Diagnostic studies on Li-battery cells and cell components

Project Id: esp_02_abraham

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Argonne National Laboratory

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Vehicle Technologies Program

This presentation does not contain any proprietary or confidential information

Overview

Timeline
- Start date: FY09 (ABRT)

  - (ATD, since 1999)
- End date: On-going
- Percent complete:

  - project on-going

Budget
- Total project funding

  - 100% DOE
- FY09: $400K

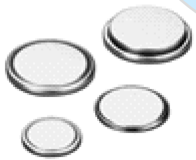
Barriers
- Calendar/Cycle Life
- Performance

Partners
- University of Illinois at Urbana-Champaign
- University of Rhode Island
- Idaho, Brookhaven, Sandia and Lawrence Berkeley National Labs

Objective and Approach

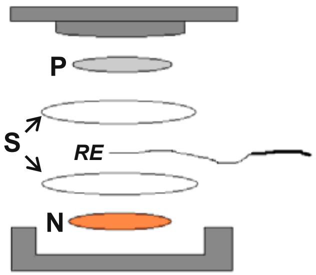
Identify Constituents and Processes responsible for Cell Performance and Performance Degradation

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

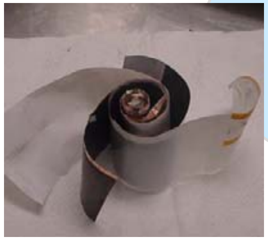


Gen X

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



Disassembly of New and Aged Cells



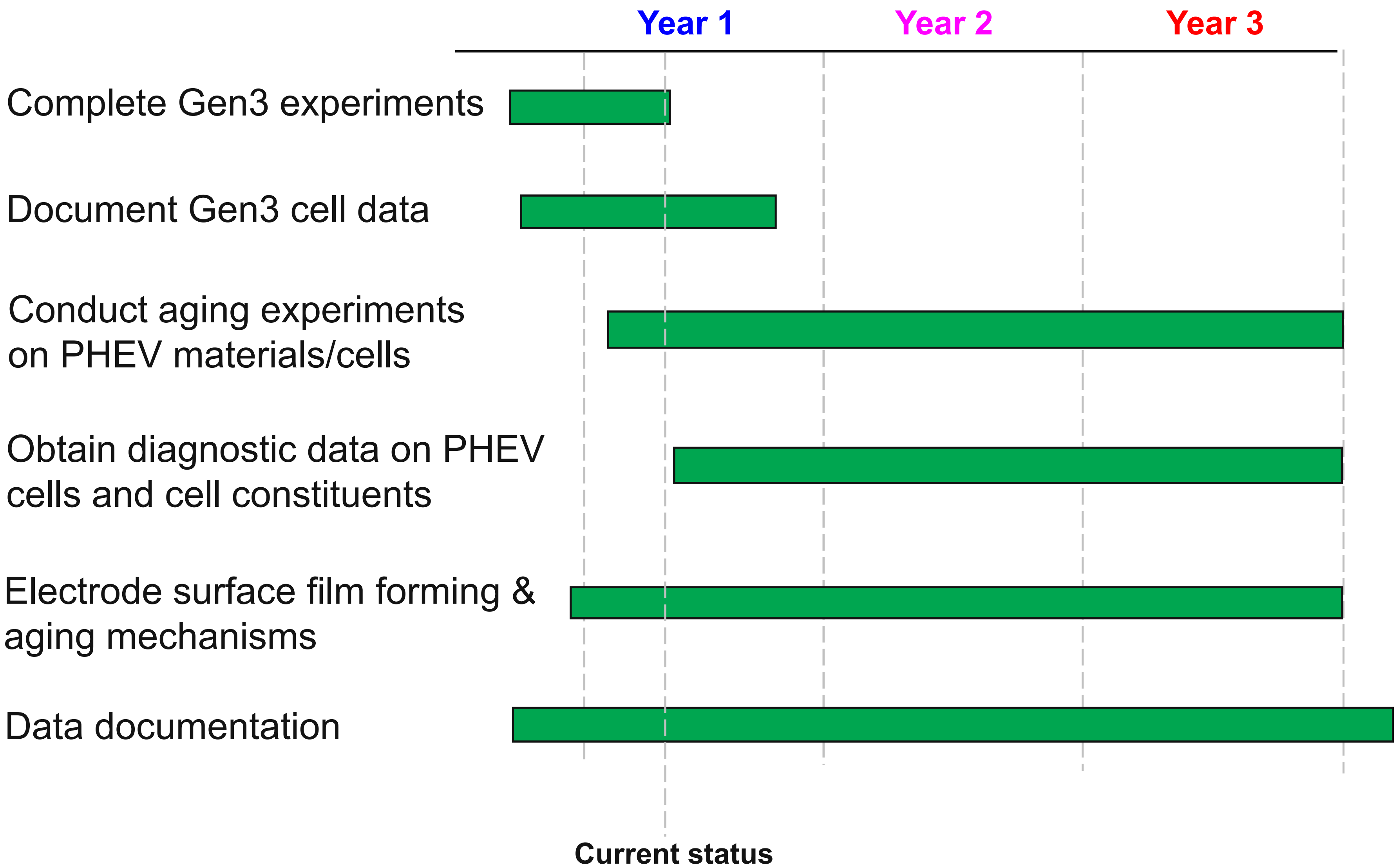
Electrode Surface & Bulk Analyses
(ANL, BNL, LBNL)

Electrolyte & Separator study
(ANL, LBNL)

(UIUC, URI)

- Suggest/implement approaches to extend cell life

Milestones


Year 1
Year 2
Year 3
Complete Gen3 experiments
Document Gen3 cell data
Conduct aging experiments on PHEV materials/cells
Obtain diagnostic data on PHEV cells and cell constituents
Electrode surface film forming & aging mechanisms
Data documentation
Current status

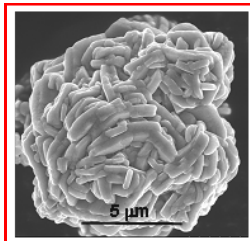
Gen3 aging studies conducted in various cell configurations

(coin cell, pouch cell, RE cell) – *consistent aging trends seen for all cells*

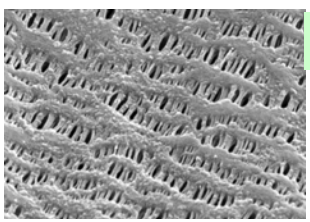
Separator color white on both positive and negative side

Cell disassembly in glove box. Electrodes initially appeared wet (sufficient electrolyte). No delamination observed, i.e., coatings adhered to current collector, even for aged cells.

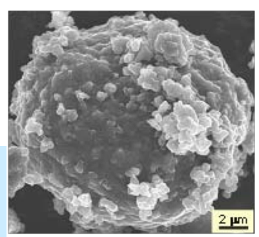
Pouch Cell Disassembly



$Li_{1.05}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.95}O_2$
Particle size ~ 5-10 µm



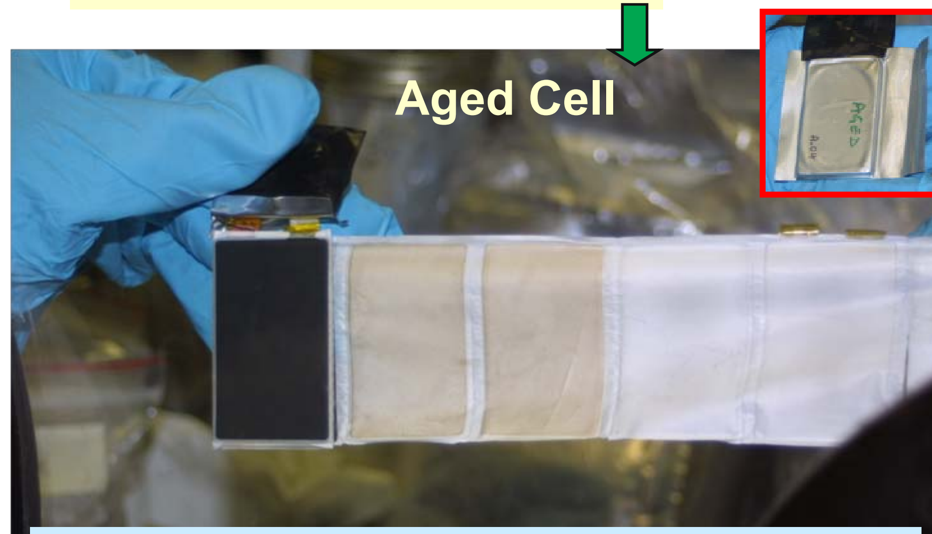
Separator



MCMB-1028 graphite
Particle size ~10 µm

Electrolyte: **3EC-7EMC + 1.2M$LiPF_6$ + x wt% $LiF_2BC_2O_4$**

Chemistry of Gen3 cells



The "darker" separator side faced the positive electrode

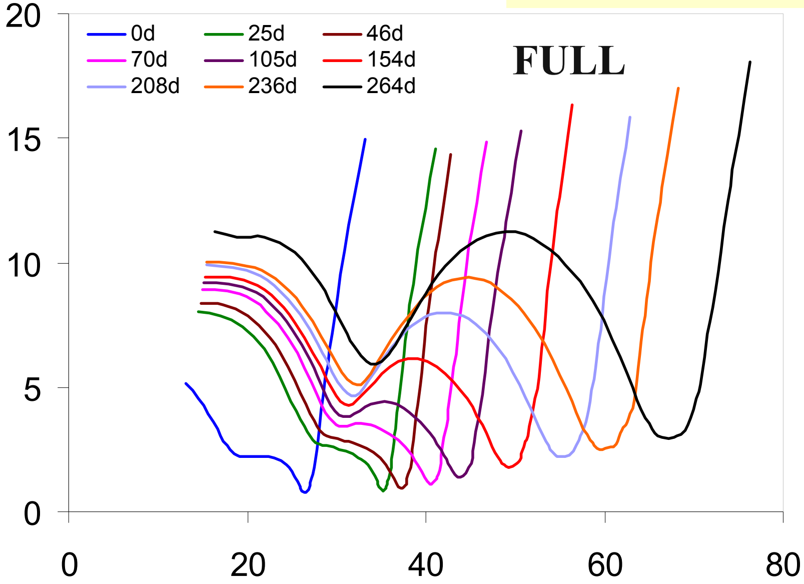
Technical Accomplishments

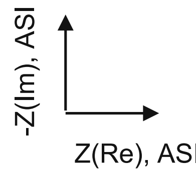
- Determined sources of performance degradation in Gen3 cells. Some highlights (*detailed in following slides*) are as follows:
  – The negative electrode is the main contributor to cell impedance rise in cells containing the $LiF_2BC_2O_4$ additive
  – The additive improves cell performance by inhibiting impedance rise at the positive, and reducing capacity loss at the negative electrode
  – The positive electrode capacity loss on aging is very small. The negative electrode showed measurable capacity loss that apparently results from pore-clogging or particle isolation.
  – Increase in negative electrode impedance has been correlated to accumulation of transition metals at this electrode upon cell aging.
  – Inhibition of positive electrode impedance rise has been correlated to presence of B-bearing oligomers, arising from $LiF_2BC_2O_4$, at the electrode surface.
- Characterized SEI layers formed on graphite electrodes cycled in cells containing various electrolytes, by XPS, FTIR and TGA, and formulated formation mechanisms based on the data.

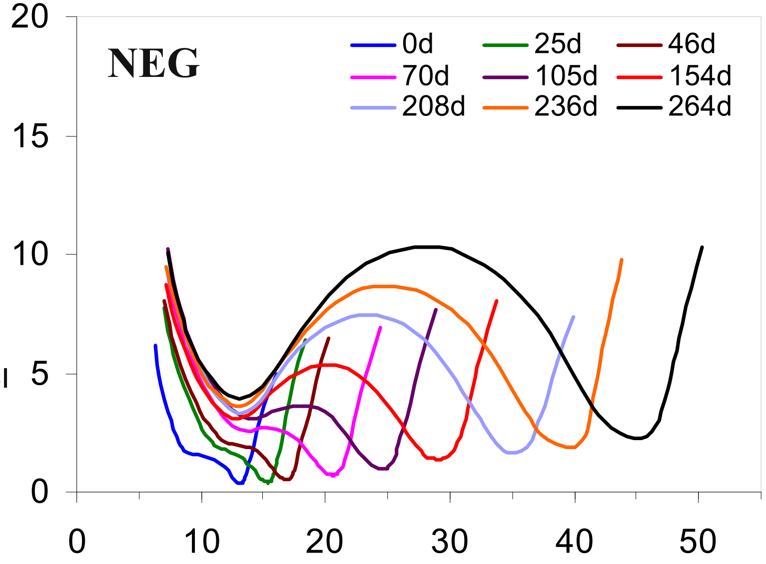
Gen3 Aging Studies – RE cells – *4V, 55°C aging*

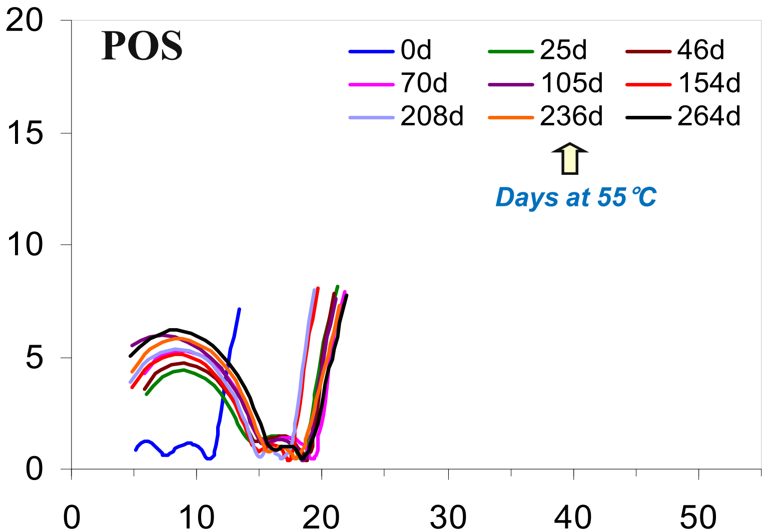
Data show that negative electrode is main contributor to cell impedance rise

Data from cells containing 3 wt% $LiF_2BC_2O_4$ electrolyte additive





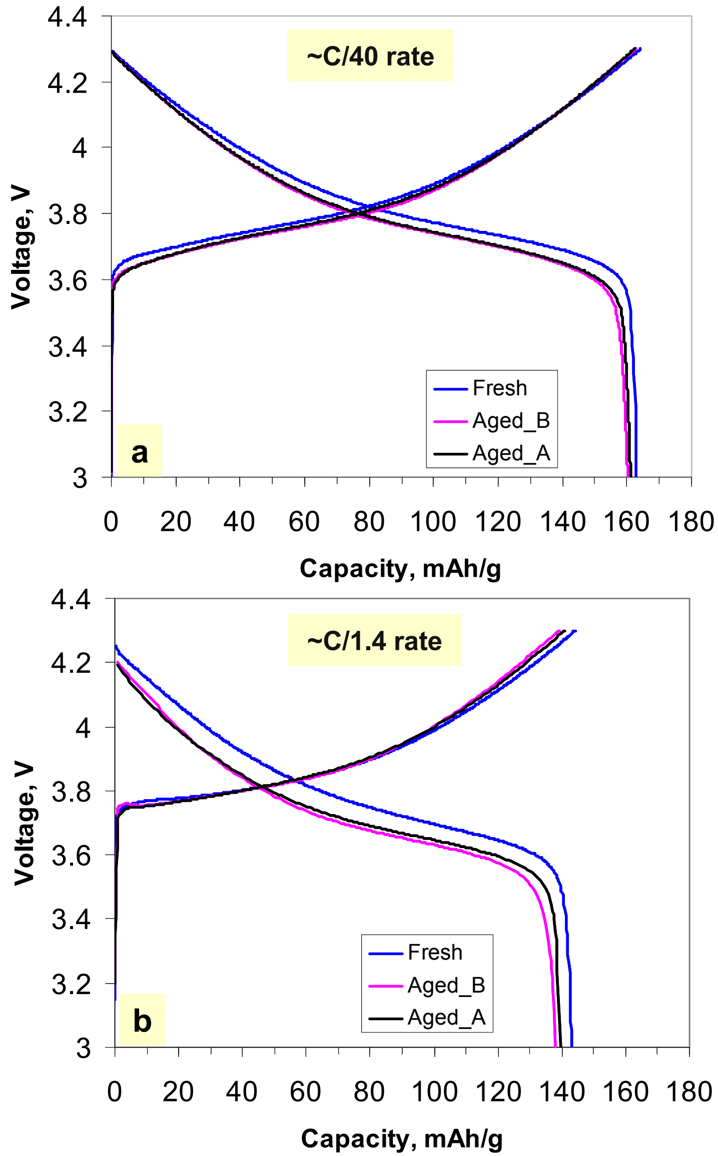




Negative Electrode: Impedance rise in frequency regime associated with electrode-electrolyte interfacial processes. This indicates that SEI layer becomes more resistive on aging

Positive Electrode: Impedance rise in frequency regime associated with electronic processes in electrode. Electrolyte additive appears to inhibit electrode impedance rise

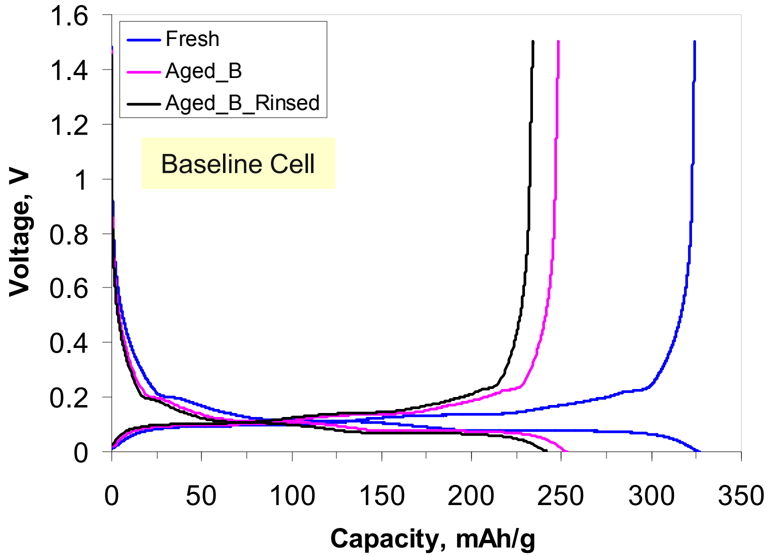
Harvested positive electrode data – capacity loss, on aging, is small

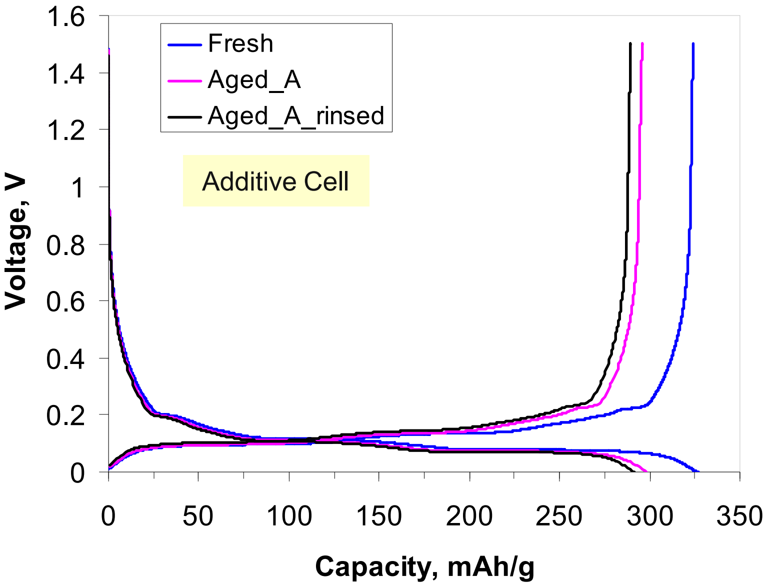


Sample	Aging condition
Fresh	None (as-received laminate)
Aged_B	4V, 38 wks at 55°C, baseline electrolyte cell
Aged_A	4V, 38 wks at 55°C, additive electrolyte cell

- No noticeable difference between fresh and aged electrode data
- Faster (~C/1.4) rate data also show little capacity difference between fresh and aged electrodes. However, aged cells show greater polarization on discharge, which is consistent with their higher impedance.

Harvested negative electrode data – capacity loss on aging

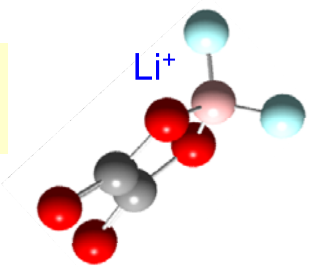




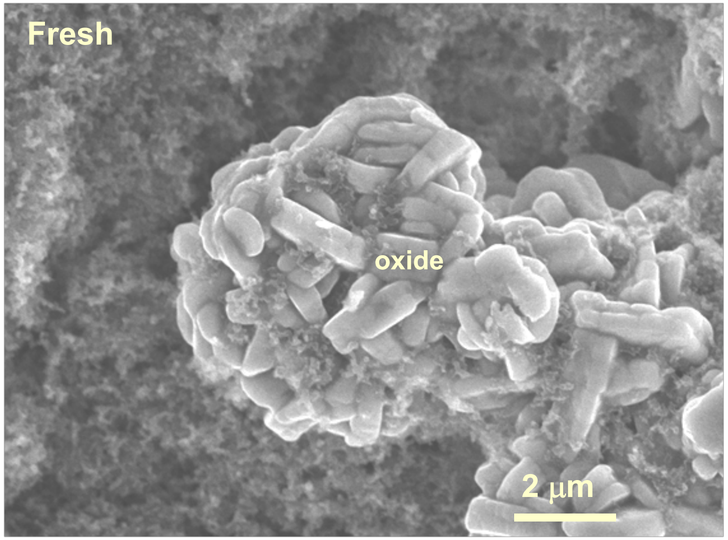
Sample	Aging condition
Fresh	None (as-received laminate)
Aged_B	4V, 38 wks at 55°C, baseline electrolyte cell
Aged_A	4V, 38 wks at 55°C, additive electrolyte cell

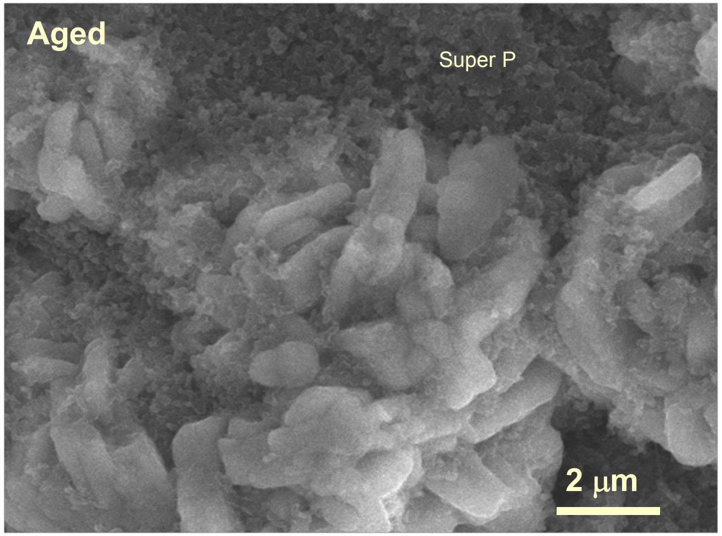
- Noticeable capacity difference between fresh and aged electrodes
- Electrode capacity loss may be from pore-clogging and/or particle isolation
- Electrolyte additive seen to be effective in reducing capacity loss
- DMC-rinse of electrodes does not help regain “original” electrode capacity

Additive
$LiF_2B(C_2O_4)$



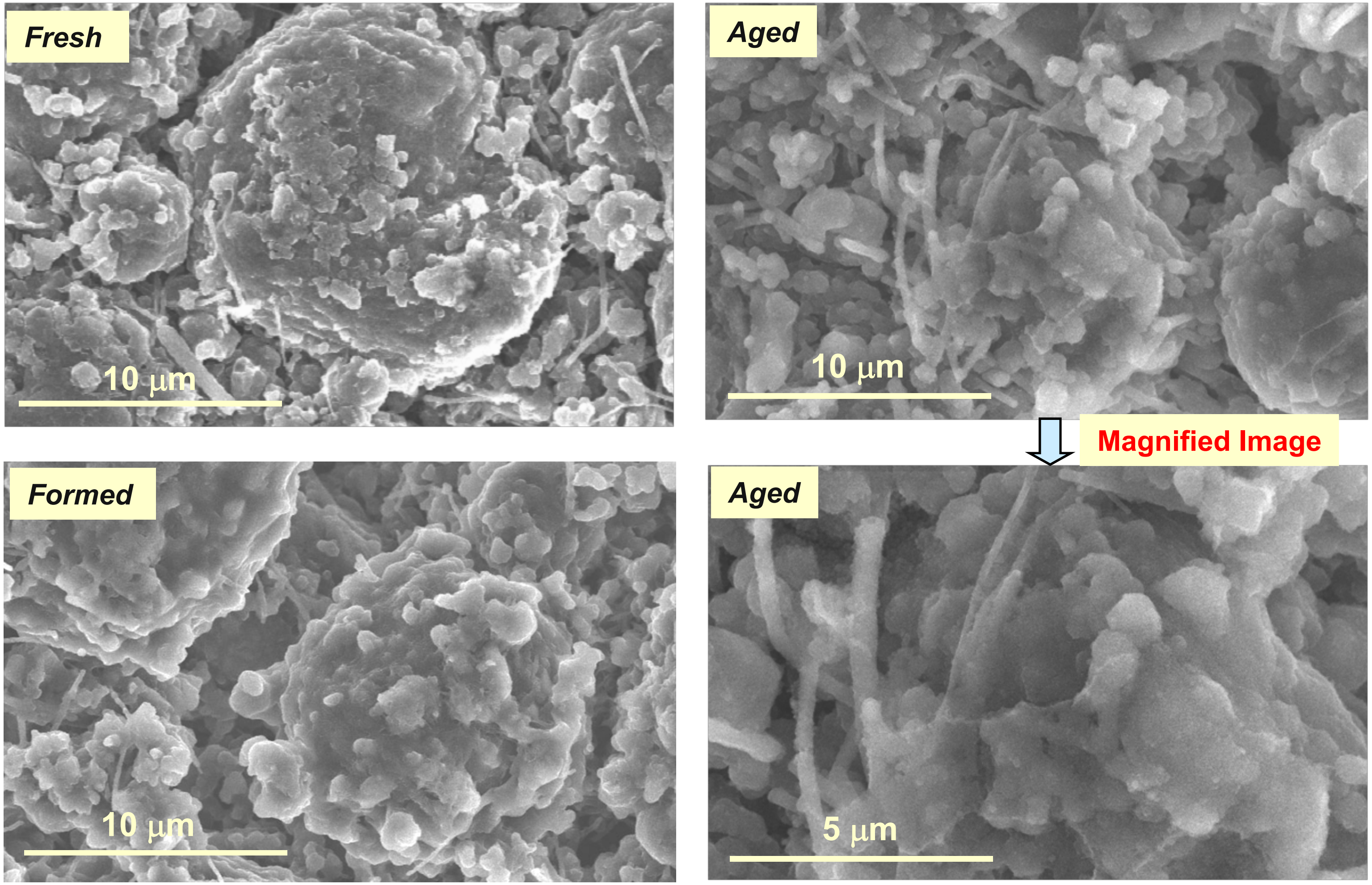
Harvested positive electrode SEM images – surface films are apparent on aged oxides





- Summary
  - ✓ The oxide secondary particles are ~ 5 to 10 μm, and made up of primary particles ~1 μm in size
  - ✓ A thin film is seen on the oxide surface after formation cycling
  - ✓ Aged electrodes show thicker films, which appeared smoother for "additive electrolyte" samples
  - ✓ There is plenty of carbon adjacent to the oxide, even in highly aged electrodes, i.e., the high-frequency arc changes in the EIS data does not appear to result from a decrease in contact between the oxide and SuperP carbons.

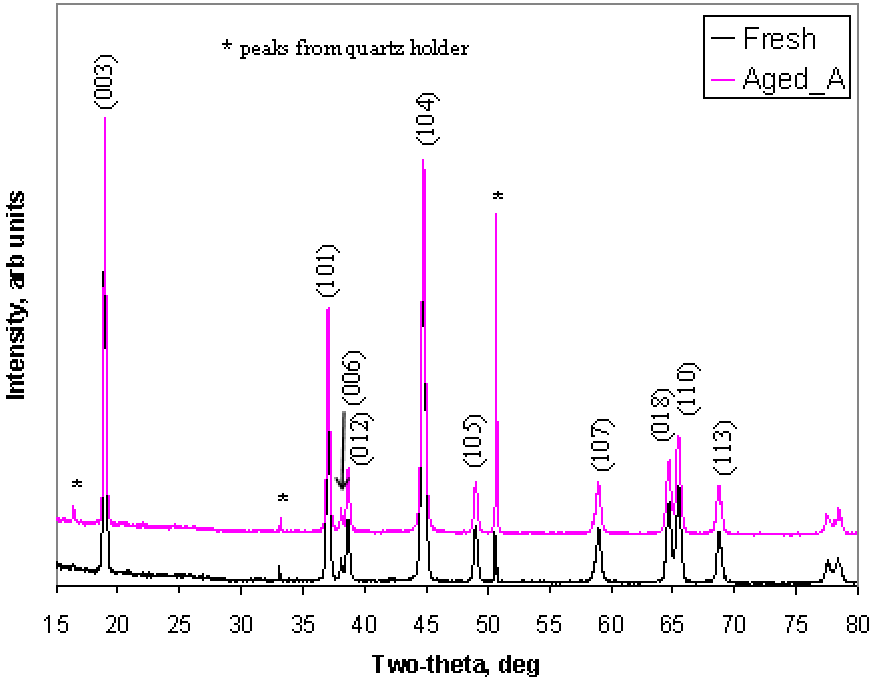
Harvested negative electrode - *thicker "surface films" on aged electrodes*



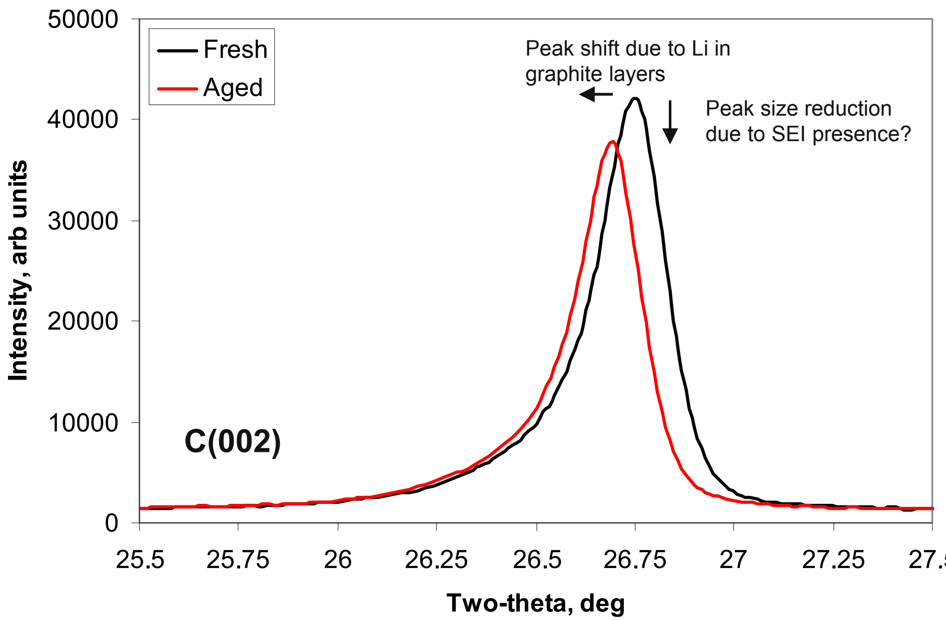
After formation cycling, the graphite and carbon fibers are covered by a very thin SEI, which thickens as the cell ages. The aged-SEI was relatively smooth on carbon fibers from additive cells and rougher on fibers from baseline cells.

with S. McLaren, UIUC

Harvested electrodes – XRD data showed no obvious damage to the electrode active materials (oxide-positive, graphite-negative)

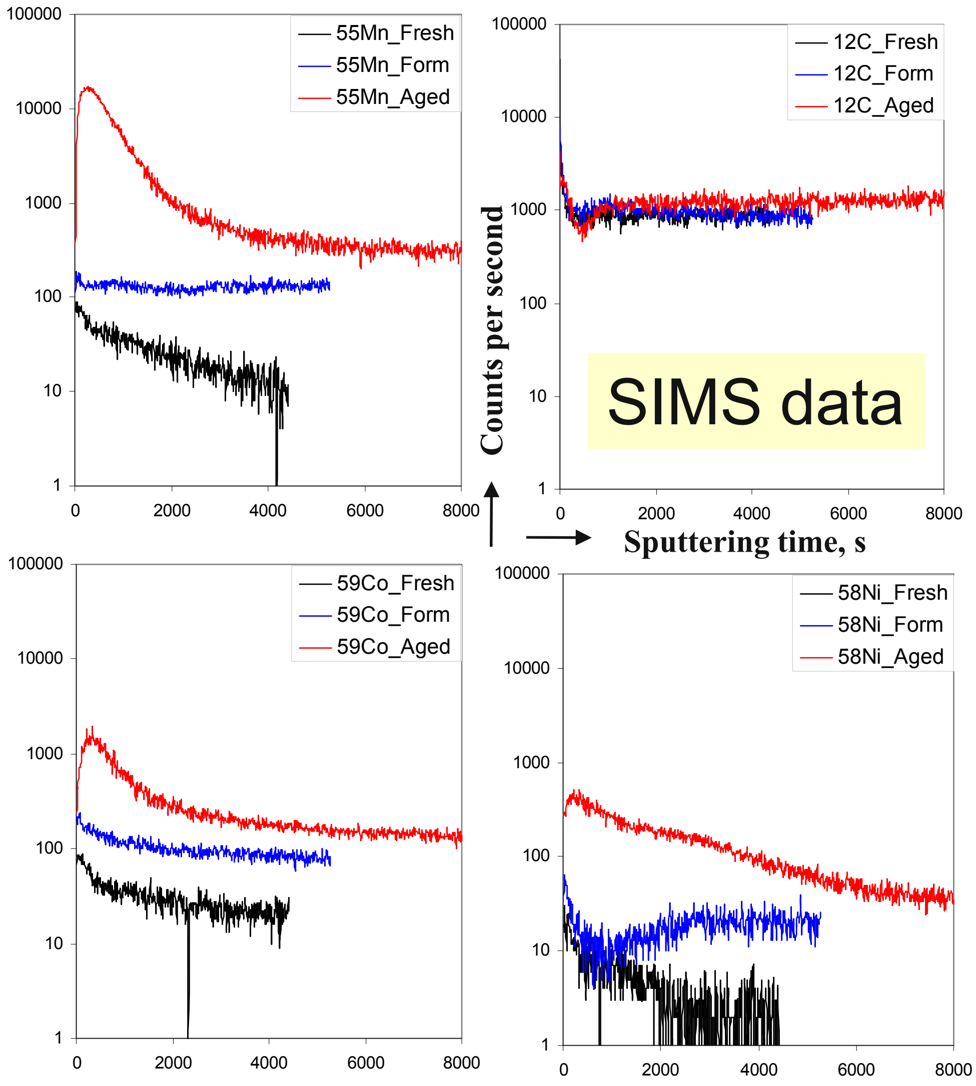


Representative XRD spectra show little difference between data from fresh and aged Gen3 positive electrodes.



The lower peak intensities of the harvested electrodes, relative to that of the fresh electrode, may be due to the SEI layer presence. Aging does not significantly affect graphite peak width or intensity.

Harvested negative electrode – Dynamic SIMS data show that transition metals (Mn, Ni, Co) accumulate at the graphite electrode on aging

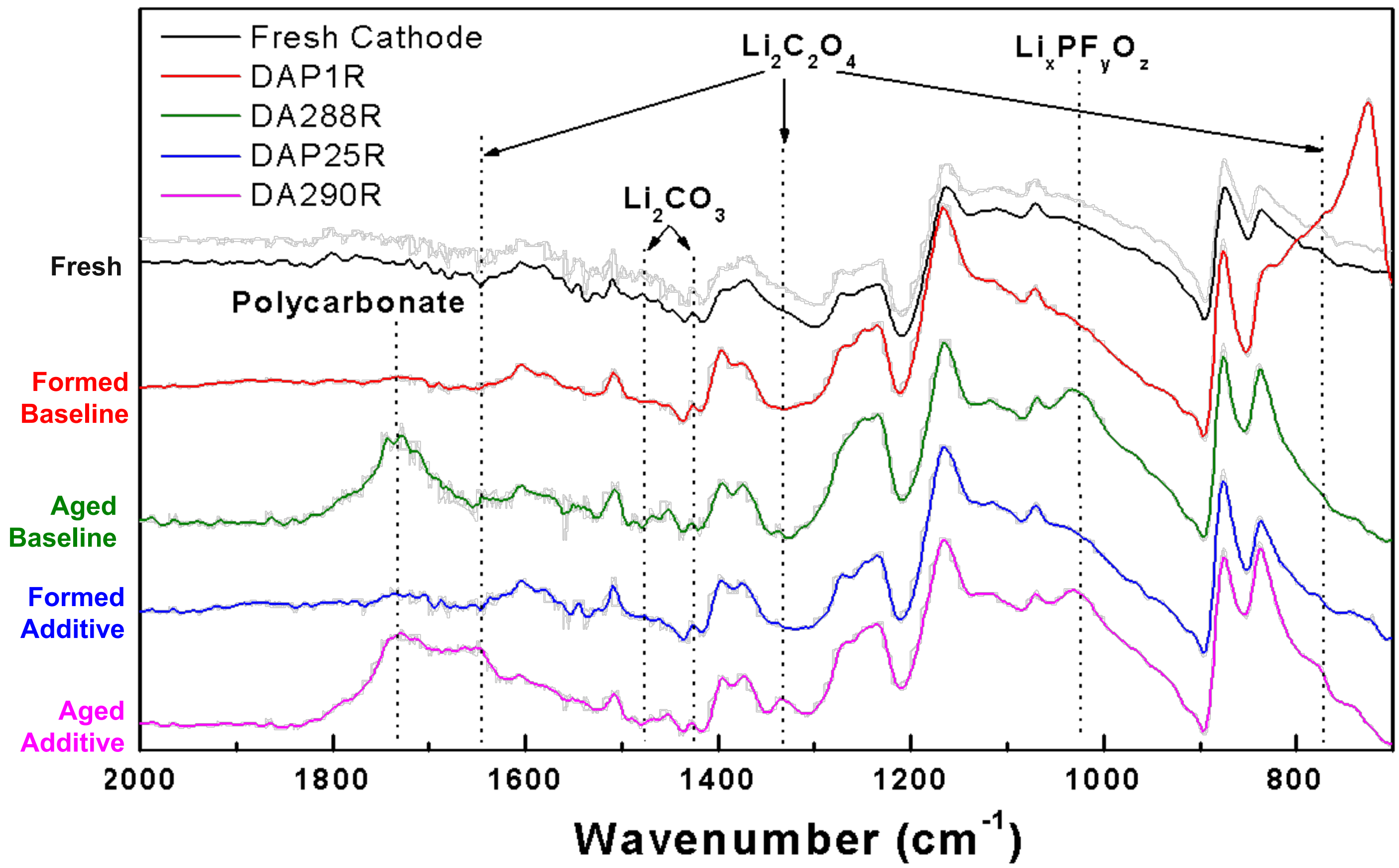


Summary

- ✓ Mn, Co and Ni counts is greater on graphite from aged cell than on graphite from formed cell
- ✓ Transition metal accumulation (~100 ppm) at graphite electrode is observed for cells, both, with and without $LiF_2BC_2O_4$ additive
- ✓ C sputtering data indicate that graphite electrode SEI is different on aged samples than on formed samples. These differences, which may include changes to morphology, constitution, and thickness of SEI, correlate with the negative electrode impedance increase induced by cell aging

D.P. Abraham, T. Spila, M. Furczon, E. Sammann, Electrochem. Solid-State Lett. 11 (2008) A226

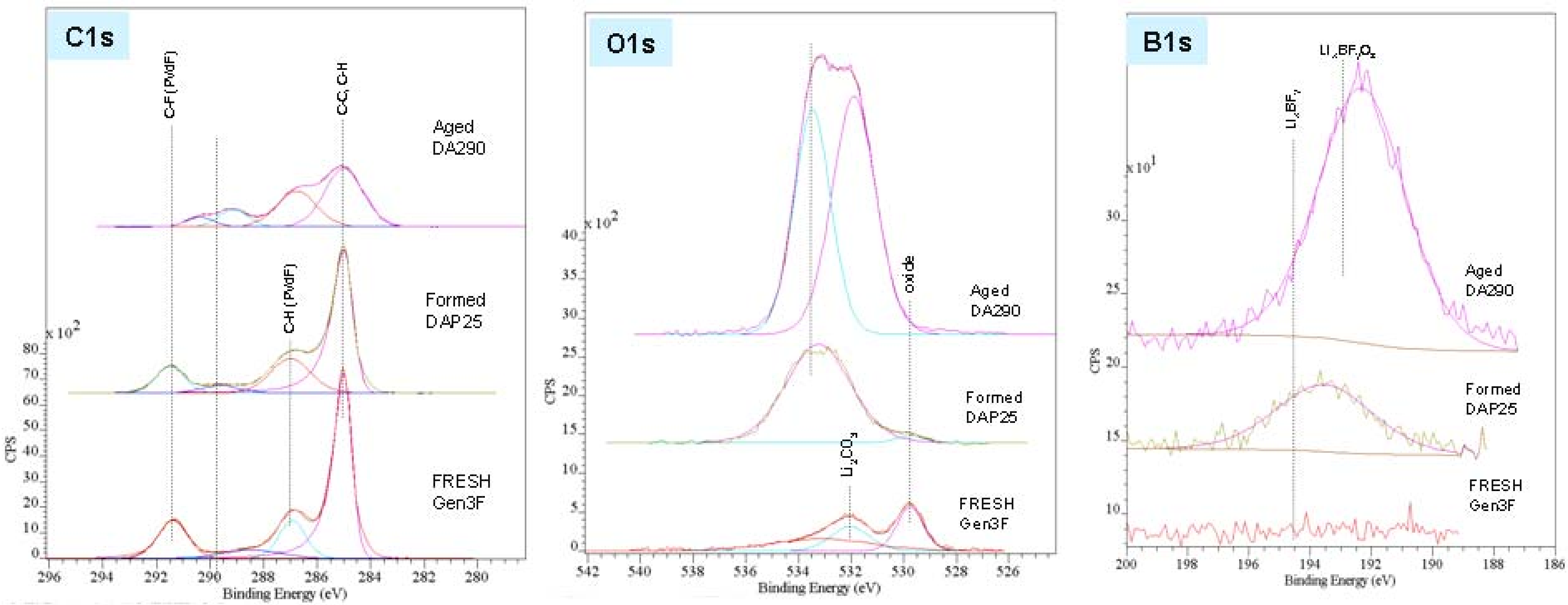
Harvested positive electrodes – FTIR data indicate changes in polycarbonate (oligomers), lithium alkyl carbonates, and $Li_xPF_yO_z$ content on aging



Surface films on electrodes harvested from the $LiF_2BC_2O_4$-additive also show presence of a lithium oxalate (or a related oxalate compound)

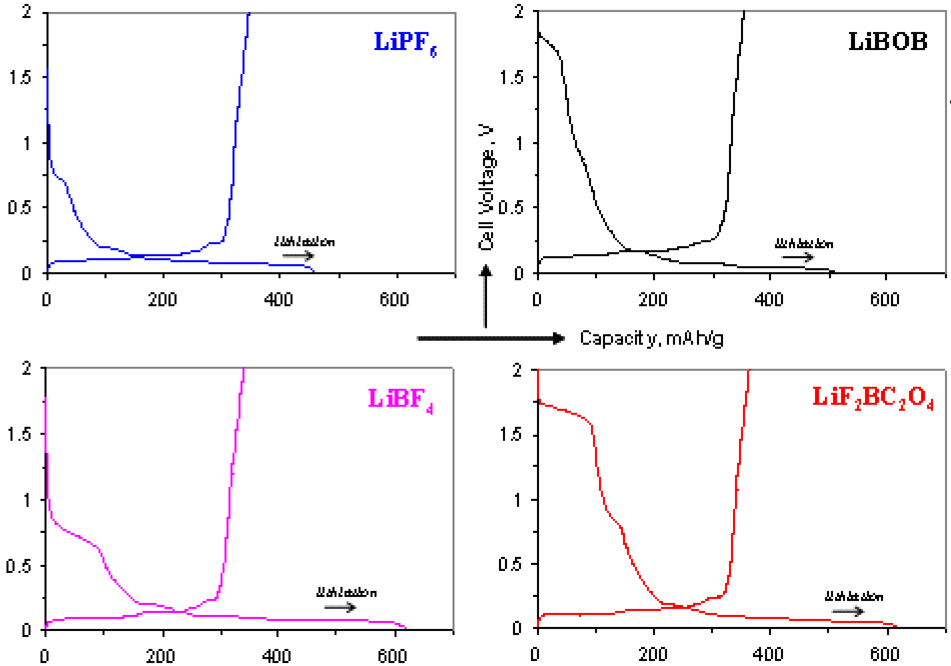
with B. Lucht, URI

Harvested positive electrodes (from additive cell) – XPS spectra show that the composition of surface films changes with cell age



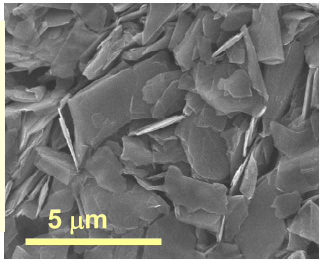
<u>Fresh</u> electrode data showed peaks from carbons and the binder. These peaks are absent in <u>aged</u> sample data indicating an overlying surface film. The <u>aged</u> sample spectra suggested the presence of various species, including ethers (ROLi), carbonates ($ROCO_2Li$), $Li_xPF_yO_z$ and $Li_xBF_yO_z$. B-bearing oligomers, arising from $LiF_2BC_2O_4$, may inhibit electrode impedance rise by forming a protective layer on the oxide.

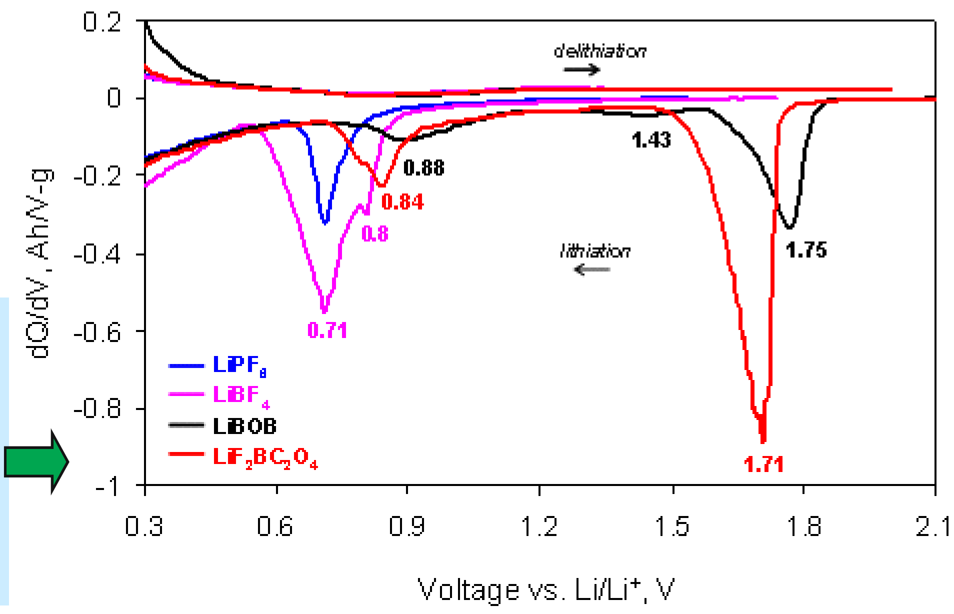
SEI films on graphite have been studied using Binder-Free (BF) electrodes - absence of PVdF binder simplifies data interpretation



First cycle lithiation-delithiation data for BF-graphite//Li cells containing various electrolytes.

SEM image showing graphite electrode

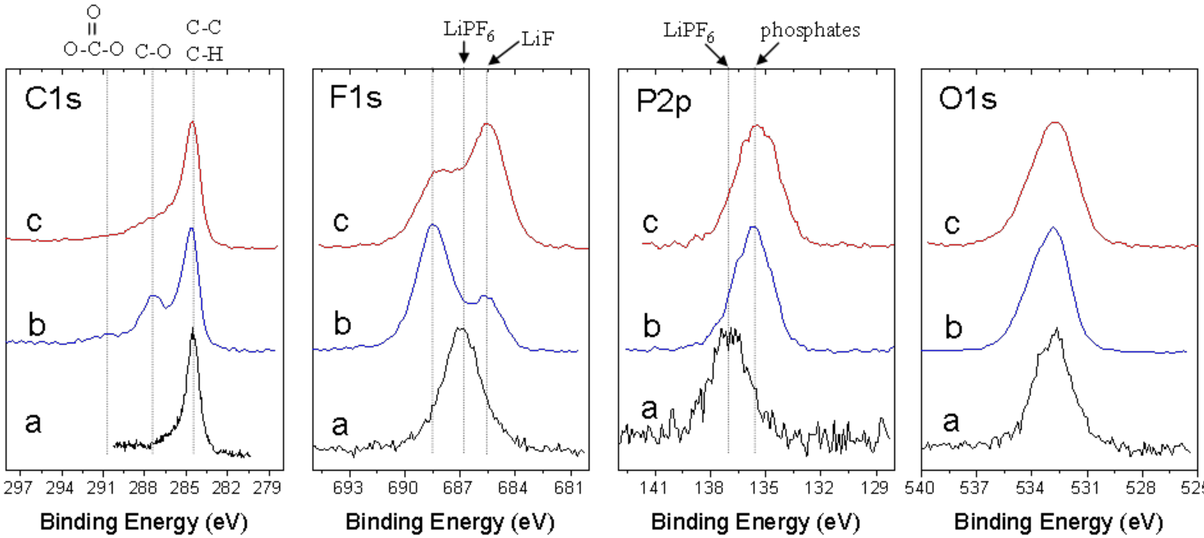




Differential capacity plots: Electrolyte reduction observed at multiple voltages (>1.5V and <1V vs. Li) for LiBOB and $LiF_2BC_2O_4$, and only <1V vs. Li for $LiPF_6$ and $LiBF_4$

A. Xiao, L. Yang, B.L. Lucht, S-H. Kang, and D.P. Abraham, J.Electrochemical Soc. 156 (2009) A318.

Typical XPS data show peaks from SEI compounds on BF-graphite electrode



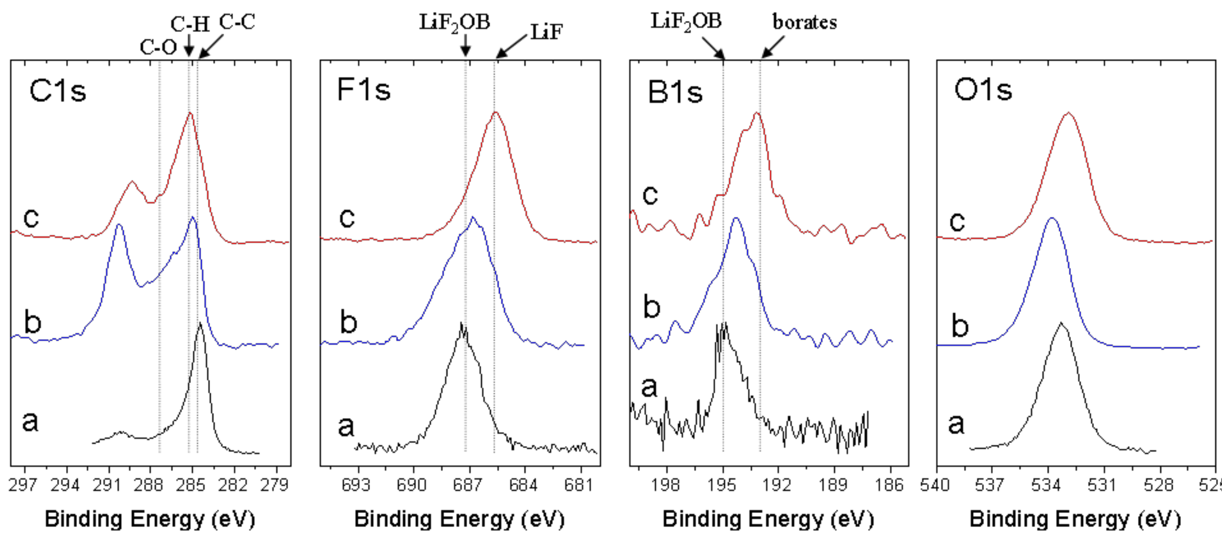
$LiPF_6$ electrolyte

Lithium alkoxides and carbonates removed upon washing, LiF and $Li_xPF_yO_z$ retained.

(a) dipped, then dried, (b) cycled, but not rinsed, and (c) EMC-rinsed

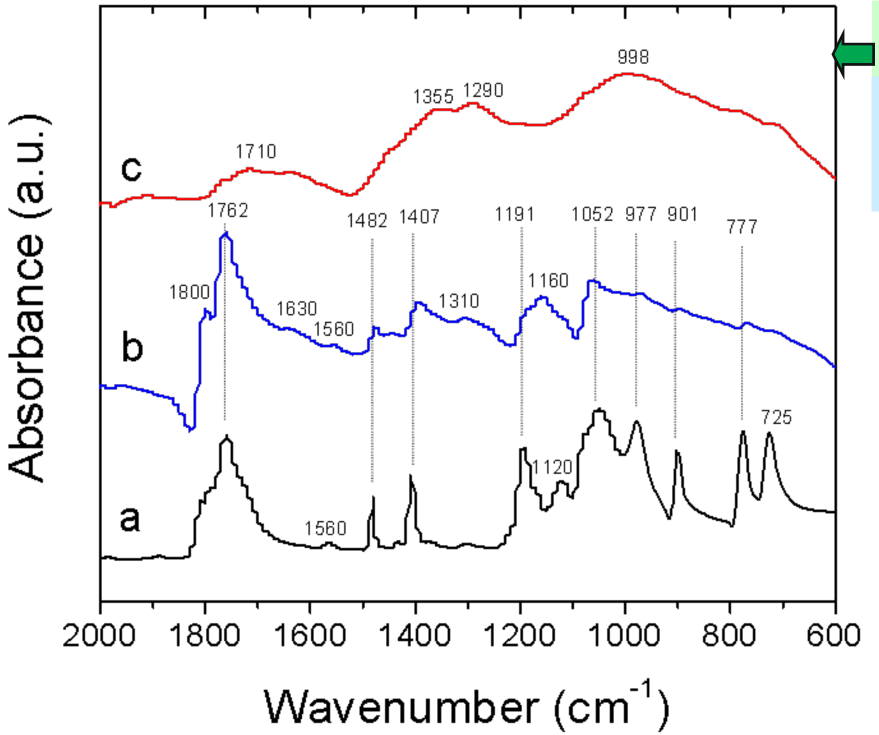
$LiF_2BC_2O_4$ electrolyte

LiF, Li_xBO_y $Li_xBO_xF_y$ and $Li_2C_2O_4$ are primary components after rinsing



A. Xiao, L. Yang, B.L. Lucht, S-H. Kang, and D.P. Abraham, J.Electrochemical Soc. 156 (2009) A318.

Typical FTIR data show peaks from SEI compounds on BF-graphite electrode



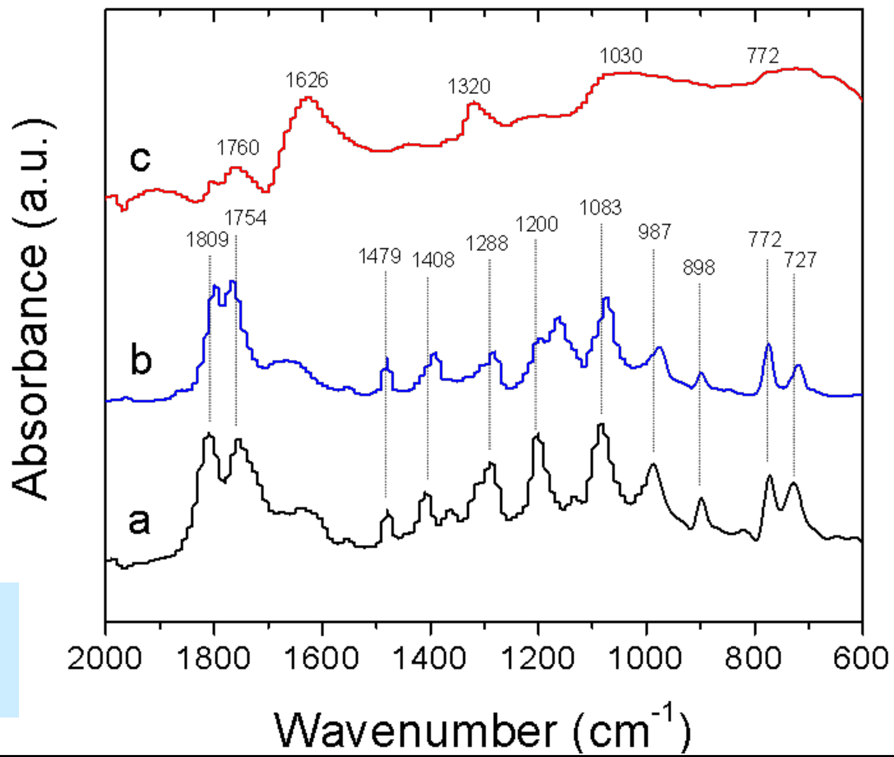
LiBF$_4$ electrolyte

EC-LiBF$_4$ on dipped sample. Li_xBO_y and $Li_xBF_yO_z$ retained after rinsing

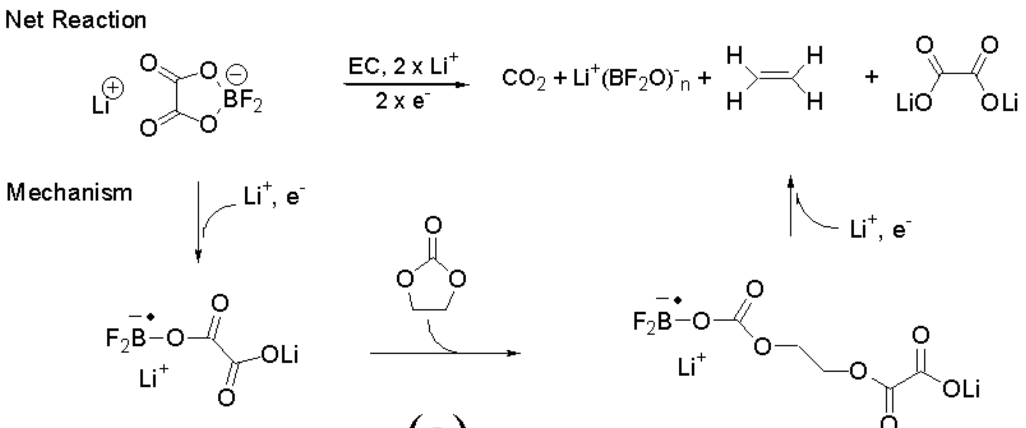
(a) dipped, then dried, (b) cycled, but not rinsed, and (c) EMC-rinsed

LiBOB electrolyte

EC-LiBOB on dipped sample. Li_xBO_y and $Li_2C_2O_4$ retained after rinsing

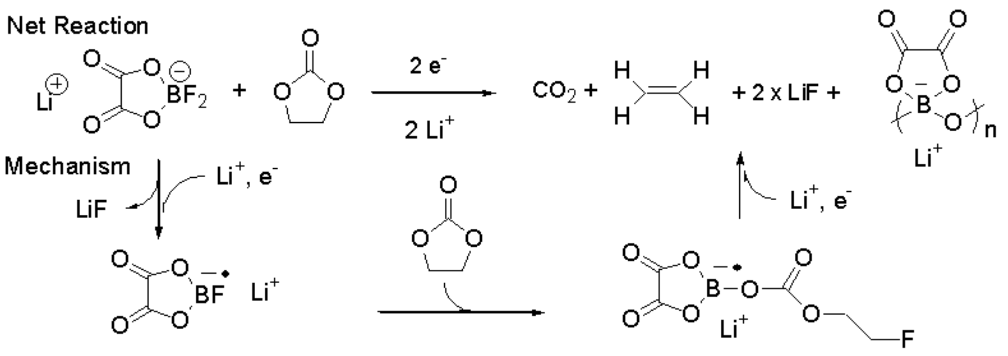


Example of reaction mechanisms postulated to explain formation of SEI constituents



(a)

(a) The reduction of $LiF_2BC_2O_4$ induces a ring-opening reaction of the salt, which coupled with a ring-opening reaction of EC generates a $Li(BF_2O)_n$ polymer and $Li_2C_2O_4$.



(b)

(b) An alternative reaction route generates the linear borate with an oxalate ligand on B and LiF. This is a more likely reaction route because LiF is known to be present in the SEI.

Work in Progress/Future Work

- "Wrap up" tests on Gen3 cells and cell constituents
  - ✓ Document data in reports and refereed journal articles
- Examine performance and performance degradation of materials and cells under PHEV test conditions (wider voltage windows, greater SOC swings, etc.)
  - ✓ Wider voltage windows may yield higher capacities but cause faster performance degradation for reasons that may include electrolyte degradation, active material bulk/surface degradation, etc.
- Continue examination of electrode surface films after formation in cells containing various electrolytes and electrolyte additives
  - ✓ Some of these experiments will be conducted on model electrodes, such as binder-free graphite electrodes and binder- and carbon-free oxide electrodes
- Examine relationship between transition metal accumulation on graphite surfaces and electrode impedance rise
  - ✓ We have established a "correlation" but is there "causation"?

Summary

- The objective of this study is to identify factors that contribute to cell performance, 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 cells containing electrodes with the Gen3 chemistry. Impedance rise is lower for cells containing the $LiF_2BC_2O_4$ electrolyte additive, which appears to form boron-bearing films that form a protective layer on the oxide electrode.
- We've characterized SEI layers that form on graphite electrodes cycled in cells containing various electrolytes, by XPS, FTIR and TGA, and formulated formation mechanisms based on the data.
- We are currently documenting data from Gen3 cells and are in the process of initiating several experiments that include the examination of performance and aging behavior of materials and cells under PHEV test conditions.