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Diagnostics at Argonne

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February 26, 2008

Presentation at the Office of Vehicle Technologies,
2008 Annual Merit Review Meeting

This presentation does not contain any proprietary or confidential information

Vehicle Technologies Program

Outline

- Purpose of Work
- Technical Barrier
- Approach
- Performance Measures and Accomplishments
- Publications
- Plans for Next Fiscal Year
- Summary

Contributors

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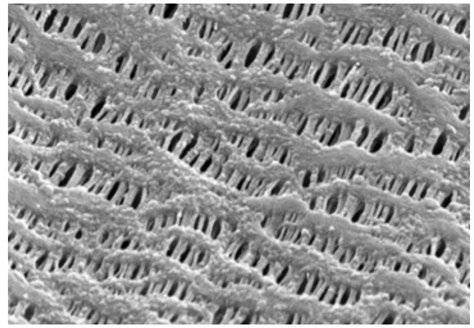
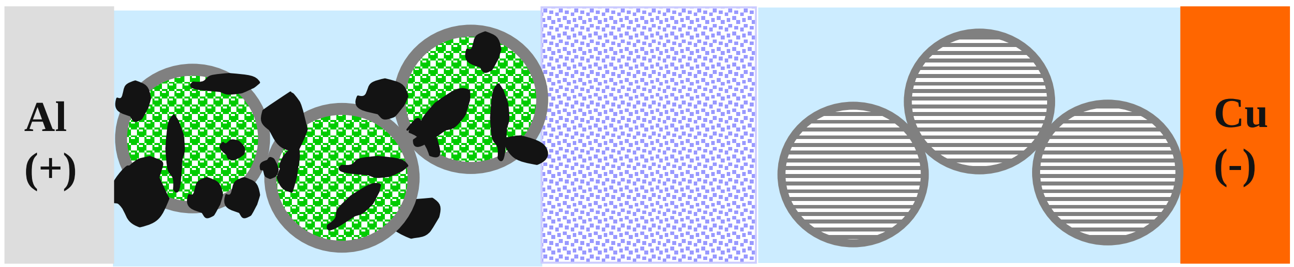
- C. Lei, UIUC
- Brett Lucht, URI

Purpose of Work- Examine Performance Degradation Mechanisms of Cells based on the Gen3 chemistry



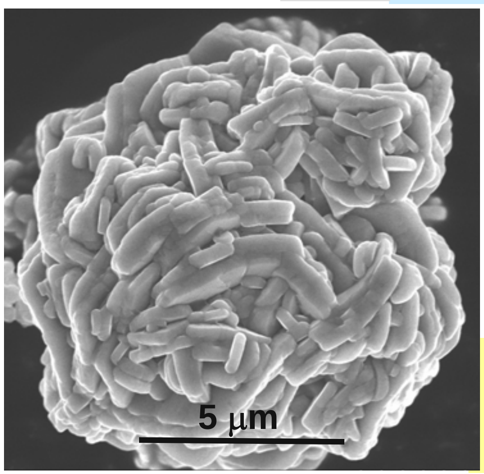
Celgard 2325 separator

Positive



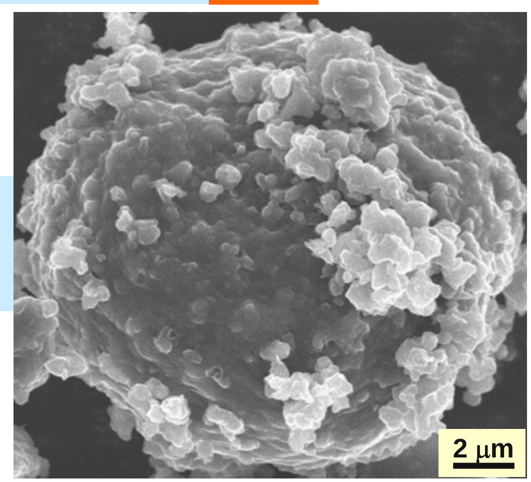
Negative

3EC-7EMC + $LiPF_6$ + $LiF_2BC_2O_4$ additive



MCMB-1028 graphite
Particle size ~10 µm

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



Major Technical Barrier

Cell Calendar and Cycle Life

- *Identifying Constituents and Processes responsible for Cell Performance Degradation should allow the selection (and optimization) of Components (electrode, electrolyte, etc.) that will enable Lithium-ion Batteries meet the 15y calendar life goal of DOE's Advanced Technology Development program*

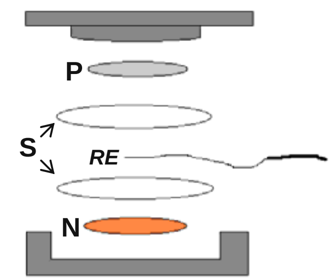
Approach

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

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

Gen3

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

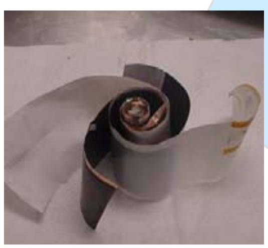


Disassembly of New and Aged Cells

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

Electrolyte & Separator study (ANL, LBNL)

(UIUC, URI)

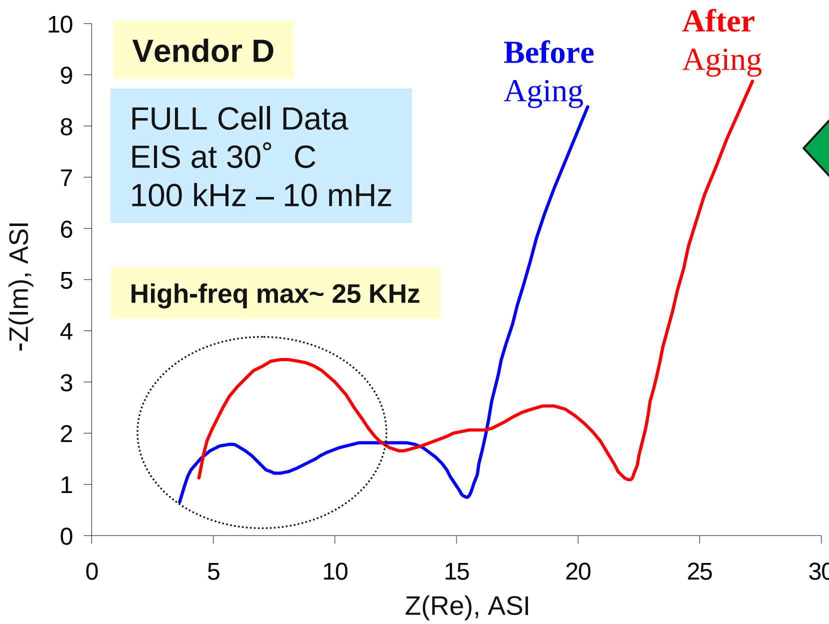


- Suggest/implement approaches to extend cell life

Performance Measure/Technical Accomplishments – FY07

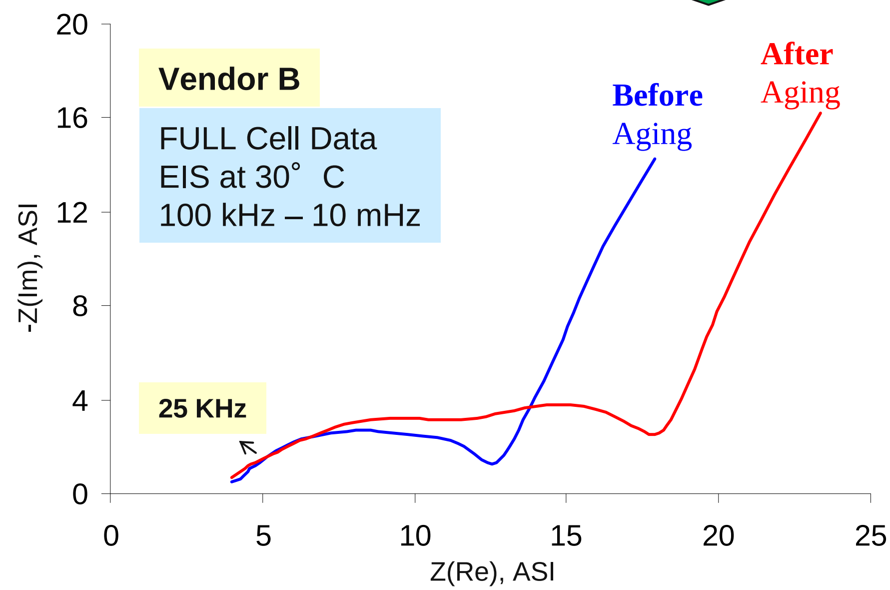
- Initiate Aging Studies of Cells containing Gen3 electrodes
  - Aging studies on cells (coin, pouch, reference electrode) were initiated with electrodes from various vendors
- Determine sources of performance degradation (capacity fade, impedance rise) in baseline Gen3 cells
  - Showed that “electrode engineering” can play a significant role in cell performance on aging, i.e., it can affect cell life
  - Showed that both positive and negative electrodes contribute to cell impedance rise. This is different from cells that contain NCA(+)//graphite(-) electrodes, where impedance rise at the NCA(+) dominates cell impedance on aging
- Determine effect of $LiF_2BC_2O_4$ electrolyte additive on performance of Gen3 cell
  - Showed that this additive improves cell performance by inhibiting impedance rise at the positive electrode

Under similar aging conditions cells prepared with electrodes from different vendors (same chemistry) show significantly different frequency response during EIS measurements



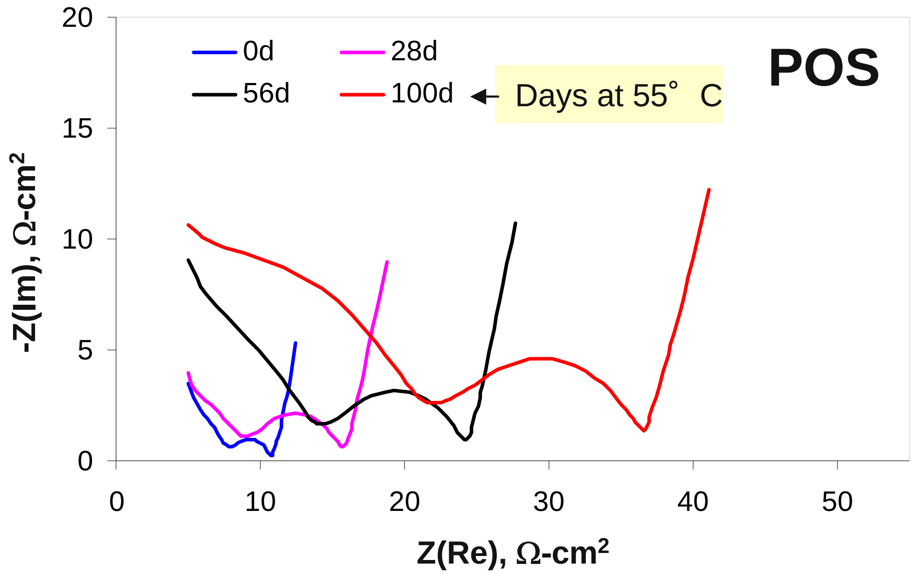
Cell impedance rise contains contributions from both high-frequency (electronic) and mid-frequency (interfacial) processes

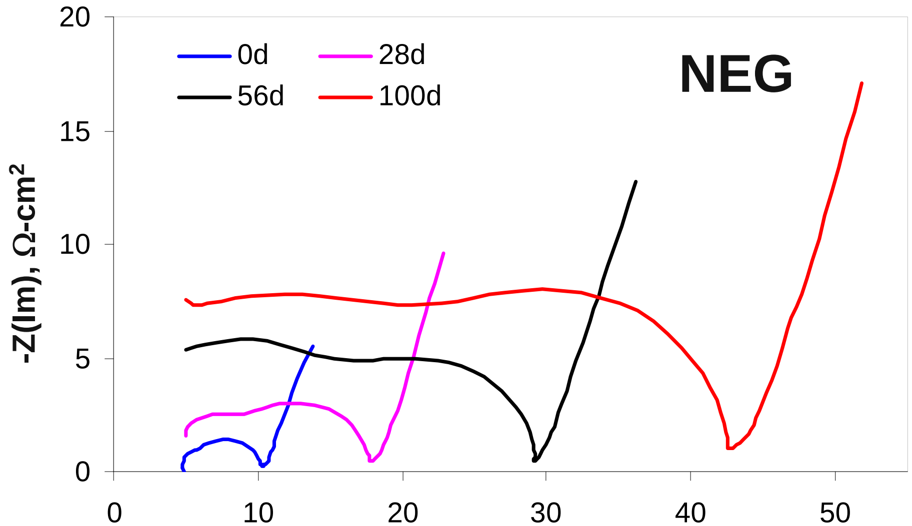
Cell impedance rise contains contributions only from mid-frequency (electrode-electrolyte interfacial) processes



This high-frequency impedance change is (a) associated with the positive electrode, and (b) is not a consequence of cell chemistry but is an electrode artifact.

Both Positive and Negative electrodes contribute to impedance rise in Gen3 electrode cells containing the baseline electrolyte

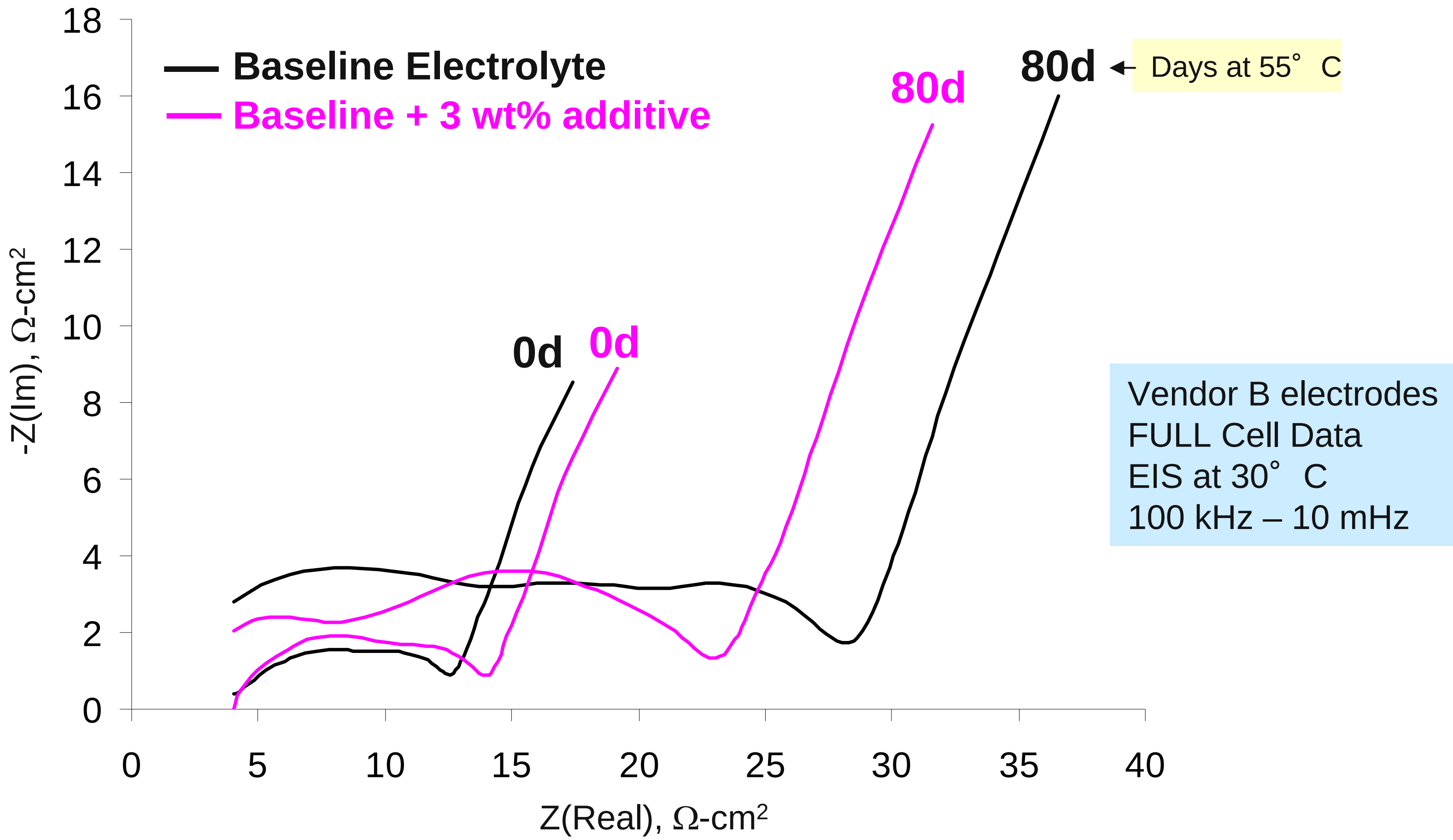




Vendor E electrodes

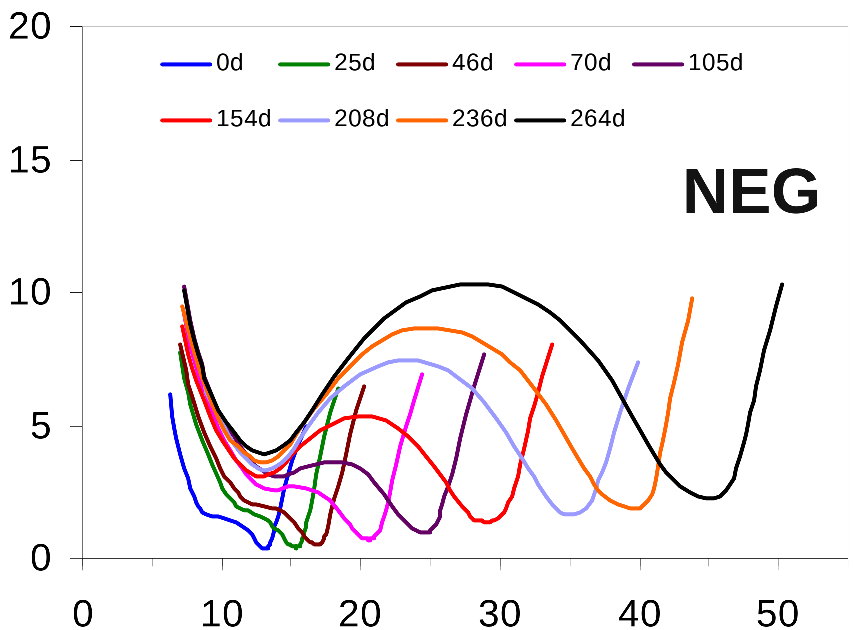
EIS data at 30° C
From a RE cell
100 kHz – 10 mHz

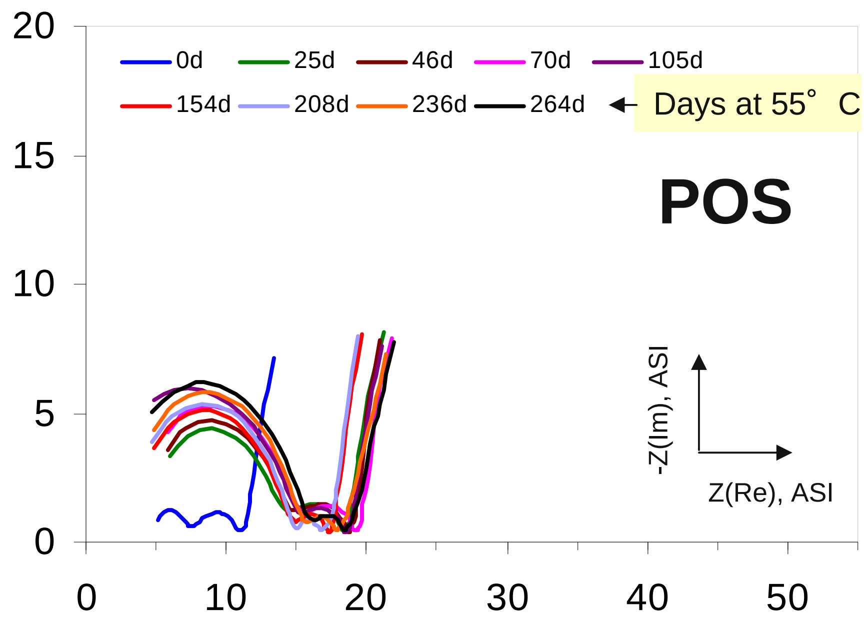
The $LiF_2BC_2O_4$ electrolyte additive reduces impedance rise (and capacity fade) on aging



Gen3 electrodes from all Vendors showed this behavior – trend is also consistent with test data on larger cells

Negative electrode impedance rise dominates cell impedance rise on aging of $LiF_2BC_2O_4$ additive bearing Gen3 electrode cells – additive inhibits positive electrode impedance rise

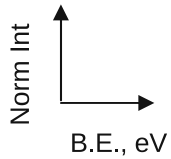




Impedance rise mainly in mid-frequency arc regime (electrode-electrolyte interfacial processes)
- Indicates that SEI layer becomes more resistive on aging

Impedance rise in high-frequency arc regime (associated with electronic processes in electrode)
-Mid-frequency arc width increase is minimal on aging

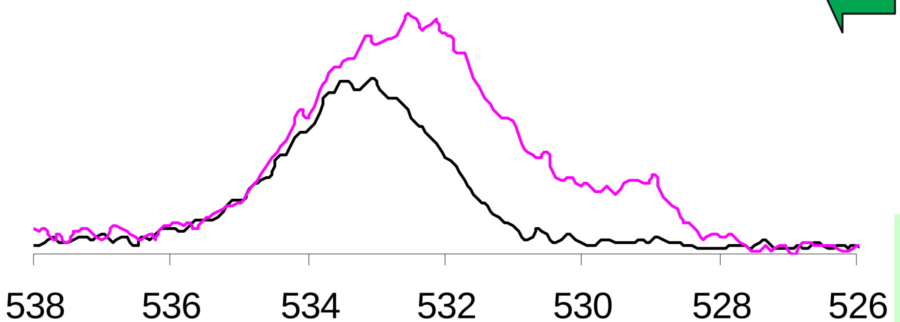
Differences in Surface Films may explain Passivation Behavior of Oxide Electrode in cells with $LiF_2BC_2O_4$ additive



After Formation

— **Baseline**
— **Baseline + add**

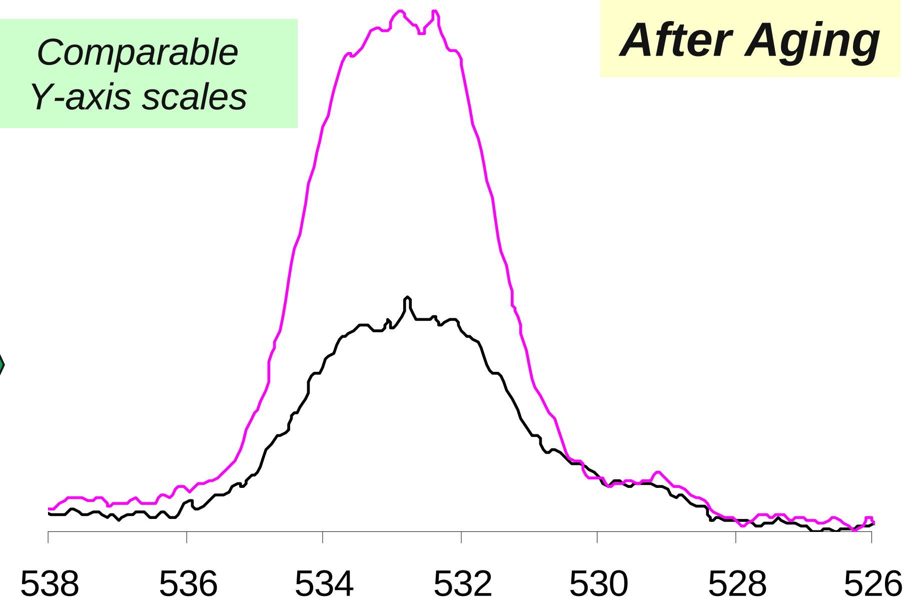
XPS spectra O1s



Some differences observed in spectra after formation cycling

Comparable Y-axis scales

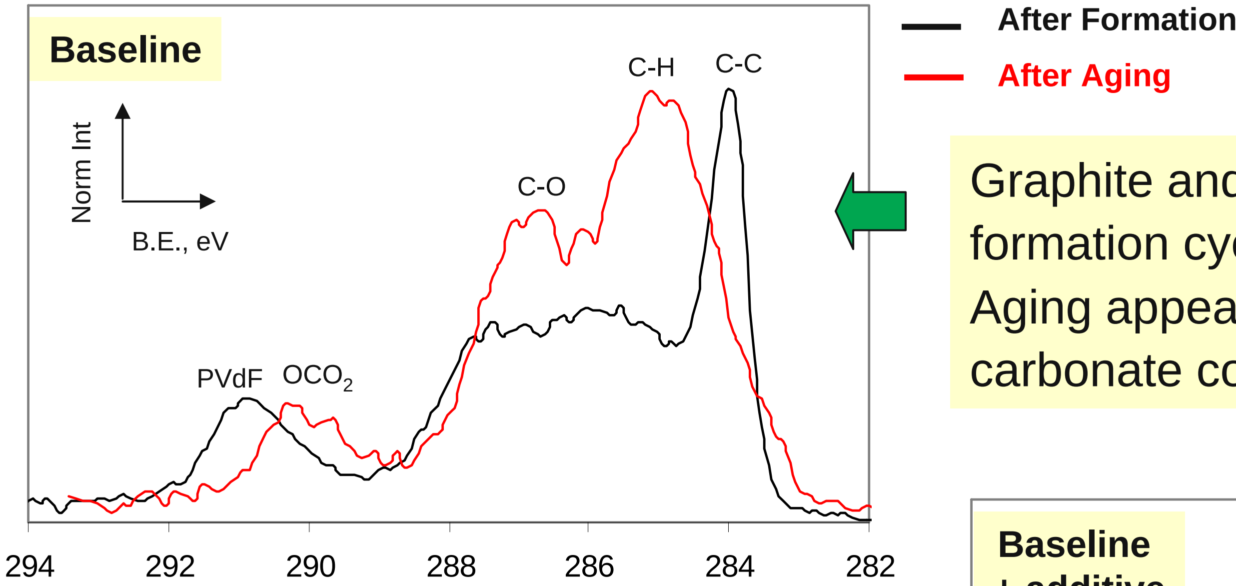
After Aging



Significant differences in O1s (& C1s XPS) spectra after aging

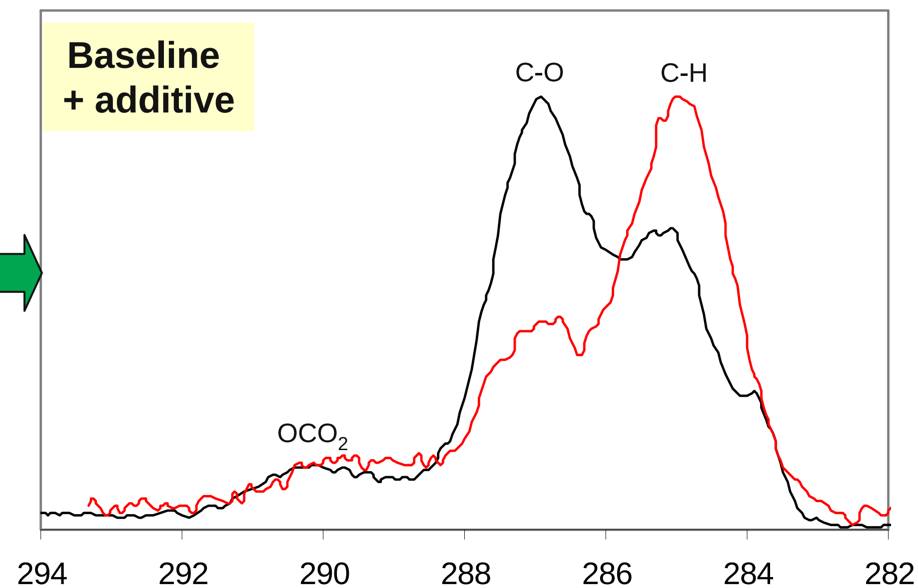
- Increased amount of oxygen-bearing species consistent with increase of ethers (oligomers?) and alkyl carbonates in cell with additive

Changes in Graphite SEI are evident on cell aging – XPS spectra – C1s



Graphite and PVdF peaks seen after formation cycling but not after aging. Aging appears to increase ether and carbonate content in SEI.

Graphite and PVdF peaks are not seen after formation cycling, which indicates that the SEI coverage is more extensive. Aging appears to modify the SEI layer



Some Relevant Publications

1. C.H. Lei, J. Bareño, J.G. Wen, I. Petrov, S.-H. Kang, D.P. Abraham, *J. Power Sources 178 (2008) 422.*
2. D.P. Abraham, S. Kawauchi, D.W. Dees, *Electrochimica Acta 53 (2008) 2121.*
3. D.P. Abraham, J.R. Heaton, S.-H. Kang, D.W. Dees, A.N. Jansen, *J. Electrochem. Soc. 155 (2008) A41.*
4. D.P. Abraham, J.L. Knuth, D.W. Dees, I. Bloom, J.P. Christophersen, *J. Power Sources 170 (2007)465.*
5. D.W. Dees, A.N. Jansen, D.P. Abraham, *J. Power Sources 174 (2007) 1001.*.
6. S.-H. Kang, D.P. Abraham*, J. Power Sources 174 (2007) 1229.*
7. Diagnostic Examination of Generation 2 Lithium-Ion cells and Assessment of Performance Degradation Mechanisms, D.P. Abraham, ed., ANL Report, ANL-05/21 (2005).

Activities for Fiscal Year 2008 (and beyond)

Physicochemical (diffraction, microscopy, spectroscopy) diagnostic examination of materials from aged cells to identify Gen3 cell degradation mechanisms.

Examine electrolytes, electrodes, and separators harvested from aged cells to answer questions that include the following:

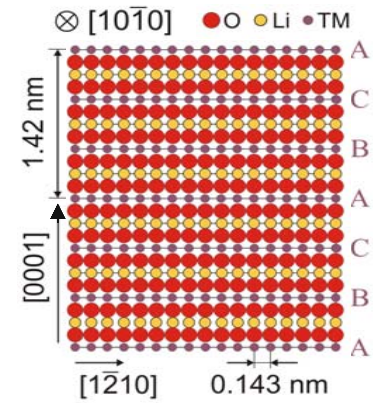
-Is there transition metal dissolution into the electrolyte? Do any of these elements deposit at the anode?

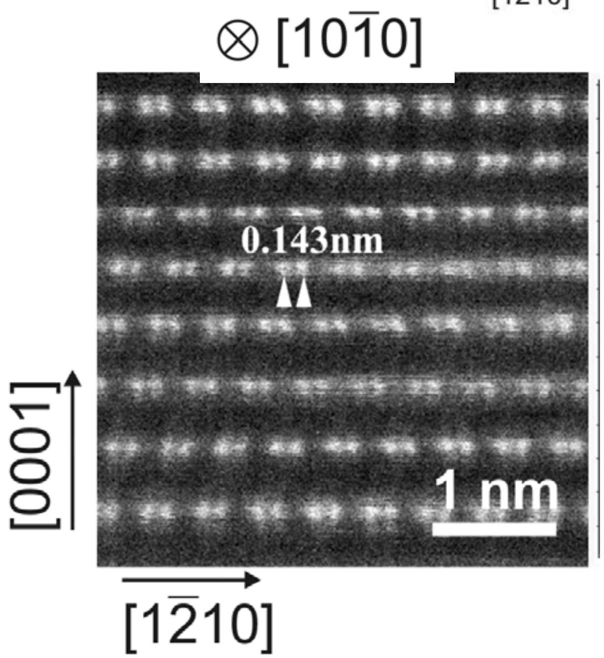
- What causes the negative electrode impedance increase in the absence, and in the presence, of the LiF_2BC_2O4 additive?

- How does the $LiF_2BC_2O_4$ additive inhibit impedance rise at the positive electrode?

- Does aging induce crystal structure changes at the oxide surface/oxide bulk?

Schematic of ideal layered structure





$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ - STEM image indicating Li presence in transition metal planes

Summary

- Development of lithium-ion batteries with 15y calendar life will enable widespread commercialization of HEVs, PHEVs and EVs. These vehicles offer the opportunity for significant petroleum displacement.
- Our approach is to develop an understanding of factors that contribute to performance degradation of lithium-ion cells. We expect to suggest and implement approaches to extend cell life.
- We've been studying the performance degradation of cells containing electrodes with the Gen3 chemistry. Both electrodes contribute to impedance rise (on aging) in cells containing the baseline electrolyte. Adding small quantities of $LiF_2BC_2O_4$ to the electrolyte additive improves cell performance by inhibiting impedance rise at the oxide electrode.
- We have published several articles and reports on diagnostic studies used to study performance degradation mechanisms in lithium-ion cells. Our data have also been presented at several conferences and DOE meetings.
- In the coming year, we will conduct detailed studies on components from fresh and aged Gen3 cells to determine cell degradation mechanisms.