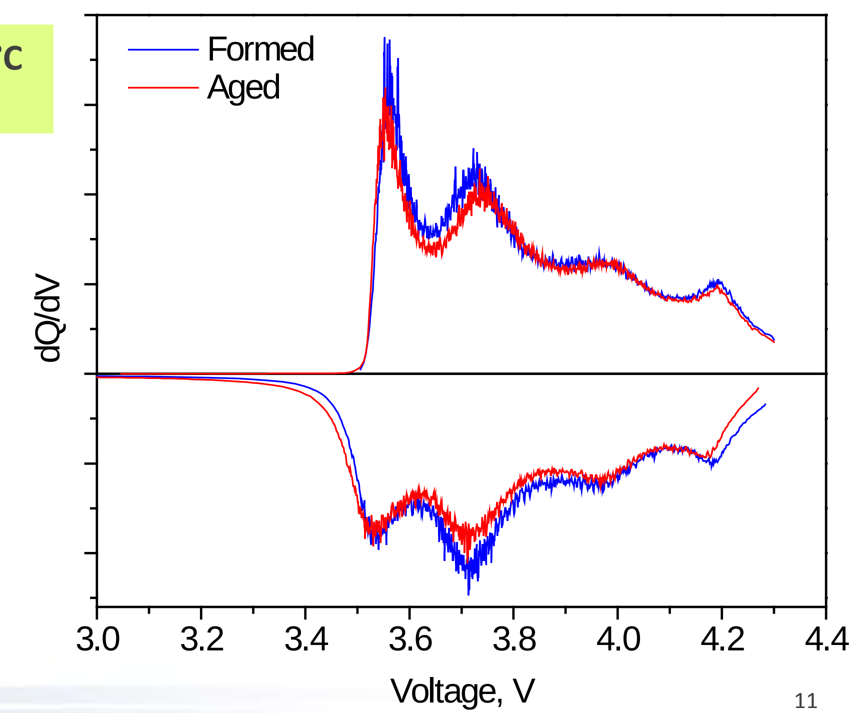
Li$^+$ consuming processes at negative electrode cause cell capacity fade



Formed and Aged samples were harvested from full cells discharged to < 2V.
Formed: 3 – 4.1V, 3X, 30C
Aged: C/1 cycling at 45°C; 4000 cycles (3.6 - 4V), 2000 cycles (3.3 - 4V), after formation cycling

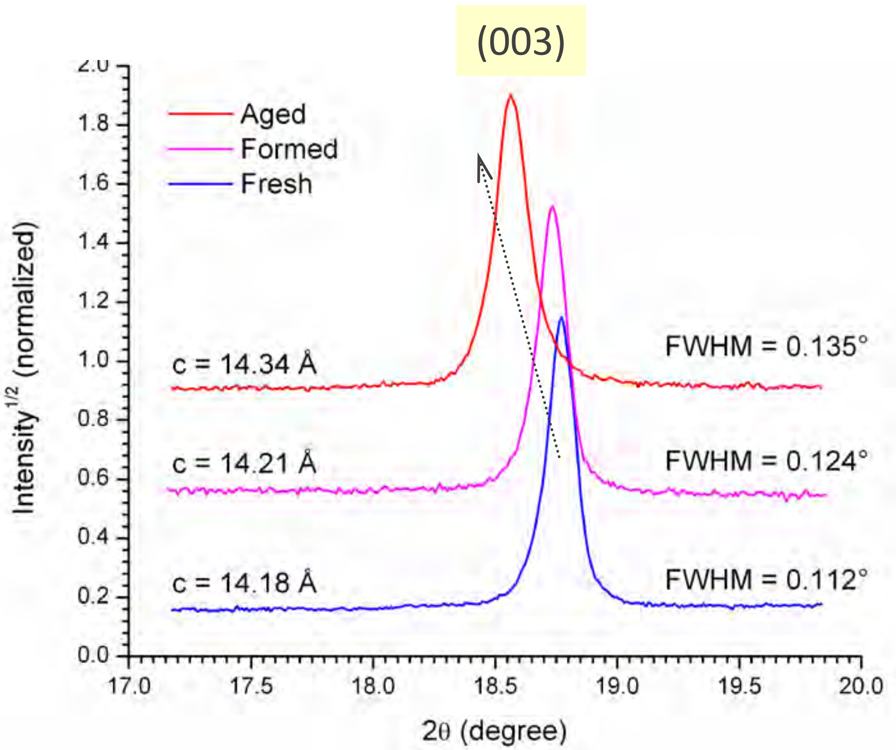
Data from coin cells with "harvested" positive electrodes, Li, and 3EC:7EMC+1.2M $LiPF_6$ electrolyte

3 – 4.3V, 30°C
~C/30 rate



Lithiation capacity of aged cell electrode is only slightly (~7%) smaller than that of formed cell electrode – also dQ/dV profiles are very similar. Data indicate (i) good oxide "phase stability", and (ii) "electronic isolation" of oxide particles (if any) is small.

X-ray diffraction (XRD) data* on positive electrodes show oxide structure changes that are consistent with Li-loss on aging



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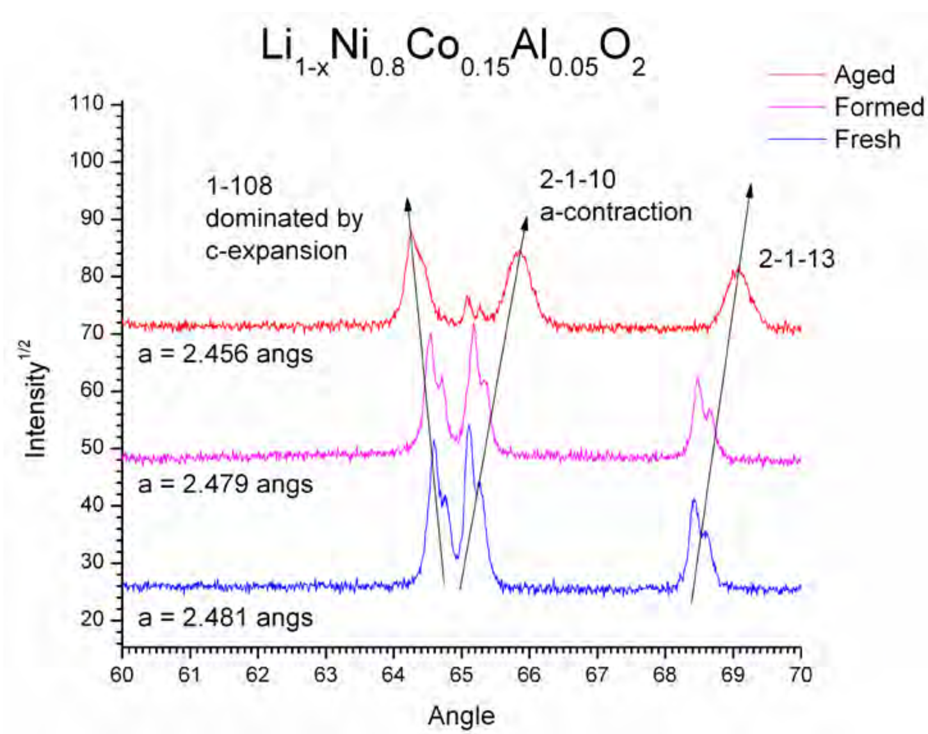


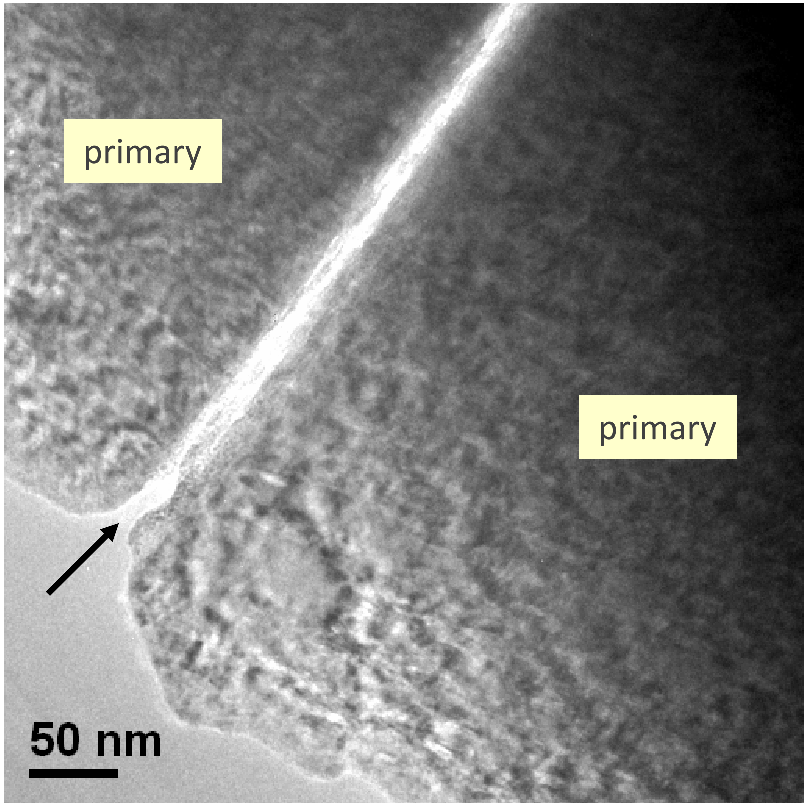
Peak shifts indicate c-axis expansion and a-axis contraction on aging

Data indicate that aged samples contain Li-deficient oxides, as expected

*with M. Sardela, UIUC

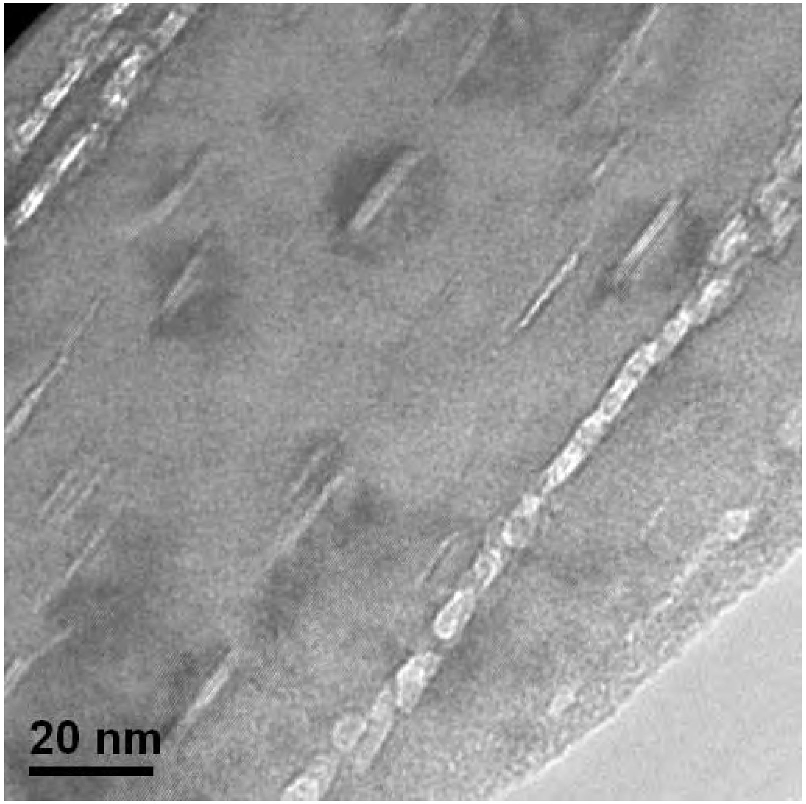
Transmission electron microscopy (TEM) data* show defects within oxide particles of aged positive electrode samples

Aged Sample: C/1 cycling at 45°C; 4000 cycles (3.6 – 4.0V), 2000 cycles (3.3 - 4.0V)



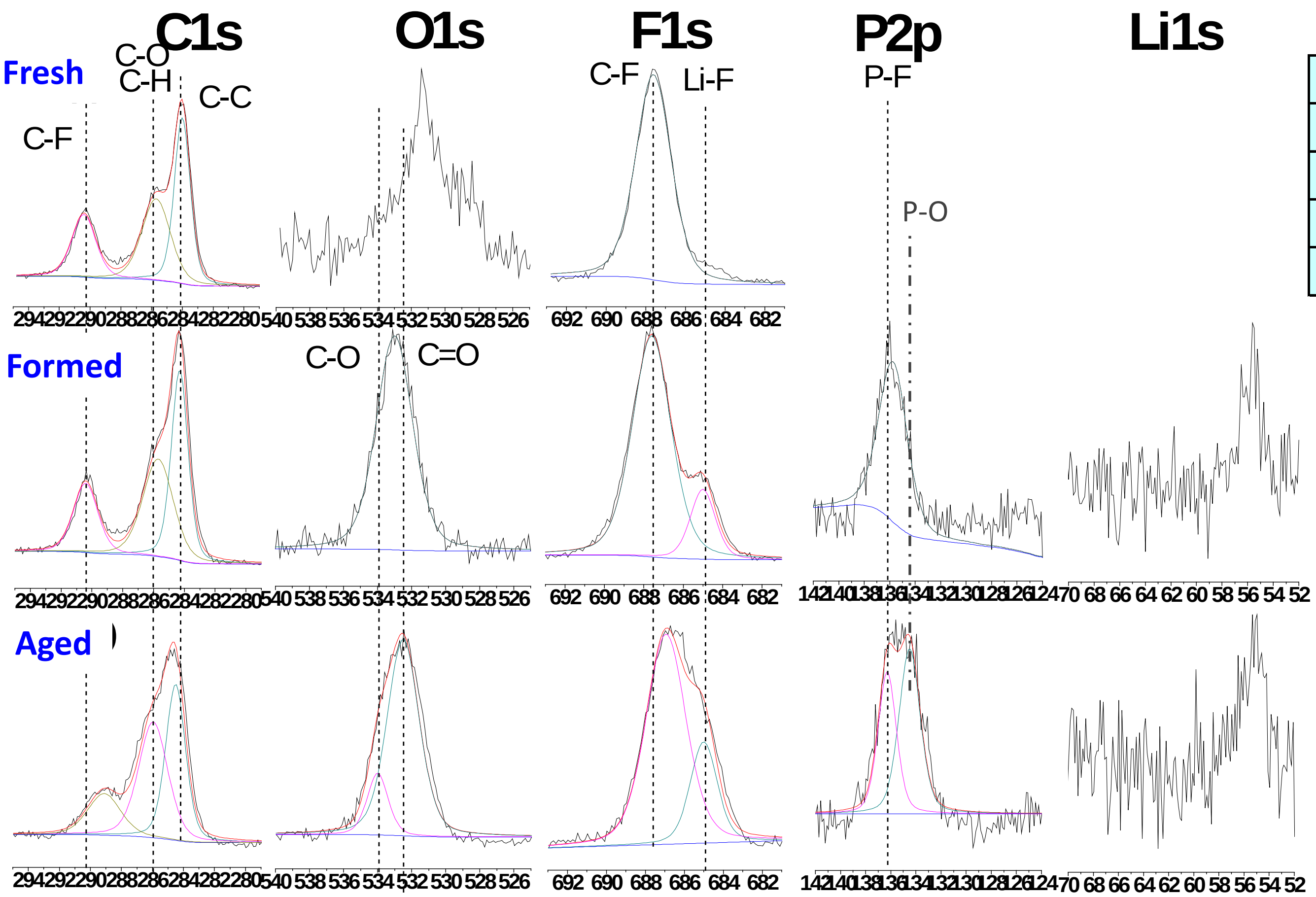
Gaps filled with electrolyte decomposition products observed between oxide primary particles

Highly aligned strings of voids; strain fields near voids



*with J.G. Wen, UIUC

X-ray photoelectron spectroscopy (XPS) data* show that positive electrode surface films change on aging



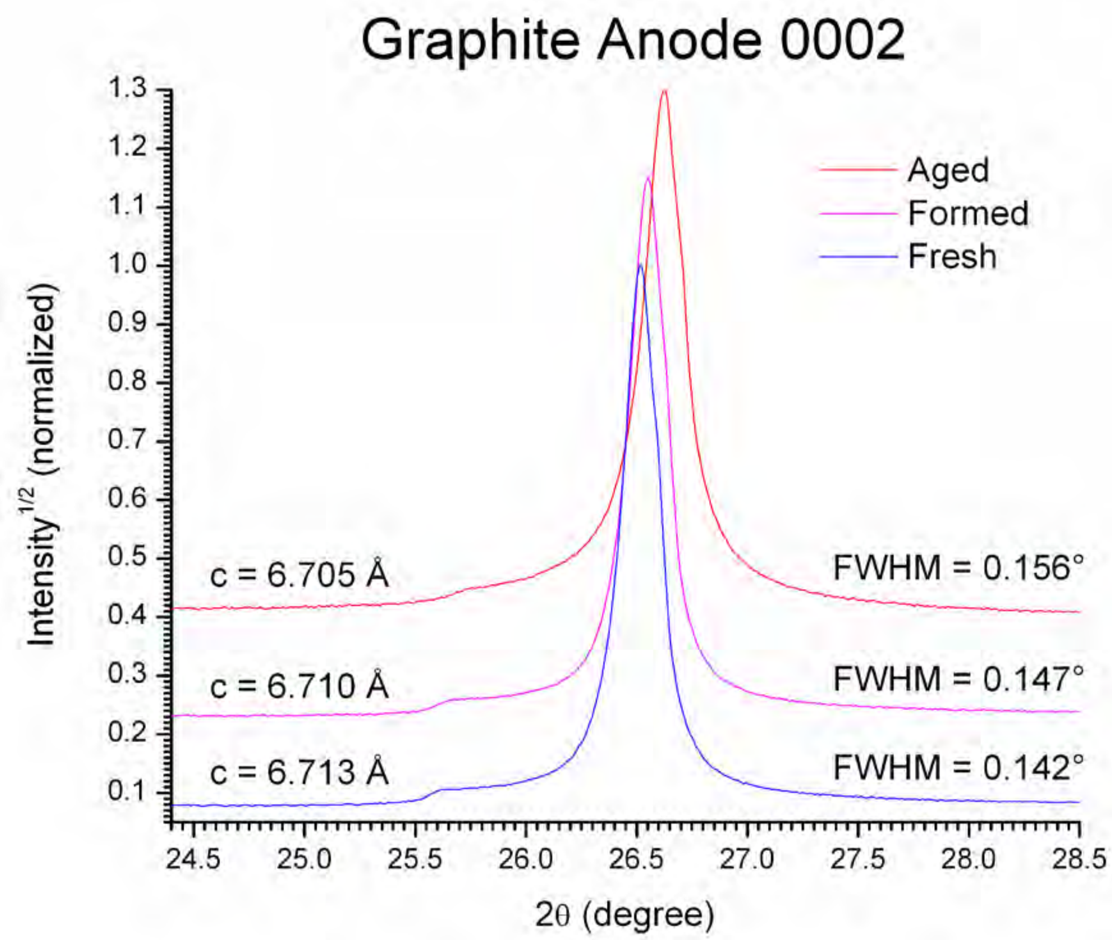
Sample	C1s	F1s	O1s	P2p	Li1s
	at%	at%	at%	at%	at%
Fresh	67	25	3		4
Formed	52	26	4	2	16
Aged	38	17	14	4	26

Aged sample shows less C and F, but more O, P and Li

Aged sample surface films appear more "inorganic", i.e., dominated by salt-decomposition products (e.g. $Li_xPF_yO_z$)

***with B. Lucht et al., URI**

Negative electrode study shows that graphite bulk structure is not damaged by cell aging process



Formed and Aged samples are from full cells discharged to < 2V.
Formed: 3 – 4.1V, 3X, 30C
Aged: C/1 cycling at 45°C; 4000 cycles (3.6 – 4.0V), 2000 cycles (3.3 - 4.0V), after formation

X-ray diffraction data* show that graphite lattice parameter and peak shape changes on aging are small

Li^+ trapped in graphite SEI appears to be the main cause of cell capacity fade

Graphite SEI changes are apparent in XPS data (not shown)

***with M. Sardela, UIUC**

Positive electrodes in next set of ABR cells will contain the high-energy layered oxides $Li(Li_xMn_aNi_bM'_c)O_2$

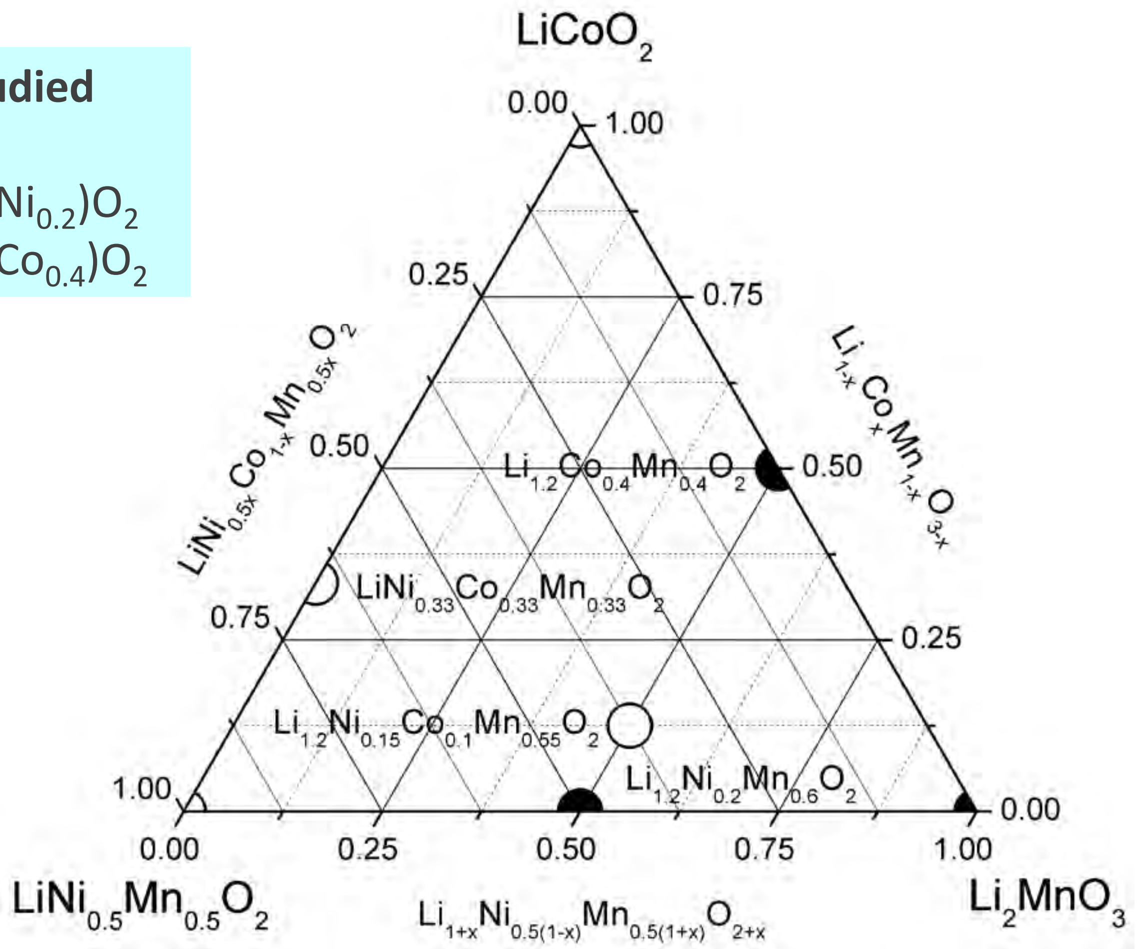
Oxide performance is related to atomic arrangements in the crystal lattice – performance degradation is associated with crystal structure changes on aging

Samples studied

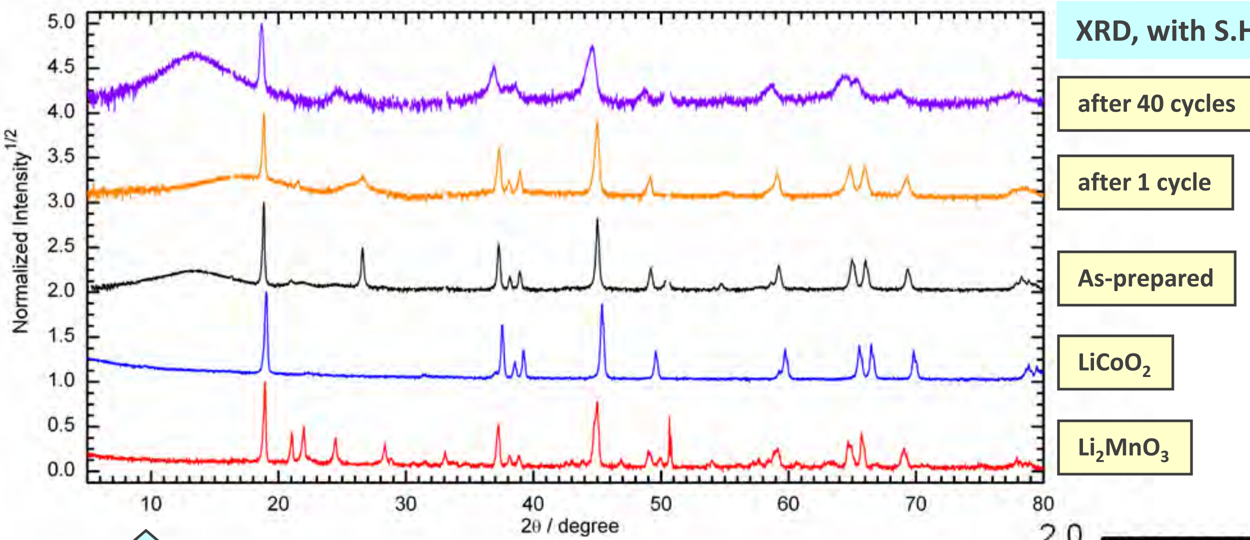
Li_2MnO_3

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

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



Long Range and Local Structure in Layered $Li(Li_xMn_aNi_bM'_c)O_2$ are being studied by X-ray and Electron Beam Techniques



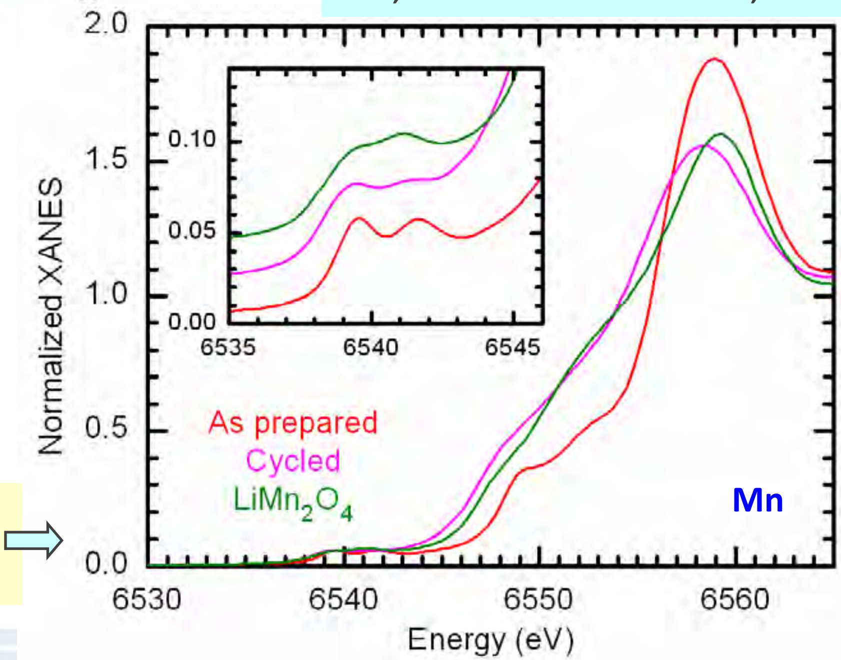
XRD, with S.H. Kang, ANL

X-ray diffraction (XRD) data provide information on long-range (average) structure of crystal lattice

XRD data of $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ samples show no obvious evidence of new phase formation after cycling

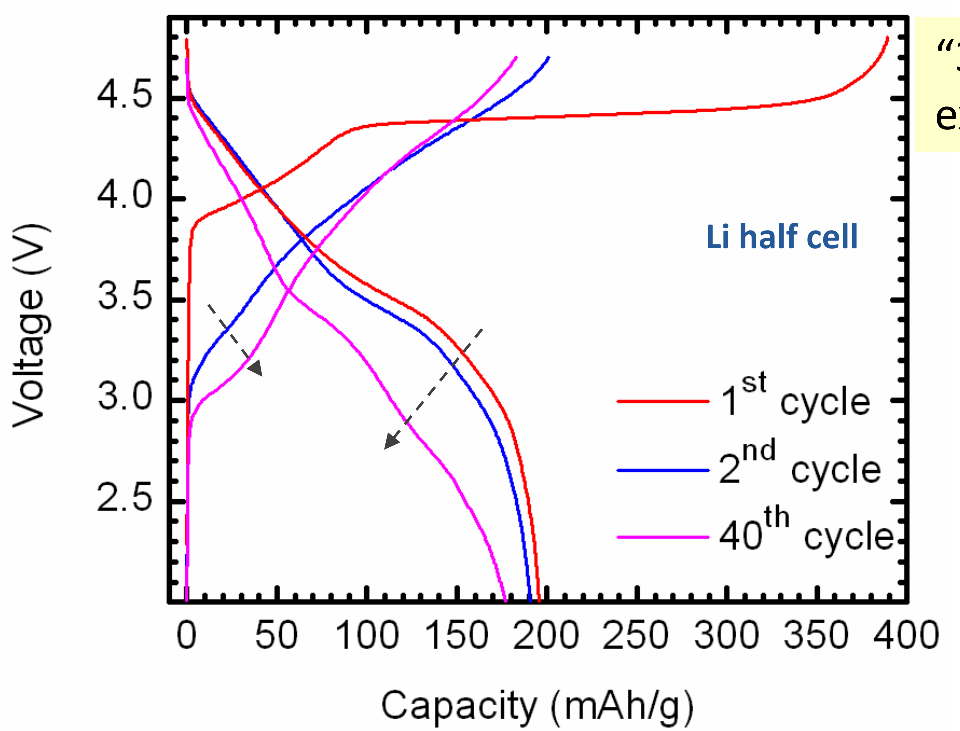
X-ray absorption spectroscopy (XAS) data provide information on local arrangements in lattice

XAS, with M. Balasubramanian, ANL



XAS data from cycled $Li(Li_{0.2}Mn_{0.4}Co_{0.4})O_2$ samples show evidence of Mn-reduction

Voltage profile changes observed in oxides from cycled/aged cells may be caused by presence of spinel phase



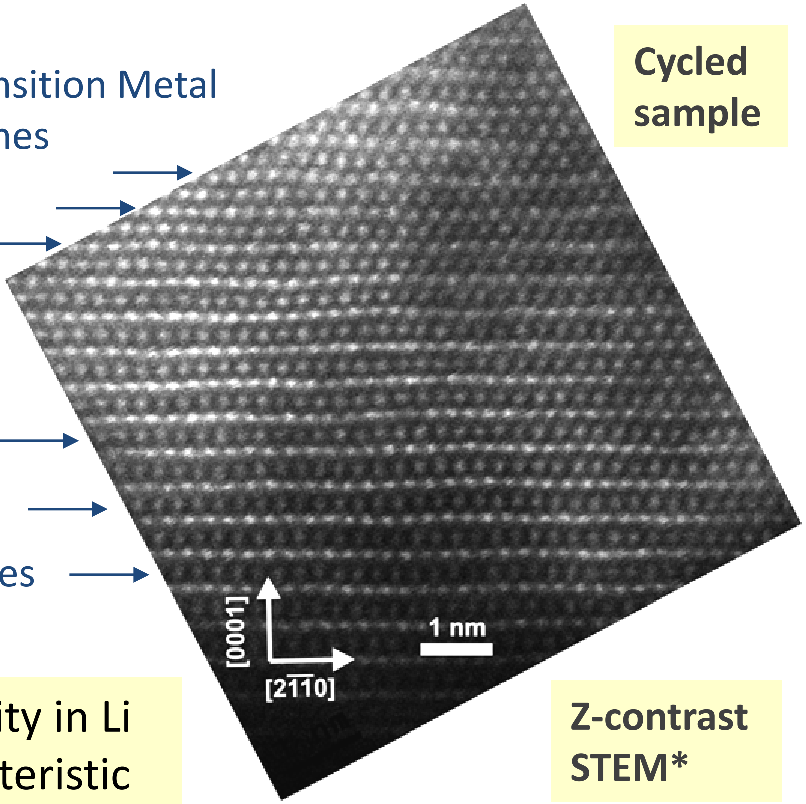
“3V region” grows at expense of “4V region”

with S.H. Kang, ANL

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

Transition Metal planes

TM in Li-planes



Cycled sample

Periodic intensity in Li layers is characteristic of spinel structure

Z-contrast STEM*

*with J.G. Wen, UIUC

Collaborations

- **Partners**
  - Argonne Colleagues (S.H. Kang, M. Balasubramanian, D. Dees, A. Jansen)
    - Collaborations on developing new material systems, better electrode formulations, advanced diagnostic techniques, enhanced data for cell performance degradation modeling
  - University of Illinois (J.G. Wen, M. Sardela, R. Haasch, S, McLaren, I. Petrov)
    - Collaborations to determine aging-related changes in electrode and separator materials
  - University of Rhode Island (B. Lucht et al.)
    - Collaborations to determine cycling-related changes at the electrode-electrolyte interface
  - Colleagues at other National Labs
    - Collaborations to effectively use the diagnostic tools/expertise at various labs to identify/solve performance degradation challenges
- **Technology Transfer**
  - Knowledge generated during the course of our diagnostic studies is shared with colleagues in US battery industry through presentations, articles, and reports

Work in Progress/Future Work

- "Wrap up" studies on PHEV baseline cell and cell constituents
  - Document data in reports; share information with academic and industry colleagues
- Initiate characterization and aging experiments on electrodes and electrode constituents identified for the next set of ABR PHEV cells
  - Examine initial electrochemical performance of materials, electrodes and cells
  - Determine electrochemical performance changes on aging under PHEV-relevant test conditions (wider voltage windows, etc.)
  - Conduct diagnostic tests to explain the electrochemical behavior of materials, electrodes, and cells
  - Recommend solutions to improve performance and mitigate performance degradation
- Continue structure investigations of $Li(Li_xMn_aNi_bM'_c)O_2$ compounds
  - Identify causes and recommend solutions to mitigate crucial challenges that may hinder commercialization, which include first cycle irreversibility, structural stability, and power delivery capability

Summary

- The objective of this study is to identify factors that contribute to cell performance and performance degradation characteristics (capacity fade, impedance rise) on long-term storage/cycling.
- 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 performance degradation of electrodes and cells with the PHEV baseline chemistry. Our data show that cell impedance rise on aging arises from processes at the positive electrode, whereas cell capacity loss can be attributed to processes at the negative electrode. The impedance rise can be correlated to structural defects within oxide particles and the increasingly inorganic nature of positive electrode surface films, whereas cell capacity fade appears to result from Li loss during graphite SEI dissolution/reformation.
- We've been studying the structure and structural rearrangements in layered $Li(Li_xMn_aNi_bM'_c)O_2$ compounds using X-ray, electron beam, and electrochemical techniques. Our data show that as-prepared oxides contain an intimate mixture of Li_2MnO_3-like and $LiMO_2$-like (M=Co, Ni) areas, ~1-2 nm size, which are integrated and interconnected at the atomic scale. The voltage-profile depression displayed by these oxides may be related to spinel-like phases that form during cycling/aging.