

# Mitigating Performance Degradation of High-Energy Lithium-Ion Cells

Project Id: ES032

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*Along with the Cell Fabrication Facility Team*

DOE Vehicle Technologies Program Annual Merit Review

Arlington, VA

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# Overview

## Timeline

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 25%

## Budget

- FY13: \$450K  
(as part of CFF Effort)

## Barriers

- Performance
- Calendar/cycle life
- Abuse Tolerance

## Partners

- CFF Team at Argonne
- Army Research Laboratory
- Univ. of Illinois, Urbana-Champaign, Univ. of Rhode Island and Purdue Univ.
- Researchers at Brookhaven, Idaho, 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.

## Milestones

- Determine sources of impedance rise and capacity fade during extensive cycling of cells containing various electrochemical couples  
September 2013 (on schedule)
- Recommend solutions that can improve the electrochemical performance and life of cells by 30% at 30 °C and 15% at 55 °C  
September 2013 (on schedule)

# 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

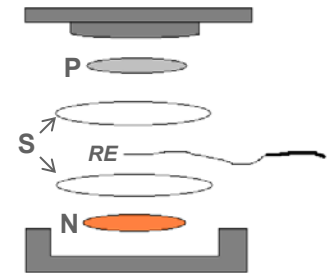
Coin, pouch, prismatic, cylindrical cells



## Electrochemical Couples

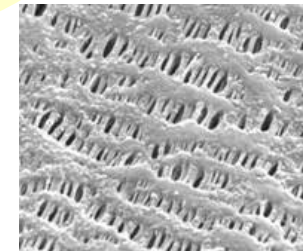
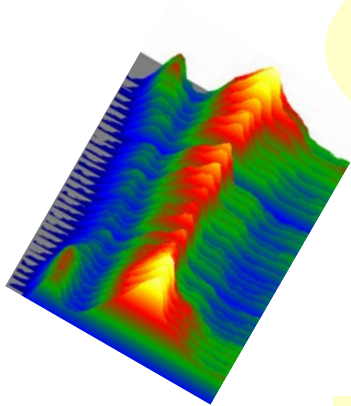
## Electrochemistry

Reference Electrode cells – identify cell components responsible for impedance rise



## Disassembly of New and Aged Cells

Electrode Surface & Bulk Analyses  
Electrolyte & Separator study



Suggest/implement approaches to extend cell life

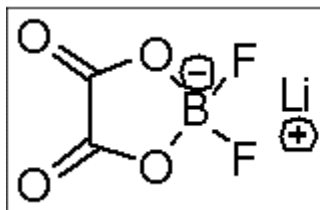
# Technical Accomplishments and Progress - 1

- **Established electrode contributions to performance degradation**
  - Positive electrode is main contributor to cell impedance rise
  - Li- trapping in the graphite electrode SEI is main cause of cell capacity fade
- **Selected Upper Cutoff Voltage (UCV) for Cell Aging**
  - Cell impedance rise increases with increasing UCV for cycling
  - Recommended an UCV of 4.4V to prolong cell life. Recommended Testing at higher UCVs to accelerate cell aging
- **Reformulated the positive electrode to enhance cell life**
  - Recommended against use of graphite for high-voltage cycling ( $> 4.5\text{V}$  vs. Li) because  $\text{PF}_6^-$  intercalation disorders the graphite structure and contributes to impedance increase at the oxide-carbon interface.
  - Recommended lowering the PVDF content in the electrode to reduce stresses that are induced by the calendaring process.
  - Recommended 92:4:4 (oxide:carbons:binder) ratio as the new formulation

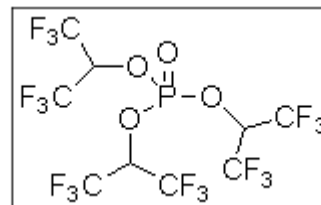


# Technical Accomplishments and Progress - 2

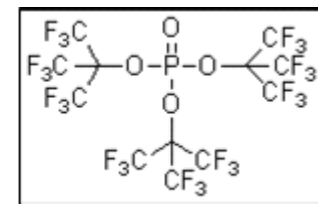
- **Demonstrated effect of alumina in the positive electrode**
  - ALD-based alumina coatings on the positive electrode improve capacity retention and reduce impedance rise in Full Cells
  - Addition of alumina powder to the positive electrode improves capacity retention but does not affect impedance rise in Full cells
- **Identified effect of select electrode additives on cell performance**
  - Addition of 2 wt%  $\text{LiF}_2\text{BC}_2\text{O}_4$  to baseline electrolyte lowers positive electrode (and, therefore, cell) impedance rise
  - Cells containing a LiDFOB+LiBOB mixture added to baseline electrolyte display enhanced capacity retention and lower impedance rise.
  - Cells with HFiP additive (ARL) show lower impedance rise than baseline cells, but performance is inferior to  $\text{LiF}_2\text{BC}_2\text{O}_4$ -bearing cells
  - Cells with PFBP additive (ARL) show higher impedance after both formation and long-term cycling



$\text{LiF}_2\text{BC}_2\text{O}_4$



HFiP



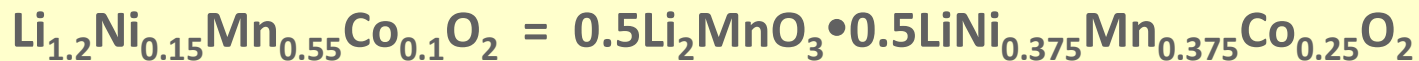
PFBP

# Chemistry of ABR-1 cells

ABR-1S(+)	ABR-1S(-)
<b><u>Positive Electrode:</u></b>	<b><u>Negative Electrode:</u></b>
86%wt $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$	89.8 %wt ConocoPhillips A12 graphite
8%wt Solvay 5130 PVDF binder	6%wt KF-9300 Kureha PVDF binder
4%wt Timcal SFG-6 graphite	4 %wt Timcal Super P
2%wt Timcal Super P	0.17 %wt Oxalic Acid
6.64 $\text{mg}/\text{cm}^2$ active-material loading density	5.61 $\text{mg}/\text{cm}^2$ active-material loading density
37.1% electrode porosity	26% electrode porosity
35- $\mu\text{m}$ -thick coating	40- $\mu\text{m}$ -thick coating
15- $\mu\text{m}$ -thick Al current collector	10- $\mu\text{m}$ -thick Cu current collector

Electrolyte: EC:EMC (3:7 by wt.) + 1.2M  $\text{LiPF}_6$

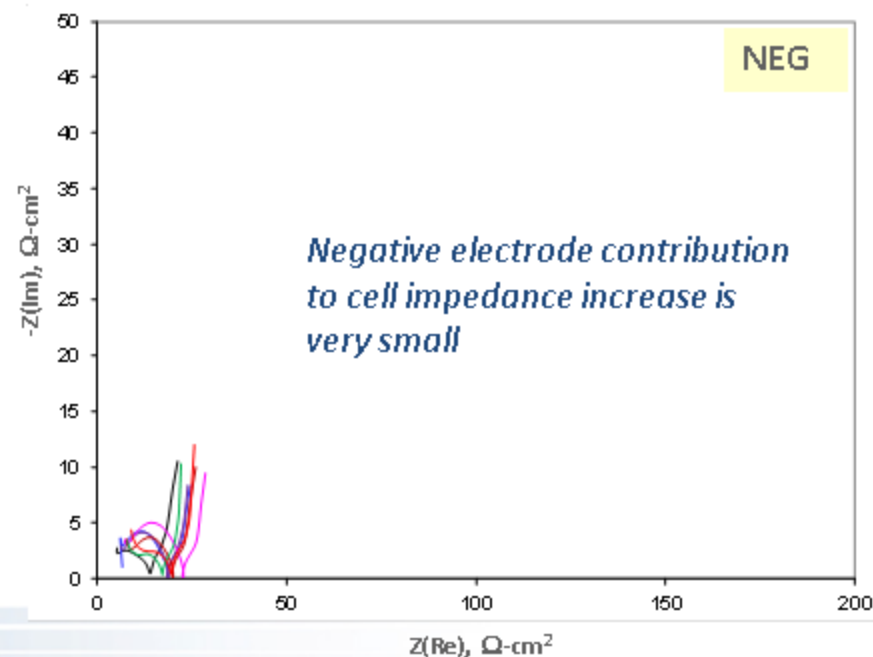
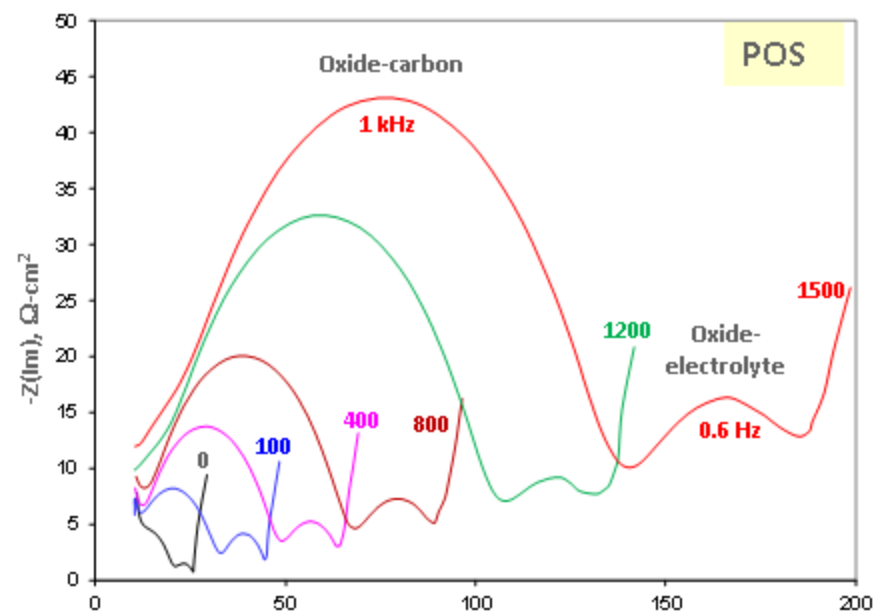
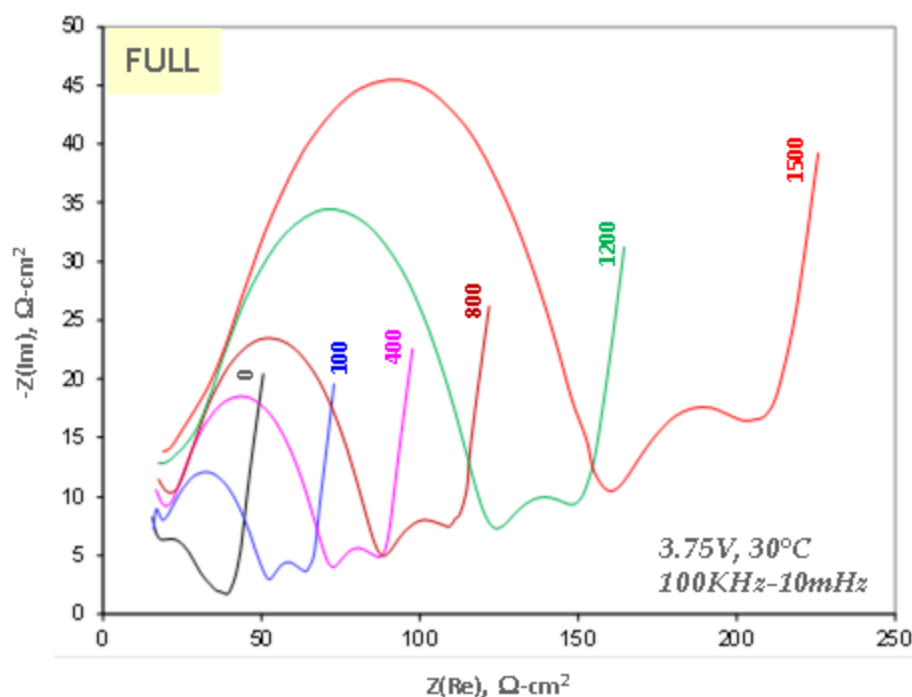
Separator: Celgard 2325



Integration and interconnection of  $\text{LiMO}_2$ -like (rhombohedral) and  $\text{Li}_2\text{MnO}_3$  (monoclinic) structures at the atomic level

# Cells show impedance rise on aging

After 30° cycling in the 2.5-4.4V voltage window - up to 1500 cycles



## Reference Electrode Cell Data

The Full Cell impedance increase is mainly from the Positive Electrode, at the oxide-carbon (high-frequency arc) and oxide-electrolyte (mid-frequency arc) interfaces.

Ref: Li et al. J. Electrochem. Soc. 160 (2013) A3006

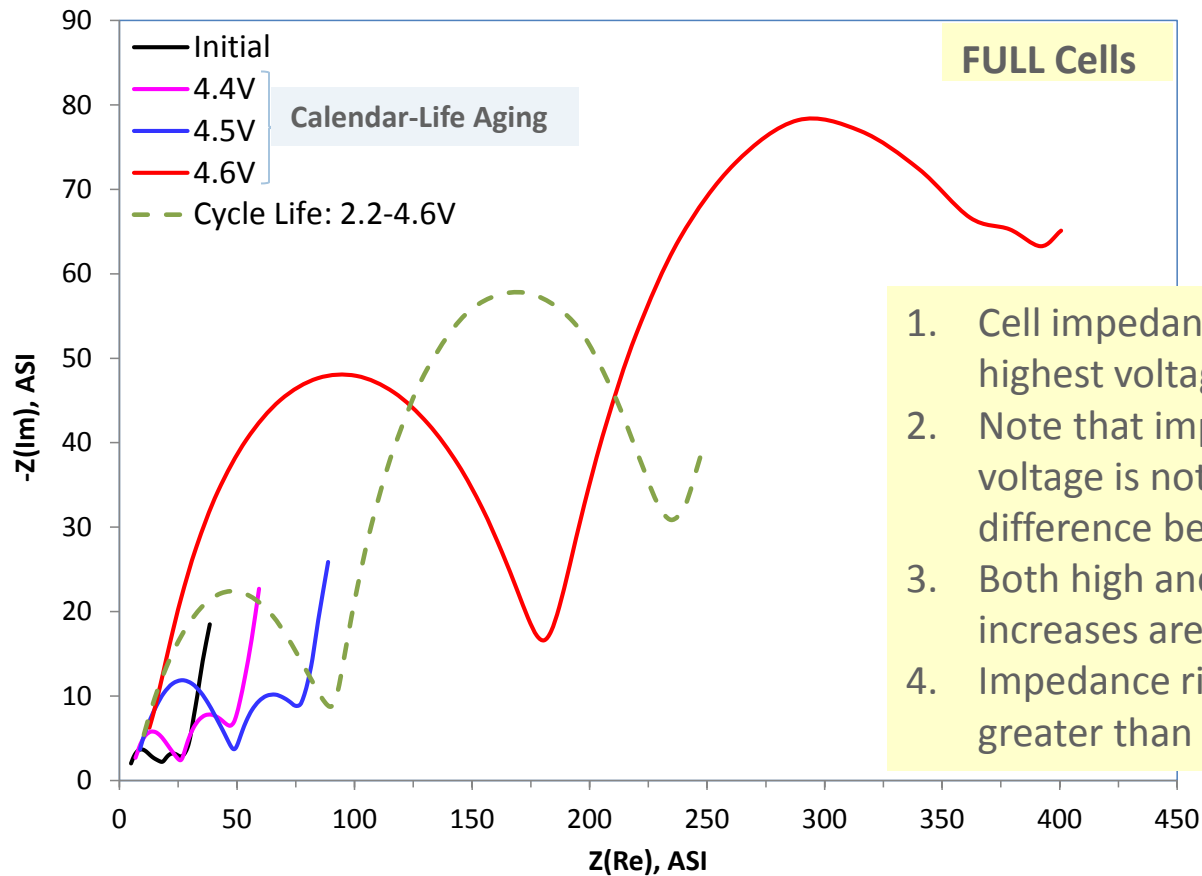




# Selection of Upper Cutoff Voltage (UCV) for Cell Testing

Full Cells, EIS data, 3.75V, 30°C, 100 kHz-0.01Hz

Calendar Life Aging, 356h, 30°C, 4.4, 4.5, 4.6V. The 2.2 - 4.6V cycle life test took 356h



1. Cell impedance increase is greatest at the highest voltage.
2. Note that impedance increase vs. cell voltage is not linear – there is a significant difference between the 4.5 and 4.6V hold.
3. Both high and mid-frequency arc increases are affected by cell voltage
4. Impedance rise for cell held at 4.6V is greater than for 2–4.6V, 10-cycles, cell

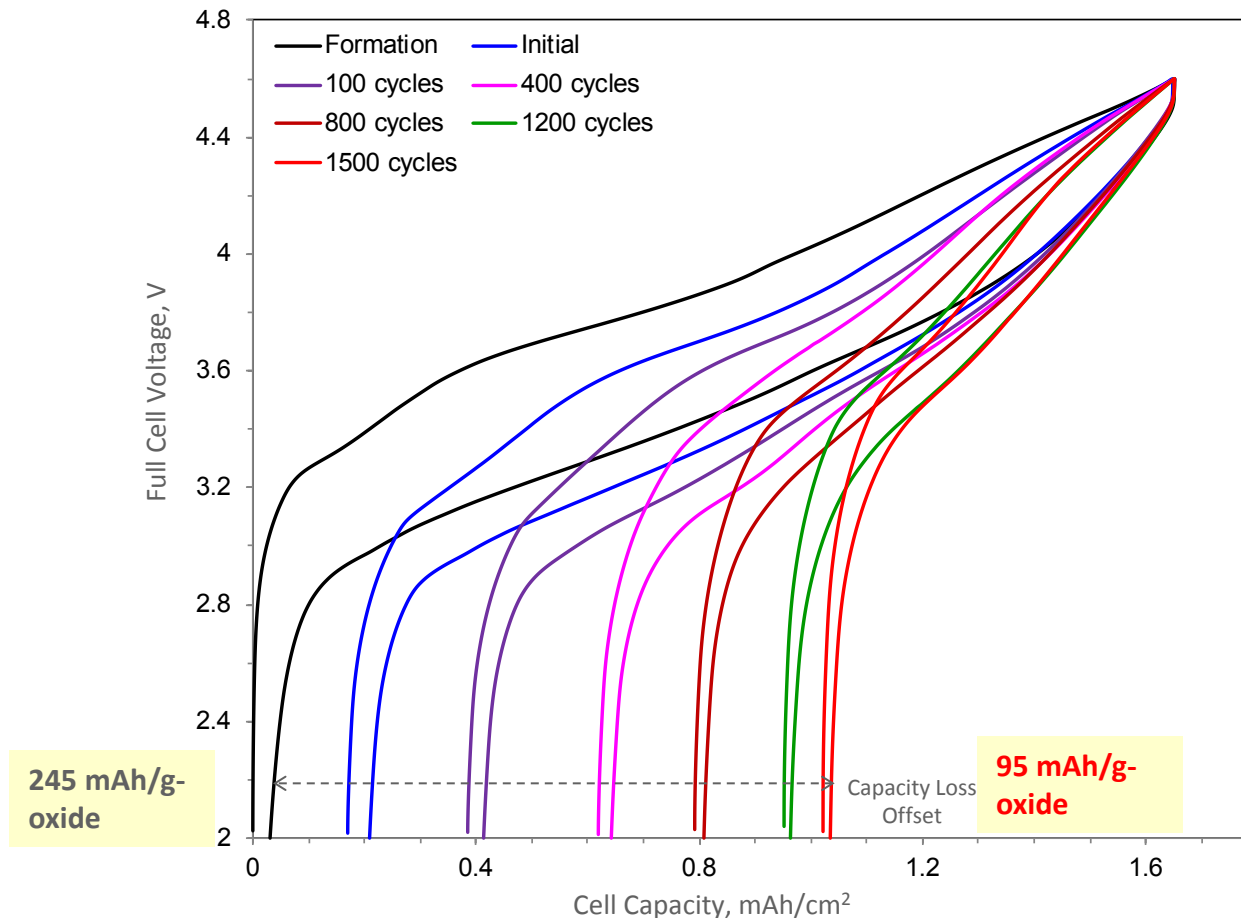
The Upper Cutoff Voltage has a significant effect on cell performance degradation  
Recommended an UCV of 4.4V to minimize cell impedance rise



# Cells show capacity loss on aging

After 30° cycling in the 2.5-4.4V voltage window - up to 1500 cycles

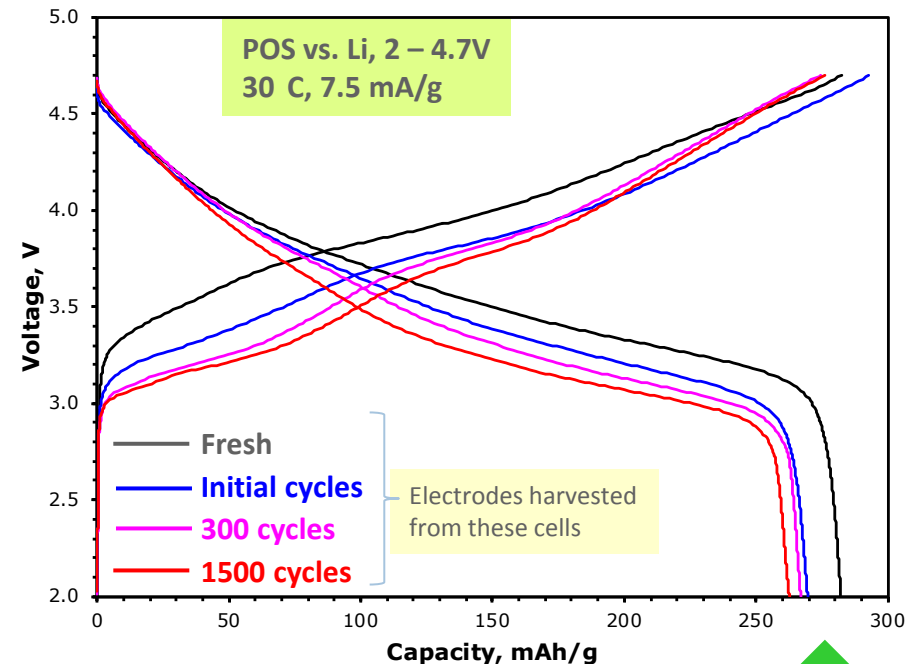
Cell capacity decreases on cycling, even at 30°C



Capacity loss is greater at higher upper-cutoff voltages, at higher temperatures, and for wider voltage cycling windows

Ref: Li et al., J. Electrochem. Soc. 160 (2013) A3006

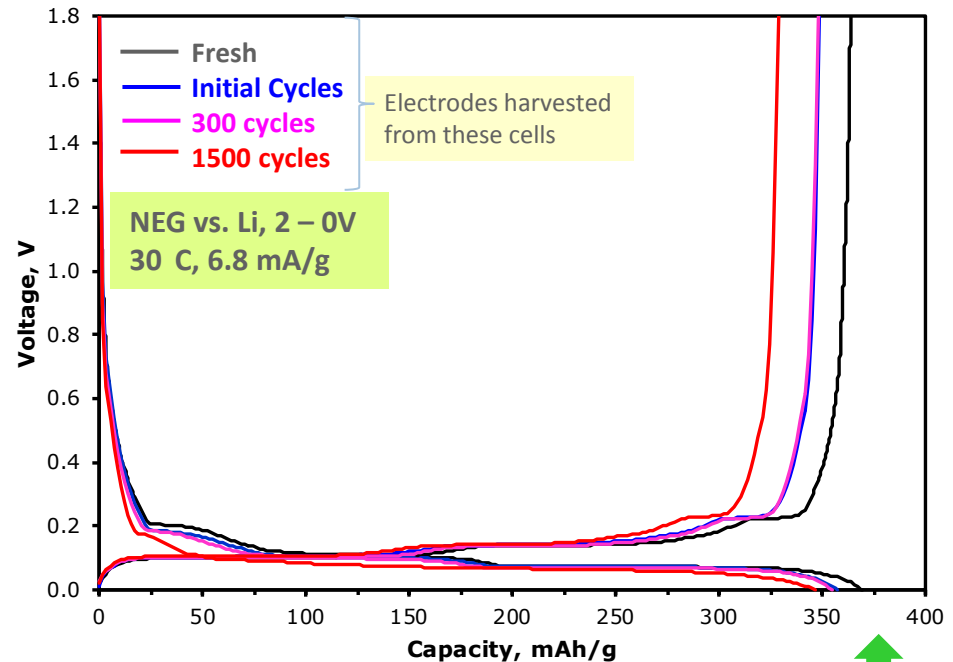
# Capacity Fade: Data from “harvested” positive and negative electrodes (vs. Li) show that bulk-structure contributions of oxide and graphite particles are small



Capacity (Fresh electrode): 282 mAh/g

Capacity (1500 cycle electrode): 262 mAh/g

Some “true” capacity loss occurs on cycling – this could be due to oxide particle isolation that may result from loss of oxide-carbon contacts or from particle surface films and/or surface structure changes.  $dQ/dV$  data indicate that the oxide structure changes on aging.

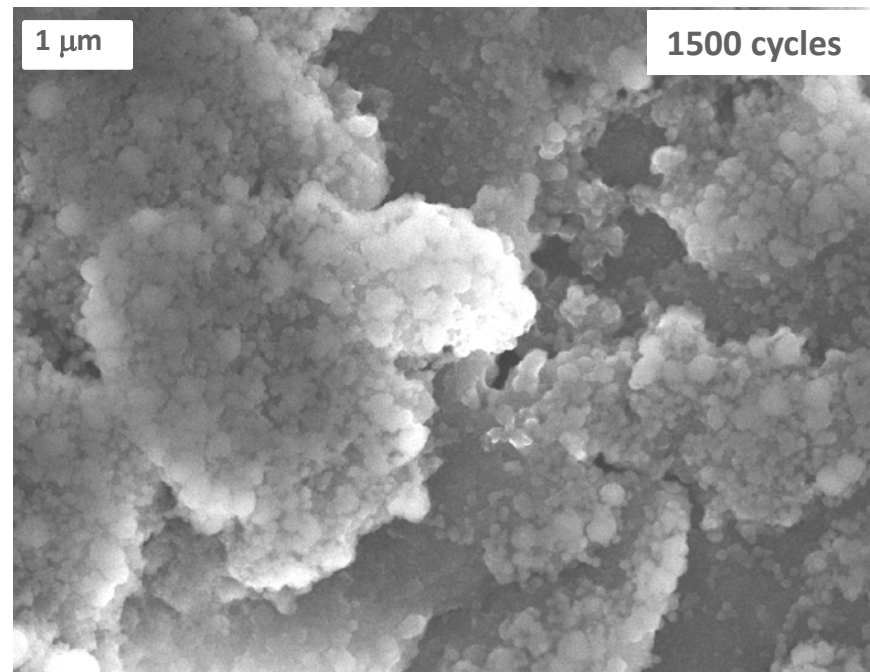
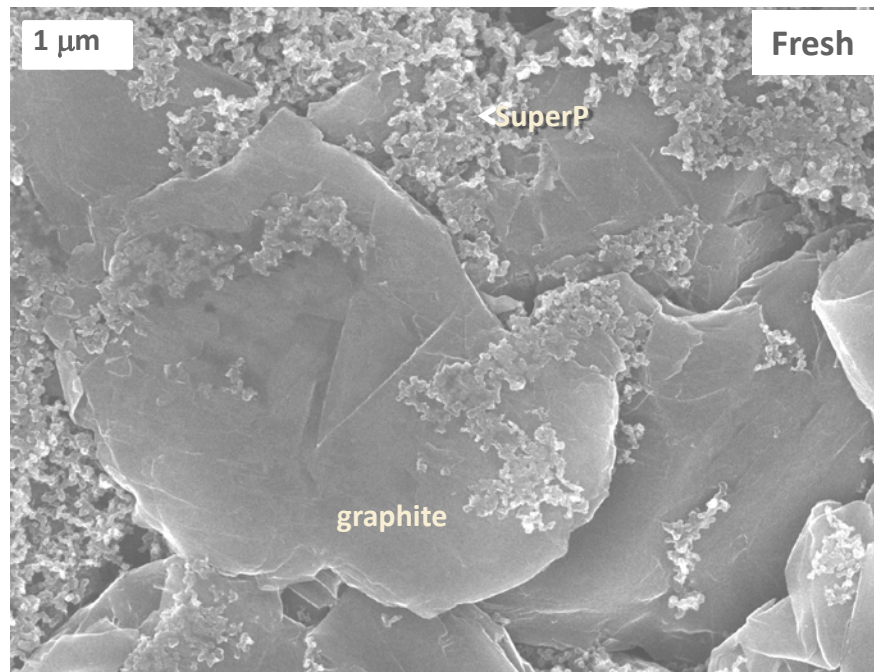


Capacity (Fresh electrode): 366 mAh/g

Capacity (1500 cycle electrode): 341 mAh/g

Some “true” capacity loss occurs on cycling – this could be due to active particle isolation that may result from thick SEI films.  $dQ/dV$  data are similar for all samples, which indicates that the graphite bulk is not damaged on cell aging

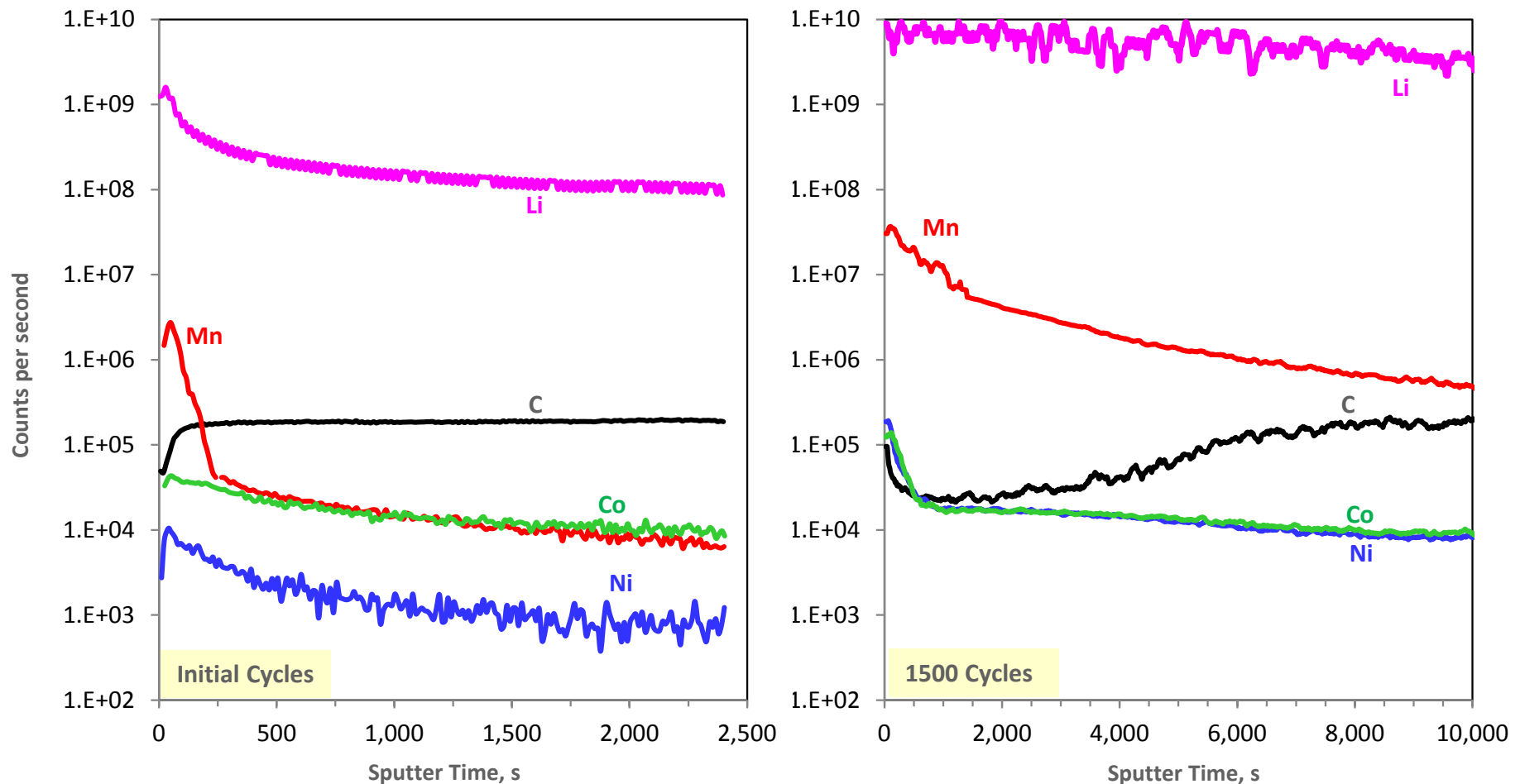
# SEI formation/dissolution/reformation reactions during cell cycling results in Li trapping



Transition metals (Mn, Ni, Co) from the oxide(+) electrode accumulate at the graphite(-) electrode and are believed to accelerate capacity fade

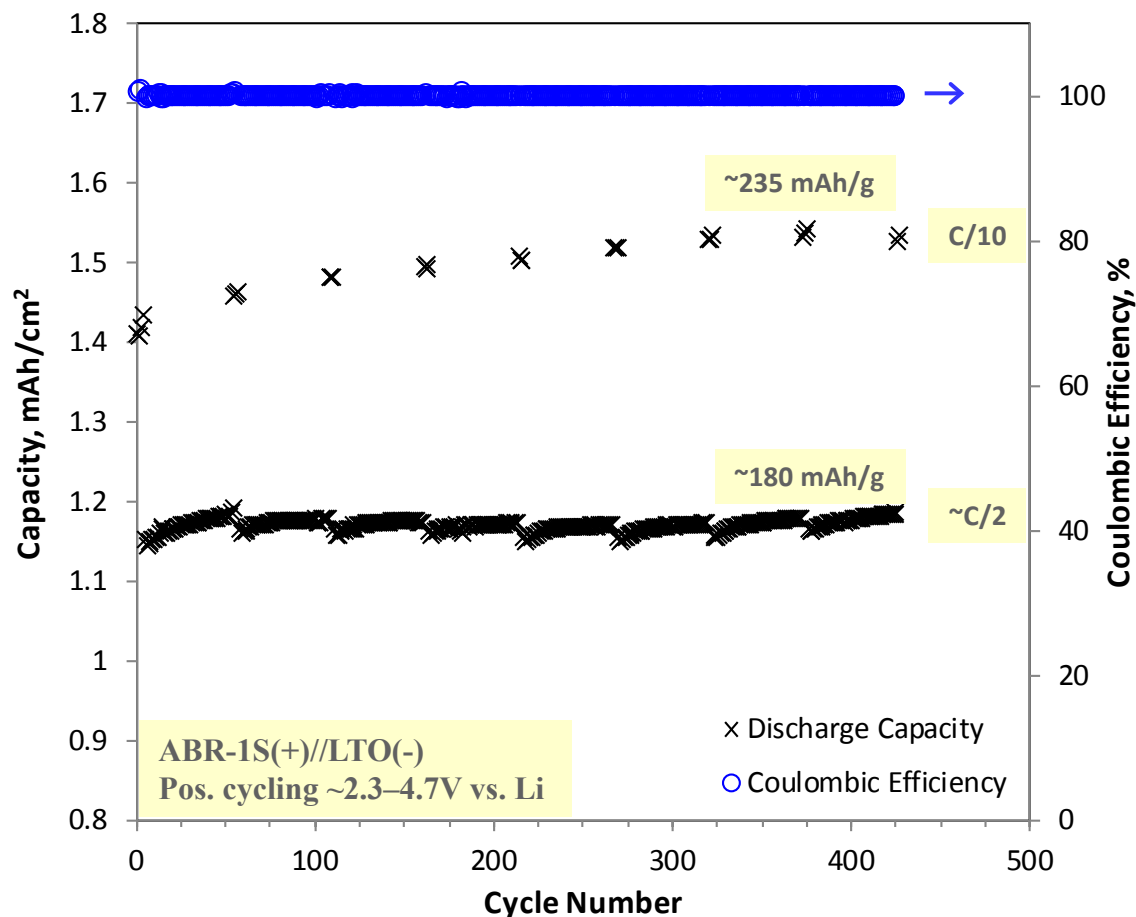
Ref: Li et al., *J. Electrochem. Soc.* 160 (2013) A3006

# SIMS sputter depth profiles show Li, Mn, Ni, Co accumulation at the graphite negative electrode



SEI is thicker after cycling/aging. This is seen from the C profiles: longer sputter times are needed to obtain steady state values for the 1500 cycle sample

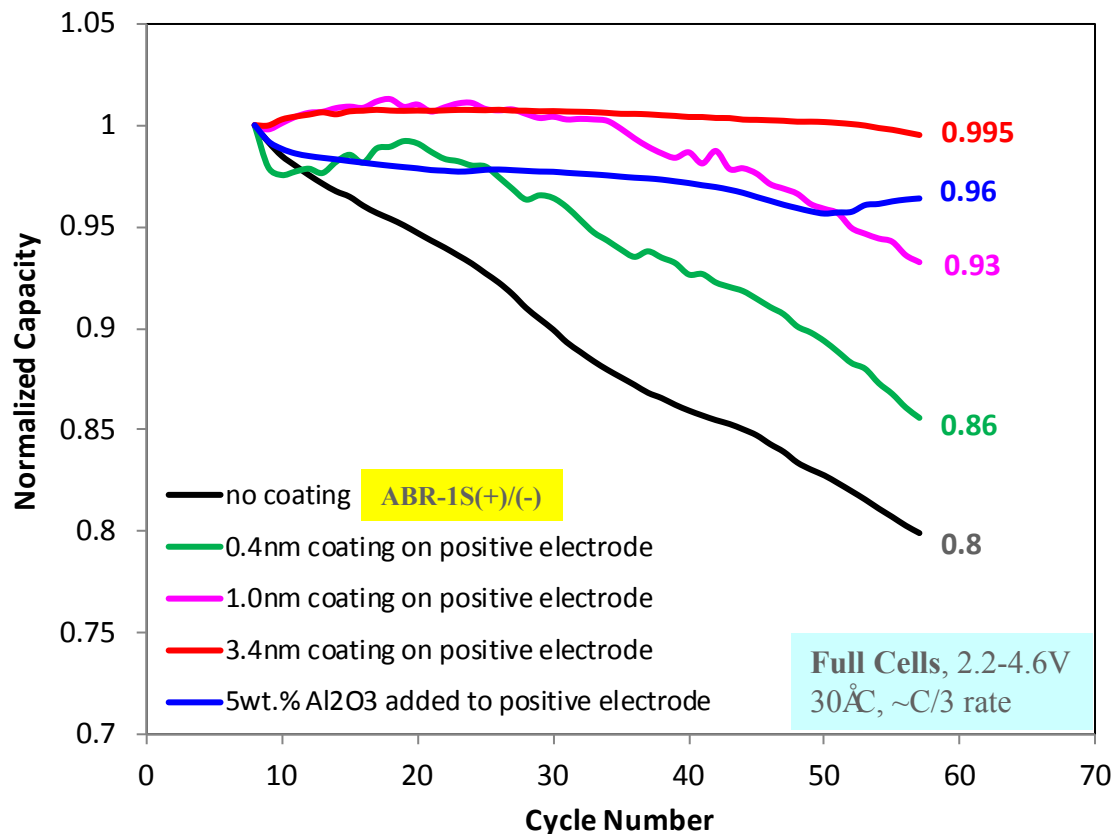
Cells containing the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (-) electrodes (coupled with the baseline positive electrode) show negligible capacity fade on cycling: 0.75–3.15V, 30 °C



These data confirm that capacity fade is manifested at the graphite-based negative electrode in our baseline ABR-1 cells

Ref: Li et al., J. Electrochem. Soc. 160 (2013) A3006

# Alumina-coating of positive electrode and/or alumina addition to positive electrode improves cell capacity retention

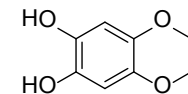
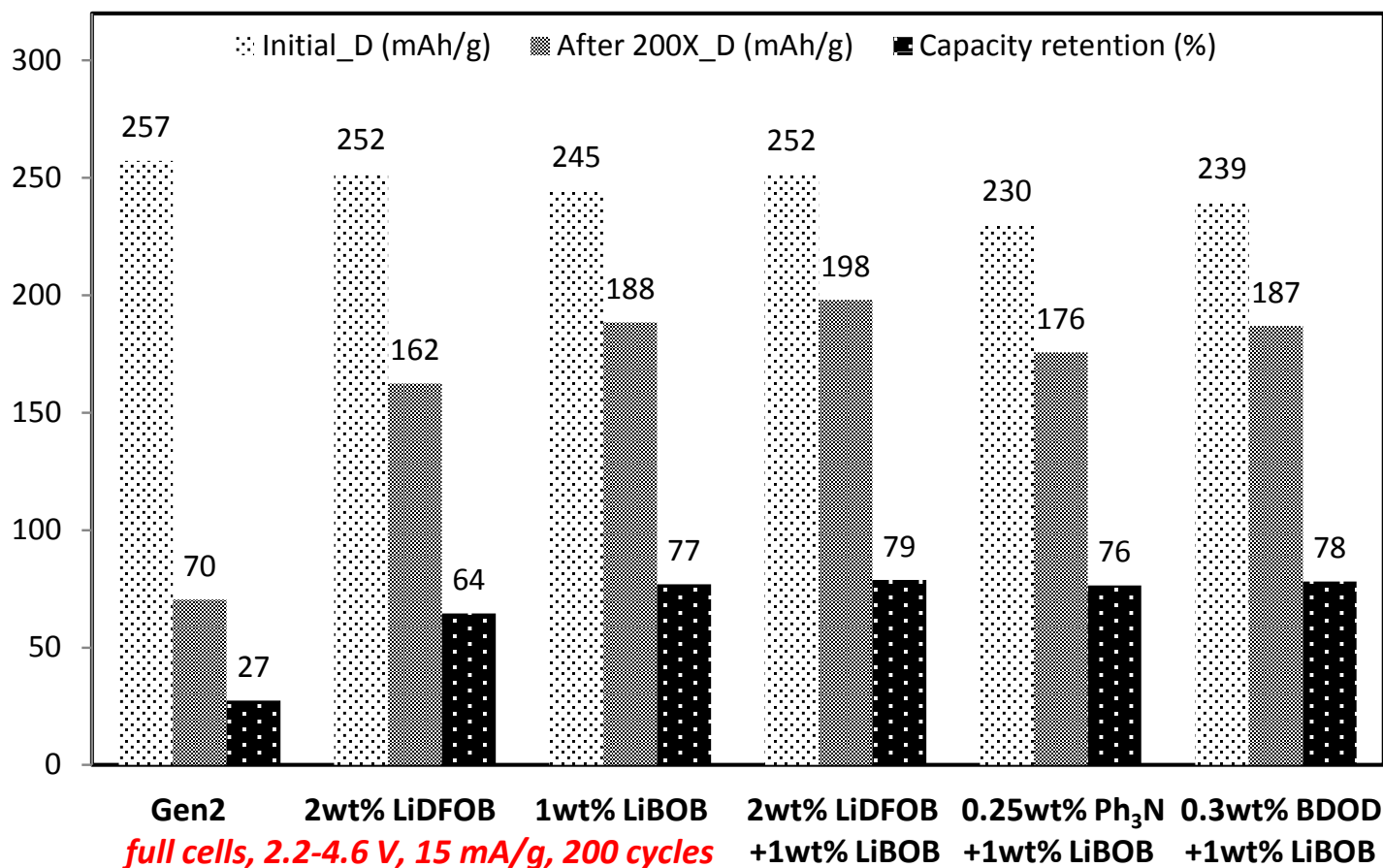


## ALD-coated electrodes

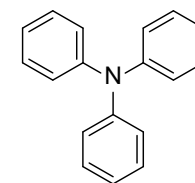
Electrode coating thickness is an estimate based on the thickness measured on a planar Si substrate

The cell containing the 3.4 nm alumina-coated positive electrode shows the best capacity retention. Alumina reduces dissolution of Mn, Ni, and Co from the positive electrode by acting as a HF-getter. Incorporation of Al-bearing species may further help stabilize the negative electrode SEI.

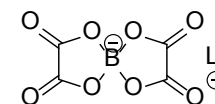
# Electrolyte additives improve capacity retention of ABR-1 cells: 2.2-4.6V, 200 cycles



1,4-benzodioxane-6,7-diol  
**BDOD**



triphenylamine  
**Ph<sub>3</sub>N**

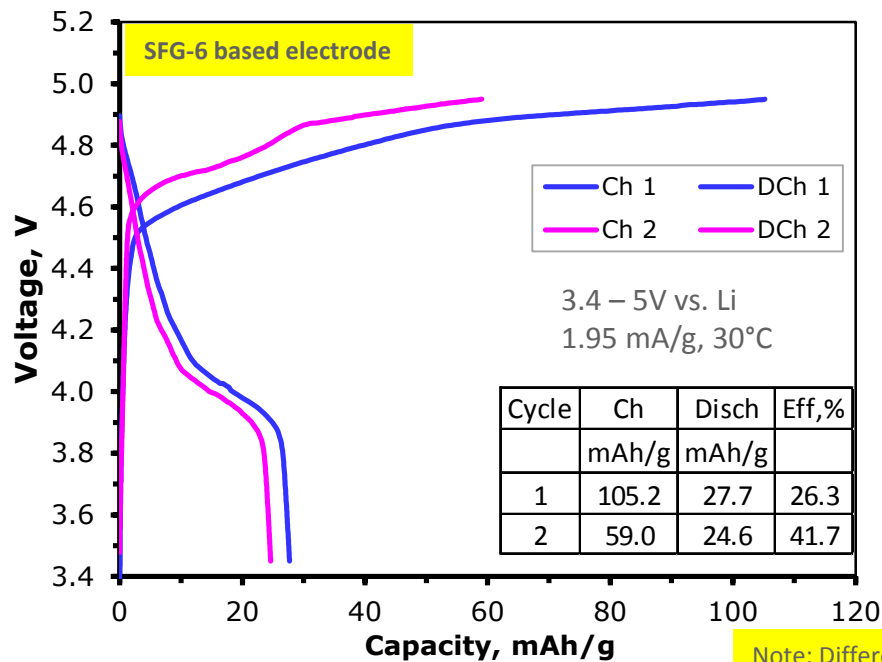


**LiBOB**

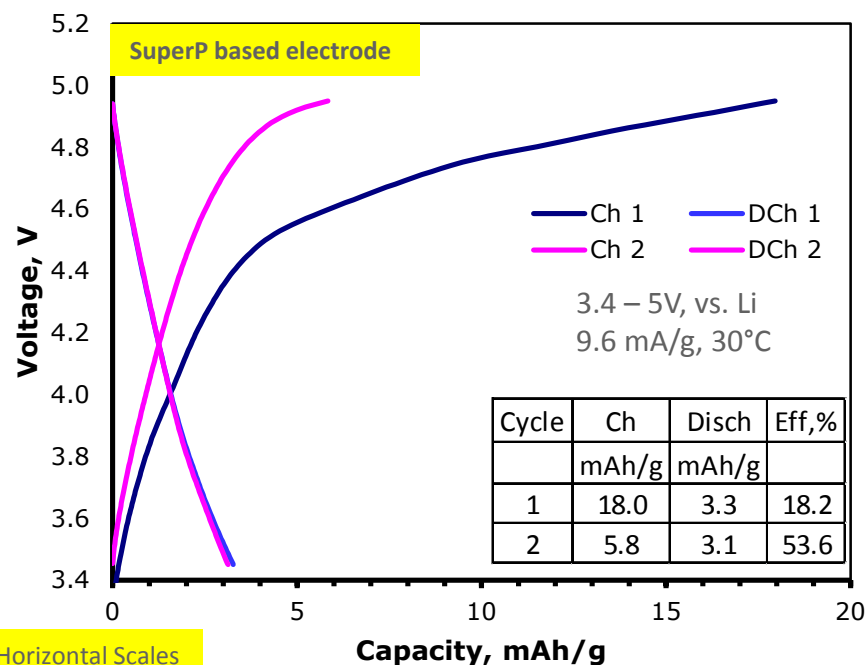
Cells containing LiDFOB (half-BOB) or a LiDFOB+LiBOB mixture added to the Gen2 electrolyte show the best performance. Therefore, these additives were recommended for the CFF cell builds.



# Positive electrode carbons, SFG-6 and SuperP, are electrochemically active at high cell voltages: 3.4 - 5V vs. Li cycles, 30 °C



The reversible capacity is probably due to  $\text{PF}_6^-$  intercalation into the graphite; this capacity increases with the upper cut-off voltage limit. Note the coulombic inefficiency; the difference between charge and discharge capacities suggests significant electrolyte oxidation on the graphite surface. All capacities decrease on cycling, but do not go to zero.

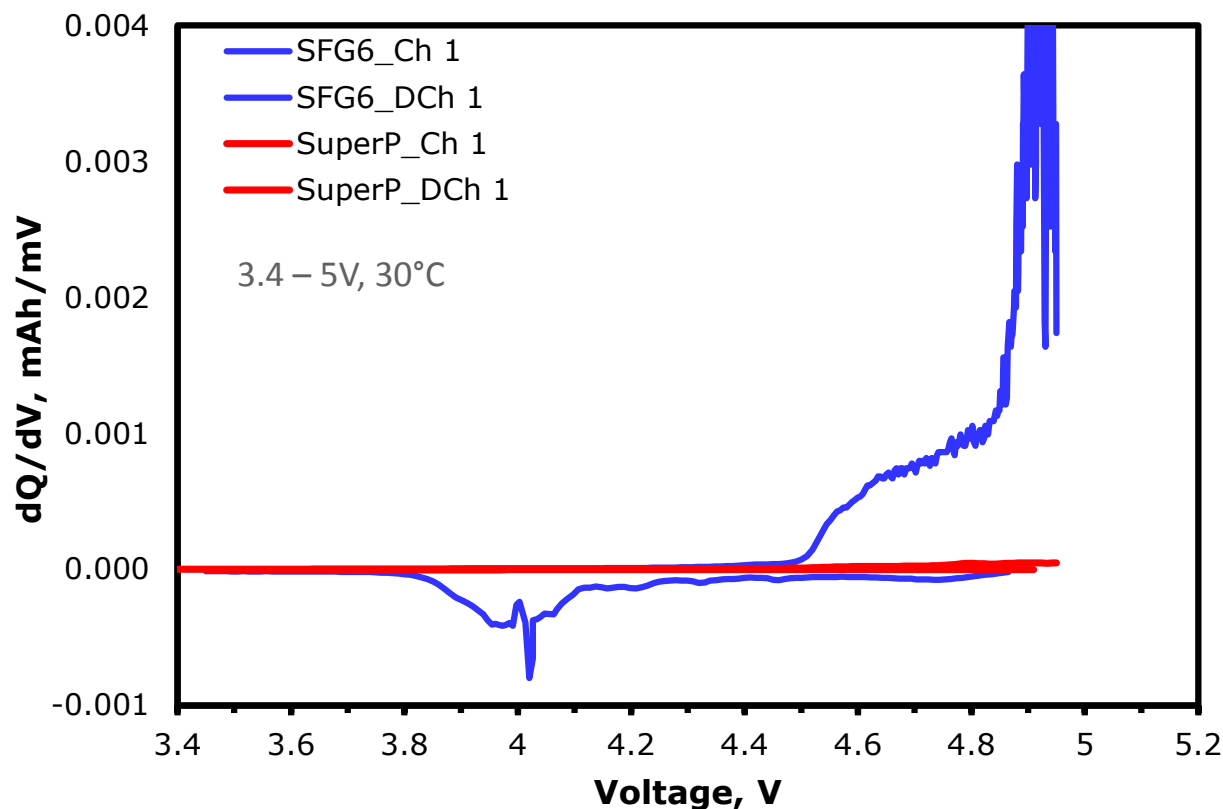


$\text{PF}_6^-$  intercalation is not expected to occur into the SuperP carbons; the reversible capacity is, therefore, small. The coulombic inefficiency is high, which again suggests significant electrolyte oxidation on the carbons. All capacities decrease on cycling but remain finite, especially the charge capacities.



## dQ/dV plots: SFG-6 and SuperP based cathodes

*Related to data from previous slide*



When plotted using the same scale, the SuperP carbon features are indistinct and barely visible. We may, therefore, conclude that  $\text{PF}_6^-$  intercalation, and electrolyte oxidation are not a significant concern for the SuperP (relative to SFG-6).

**Recommendation:** SFG-6 graphite should not be used during preparation of high-energy/high-voltages cathodes. SuperP carbons are OK; our tests indicated that positive electrodes containing TIMCAL C45 yielded the best performance.

# Positive and Negative Electrodes were reconstituted by altering oxide/carbon/binder ratios and calendaring conditions

Electrodes were prepared at CFF in 2012	Electrodes were prepared at CFF in 2012
<b>L7(C45+)</b>	<b>A002 (CFF)</b>
<b><u>Positive Electrode:</u></b>	<b><u>Negative Electrode:</u></b>
92 wt% $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ (HE5050)	91.8 %wt ConocoPhillips: CGP-A12 graphite
4 wt% Solvay 5130 PVDF binder	6%wt KF-9300 Kureha PVDF binder
4 wt% Timcal C45	2 %wt Timcal C45
	0.17 %wt Oxalic Acid
5.89 $\text{mg}/\text{cm}^2$ active-material loading density	5.16 $\text{mg}/\text{cm}^2$ A12 graphite loading density
36.1% electrode porosity	38.8% electrode porosity
26- $\mu\text{m}$ -thick coating	43- $\mu\text{m}$ -thick coating
20- $\mu\text{m}$ -thick Al current collector	10- $\mu\text{m}$ -thick Cu current collector



Only 4wt% carbons and 4 wt% binder

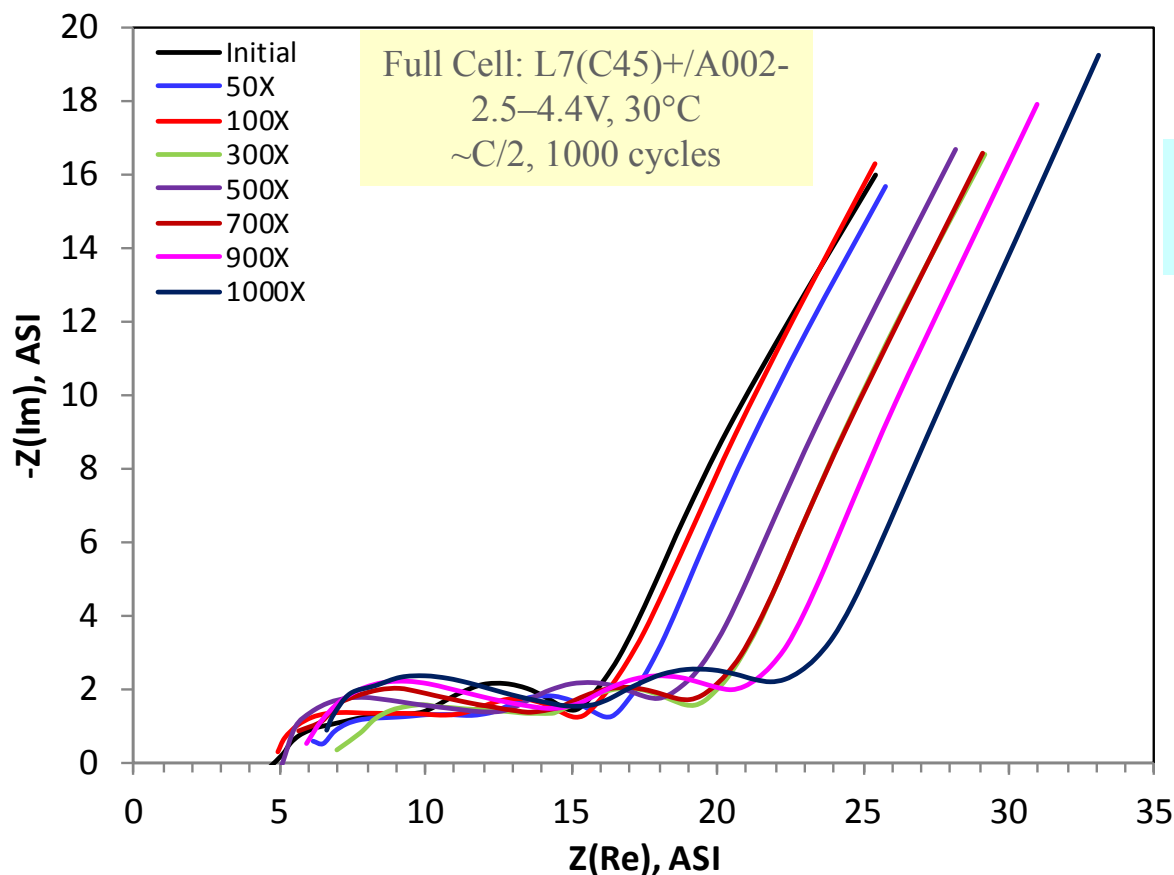


Only 2 wt% carbons

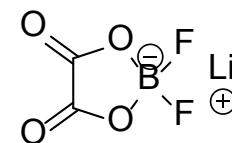
Electrolyte: EC:EMC (3:7 by wt.) + 1.2M  $\text{LiPF}_6$   
 Separator: Celgard 2325



By modifying electrode constitution and by using electrode additives we can dramatically reduce cell impedance rise



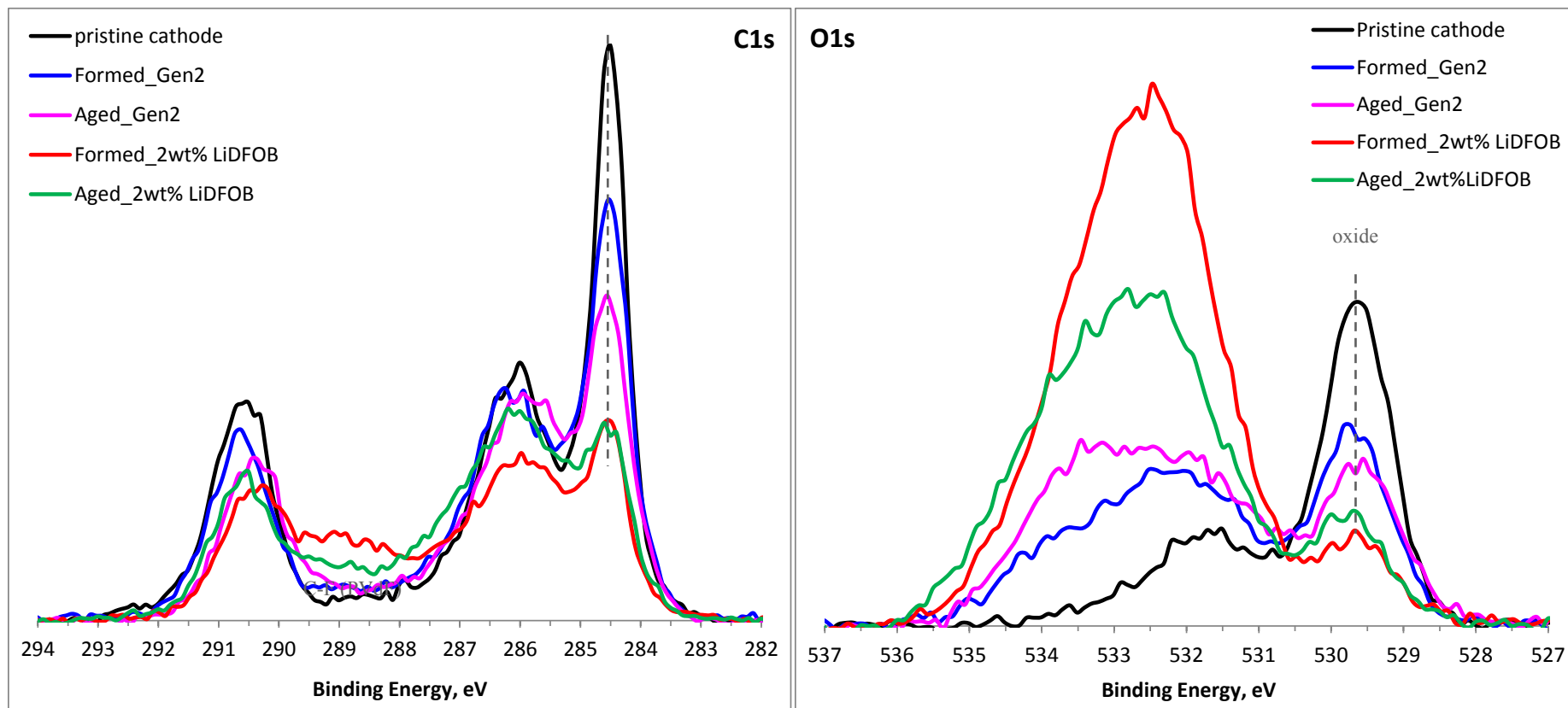
2 wt% LiDFOB added to  
baseline electrolyte



LiDFOB

Cell impedance rise is reduced by an order of magnitude  
(relative to baseline cell chemistry)

# XPS data show that LiDFOB generates surface films on the positive electrode that inhibit cell impedance rise



Our data indicate that LiDFOB also reduces on the graphite negative electrode, enhances the negative electrode SEI, and inhibits cell capacity fade

# Collaborations

- **Argonne Colleagues** (at CFF, PTF, MERF, APS, CNM, CSE)
  - Better electrode formulations, advanced diagnostic techniques, electrode and cell performance degradation modeling
- **University of Illinois** (R. Haasch, T. Spila, E. Sammann, I. Petrov)
  - Aging-related changes in cell component materials, ALD coatings/analysis
- **University of Rhode Island** (B. Lucht et al.)
  - Analyze electrolyte and electrode surface film changes
- **Purdue University** (A. Wei et al.)
  - Improve cell performance through electrolyte additives
- **Army Research Laboratory** (K. Xu et al.)
  - Improve cell performance through electrolyte additives (HFiP, etc.)
- **Brown University** (P. Guduru et al.)
  - In situ examination of stress development in electrodes during cycling
- **Colleagues at National Labs** (R. Kostecki, X.-Q. Yang, C. Daniel, K. Gering)
  - Coordinated use of diagnostic tools/expertise at various labs to identify/solve performance degradation challenges



# Work in Progress/Future Work

- Continue experiments on various LMR-NMC//Graphite couples
  - Examine effect of alternative formation cycling protocols
  - Show effect of Negative to Positive capacity ratio
  - Identify electrode additives that eliminate capacity fade
  - Determine effect of transition metal content (such as Mn) at the negative electrode on cell capacity fade.
- Examine degradation mechanisms in 5V LMNO//Graphite couples
  - Early experiments show coating delamination in the positive electrode
  - Study methods to improve adhesion between coating and current collector
- Investigate mechanisms in cells with silicon-based negative electrodes
  - How is long-term cycling performance affected by binder-type, cycling protocols, electrode coatings and electrolyte additives?
- Study performance of cells containing electrodes with water-based binders
  - How is long-term cycling performance affected by binder-type, cycling protocols, and electrolyte additives?



# Summary

## Identifying sources of performance degradation is the first step to designing long-life cells

- *Significant impedance rise during cell cycling/aging*
  - Arises mainly from the positive electrode
  - Can be reduced by reformulating positive electrode constitution, modifying oxide surface through coatings (pre-treatment), using electrolyte additives (in-situ), and by altering the cycling window
- *Significant capacity fade during cell cycling/aging*
  - Originates at the positive electrode, but manifests itself at the negative electrode –thick negative electrode SEI
  - Can be minimized by “fixing problems at the positive electrode”, such as transition metal dissolution from the oxide
- *Voltage profile changes observed during cell cycling/aging*
  - Arises from crystal structure changes
  - Solutions may include oxide surface modification, alternative synthesis techniques, oxide composition modification