Diagnostic Studies on Li-Battery Cells and Cell Components

Project Id: ES032

D.P. Abraham

Y. Li, M. Bettge, Y. Zhu

DOE Vehicle Technologies Program Annual Merit Review

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Overview

Timeline

- Start date: October 1, 2009
- End date: Sept. 30, 2012
- Percent complete: 75%

Budget

- Total project funding
  - 100% DOE
- FY10: $600K
- FY11: $600K
- FY12: $900K

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Partners

- Argonne colleagues
- University of Illinois, Urbana-Champaign
- University of Rhode Island
- Purdue University
- Brown University
- 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

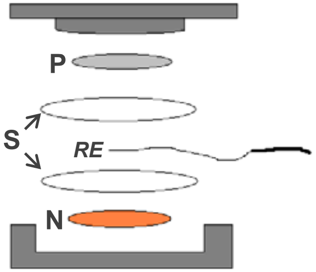
Approach

- **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

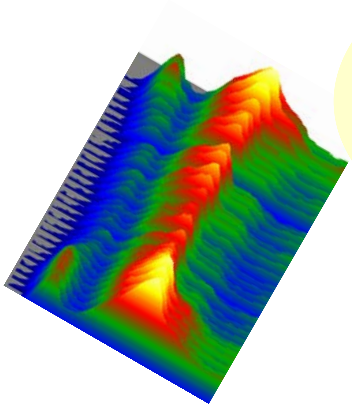


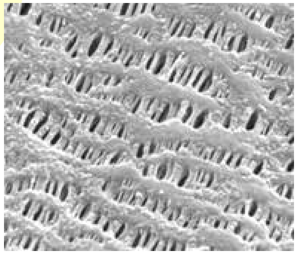
Disassembly of New and Aged Cells

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

Electrolyte & Separator study (ANL, LBNL)

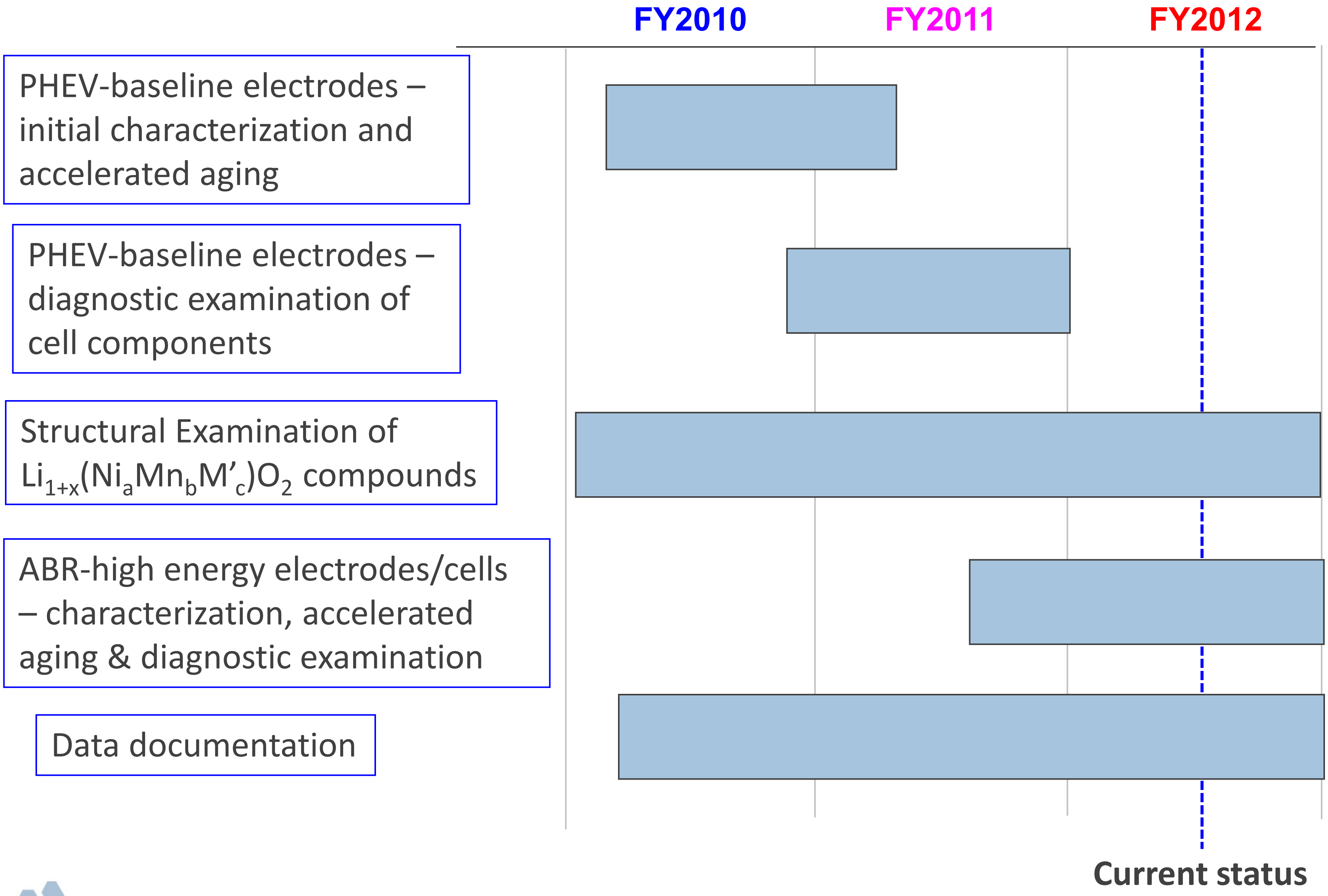
(UIUC, URI)





Suggest/implement approaches to extend cell life

Milestones



PHEV-baseline electrodes – initial characterization and accelerated aging

PHEV-baseline electrodes – diagnostic examination of cell components

Structural Examination of $Li_{1+x}(Ni_aMn_bM'_c)O_2$ compounds

ABR-high energy electrodes/cells – characterization, accelerated aging & diagnostic examination

Data documentation

Technical Accomplishments and Progress

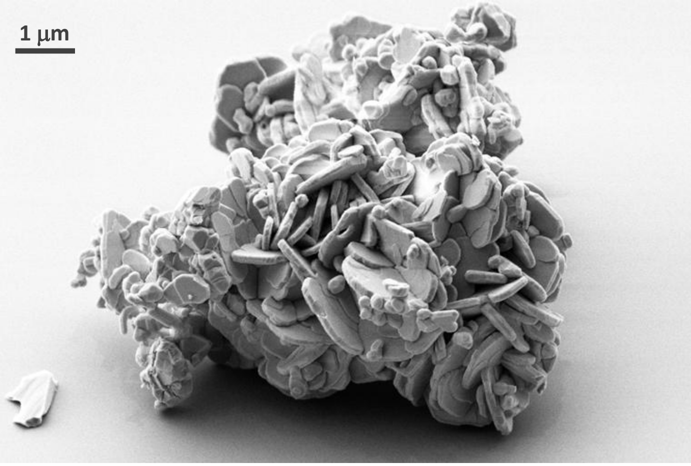
- Wrapped up studies on PHEV baseline (NCA+/Graphite-) cells and cell constituents *(met milestone)*
  - Documented data in reports. Shared information with colleagues in academia and industry through oral presentations and written communications.
- Initiated characterization and aging experiments on electrodes and cells identified for the next set of ABR cells *(met milestone)*
  - Demonstrated voltage hysteresis in $Li_{1+x}Ni_aMn_bCo_cO_2$ –based electrodes
  - Determined that the upper cut-off voltage is an important determinant of ABR cell life; performance degradation can be severe at voltages >4.6V vs. Li/Li^+
  - Correlated “cross-talk between electrodes” with cell performance degradation
  - Established that positive electrode impedance rise is the common feature in all ABR electrochemical couples tested to date.
  - Concluded that (i) electrolyte oxidation at the positive electrode is a significant contributor to cell impedance rise; (ii) lithium trapped in the negative electrode SEI is the main contributor to cell capacity fade.
- Identified targeted solutions to minimize cell performance degradation
  - Positive electrode reformulation can reduce cell initial impedance
  - Select electrolyte additives can reduce cell impedance rise and capacity fade
  - Select positive electrode coatings can reduce both cell impedance rise and capacity fade

Constitution of ABR-1 electrodes

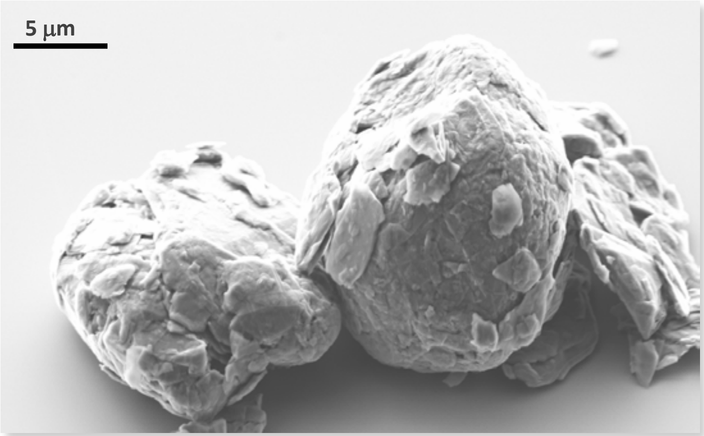
$Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ =
$0.5Li_2MnO_3$ - $0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$

ABR-1S(+)	**ABR-1S(-)**
Positive Electrode:	**Negative Electrode:**
86%wt $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$	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 mg/cm^2 active-material loading density	5.61 mg/cm^2 active-material loading density
37.1% electrode porosity	26% electrode porosity
35-µm-thick coating	40-µm-thick coating
15-µm-thick Al current collector	10-µm-thick Cu current collector

B. Polzin – Argonne CFF



Oxide primary particles consist of randomly oriented plate-like grains

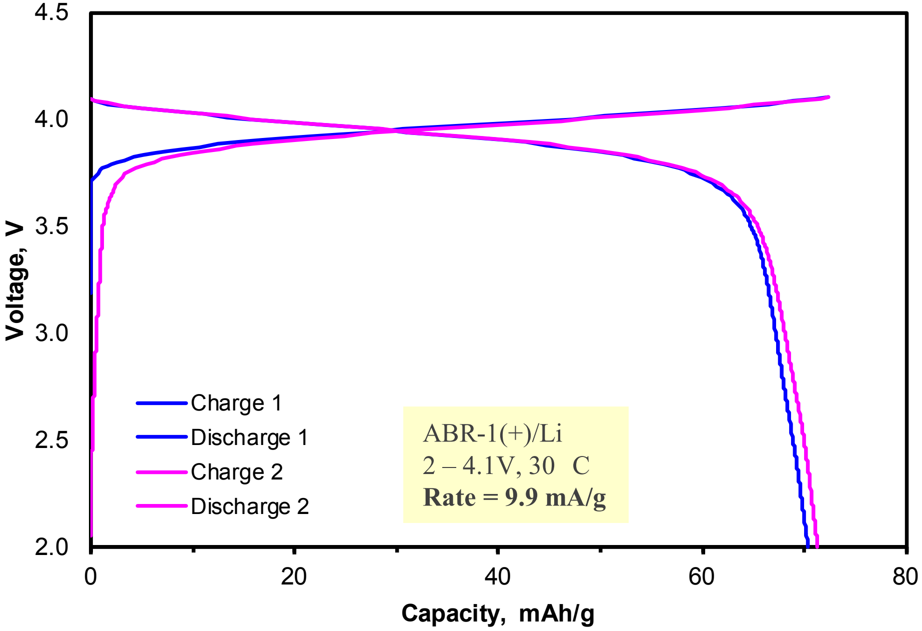


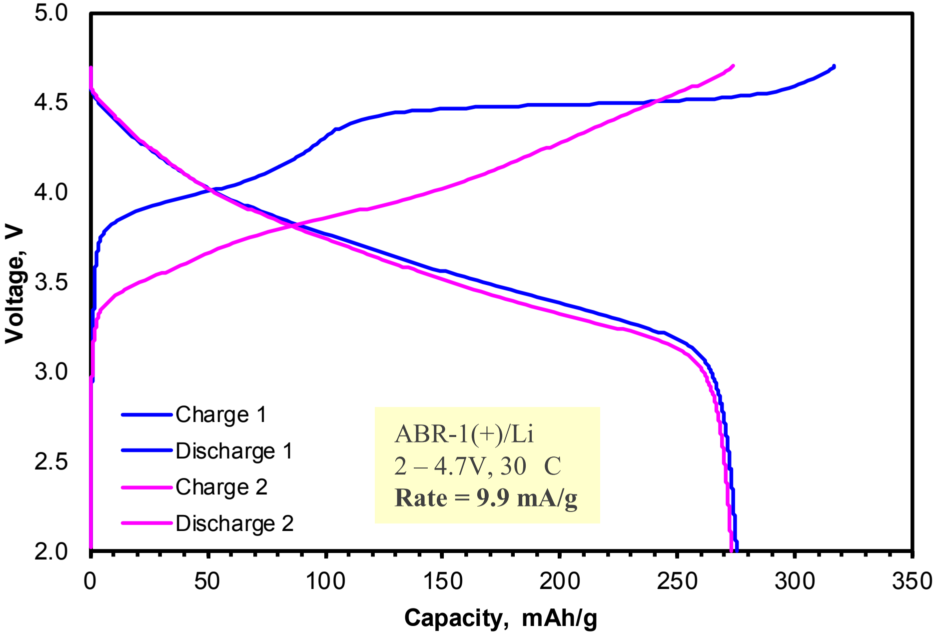
A12 graphite particles, potato-shaped morphology; surface-treated

SEM - D. Miller – Argonne-EMC

Positive electrode has to be cycled over a wider voltage window to obtain higher capacities

Data vs. Li counter electrode, 30°C, 9.9 mA/g



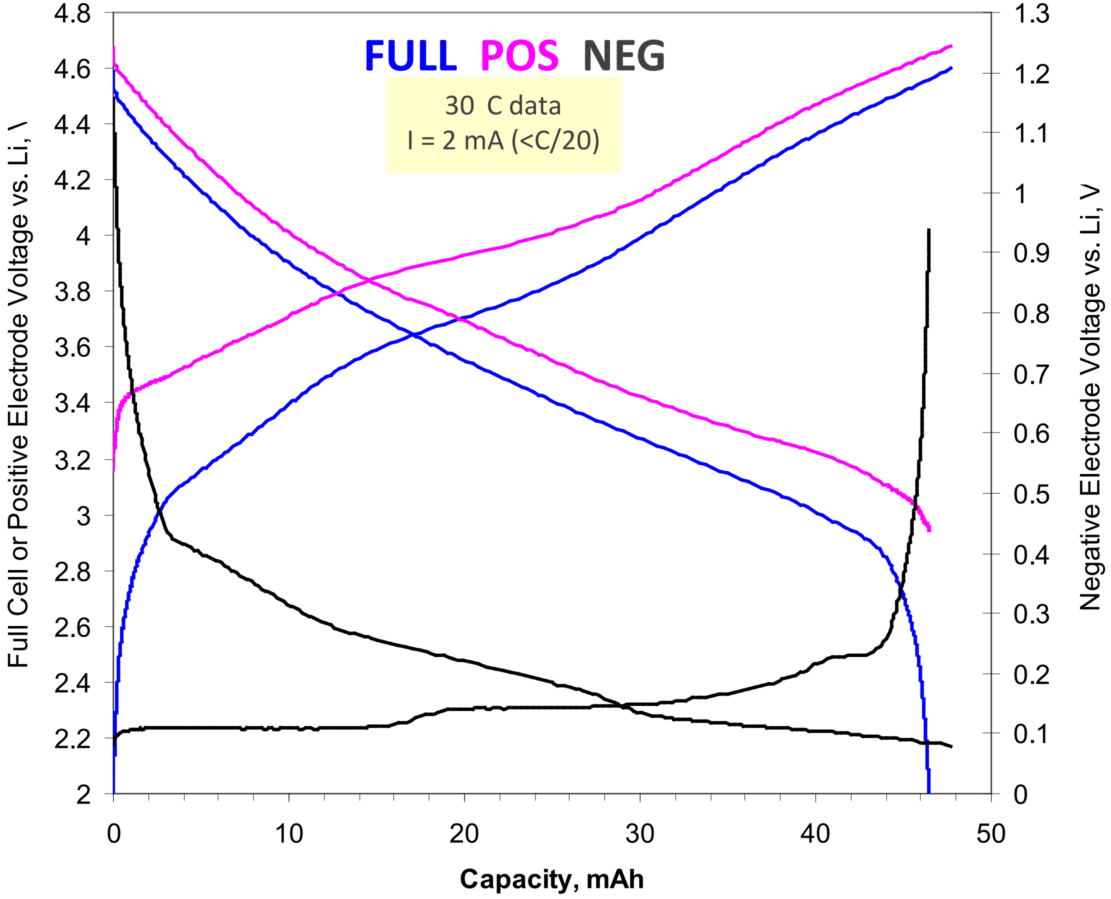


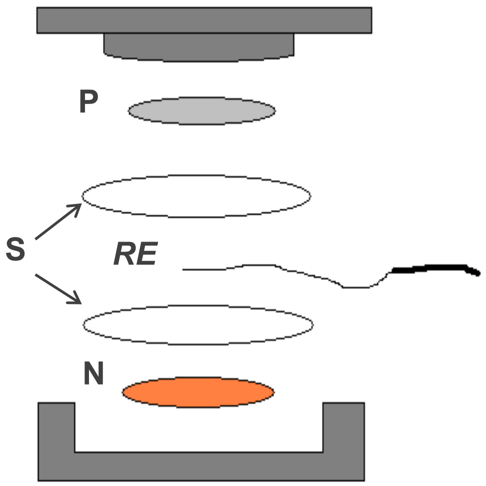
Discharge capacity (2-4.1V): 70 mAh/g
In comparison,
NCA(+)/Li(-) cells yield a discharge capacity of 150 mAh/g (2-4.1V)
NMC_333(+)/Li(-) cells yield a discharge capacity of approx. 140 mAh/g (2-4.1V)

After oxide "activation", the charge and discharge profiles are no longer symmetric
For example,
Charge capacity (3.2-4.7V): 266 mAh/g
Discharge capacity (4.7-3.2V): 235 mAh/g

Excellent data obtained on cells with and without a Reference Electrode

Cells contain
Single-sided electrodes (32 cm^2), Celgard 2325 separator
Gen2 electrolyte (1.2M $LiPF_6$ in 3EC:7EMC by wt.)





Jansen cell

Charge cycle (after formation)
Full Cell Swing = 2 to 4.6V
Positive Electrode vs. Li ≈ 3.16 to 4.68 V
Negative Electrode vs. Li ≈ 1.16 to 0.08 V

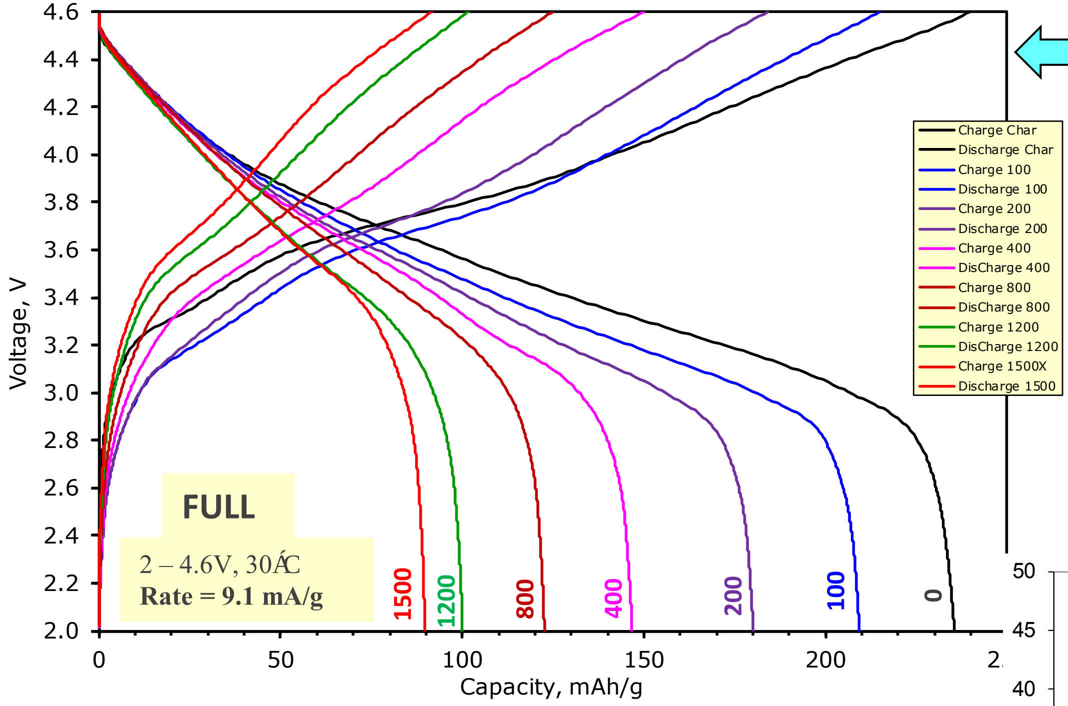
Discharge cycle (after formation)
Full Cell Swing = 4.6 to 2V
Positive Electrode vs. Li ≈ 4.67 to 2.94 V
Negative Electrode vs. Li ≈ 0.08 to 0.94 V

Cell Information

Sample Id.	Details	Nomenclature
FRESH	electrodes, no electrolyte exposure	FRESH
DA383	Few (characterization) cycles. discharged to 2V	FORMED
DA384	300 (2.5-4.4V) cycles. discharged to 2V	CYCLED
DA372	1500 (2.5-4.4) cycles. Discharged to 2V	AGED

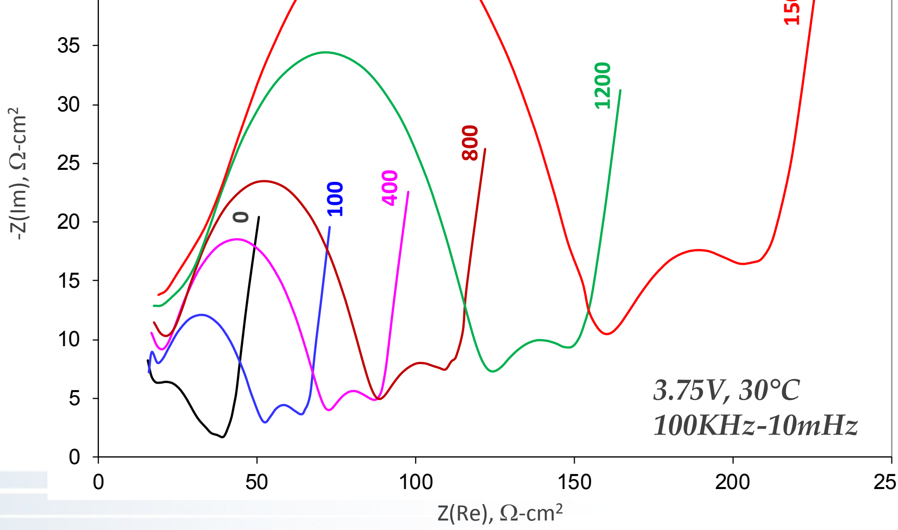
Cells show capacity loss and impedance rise on aging

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



Cell capacity decreases on cycling, even at 30°C

The 30¢C cycling creates an impedance increase in both high- and mid- frequency portions of EIS data.

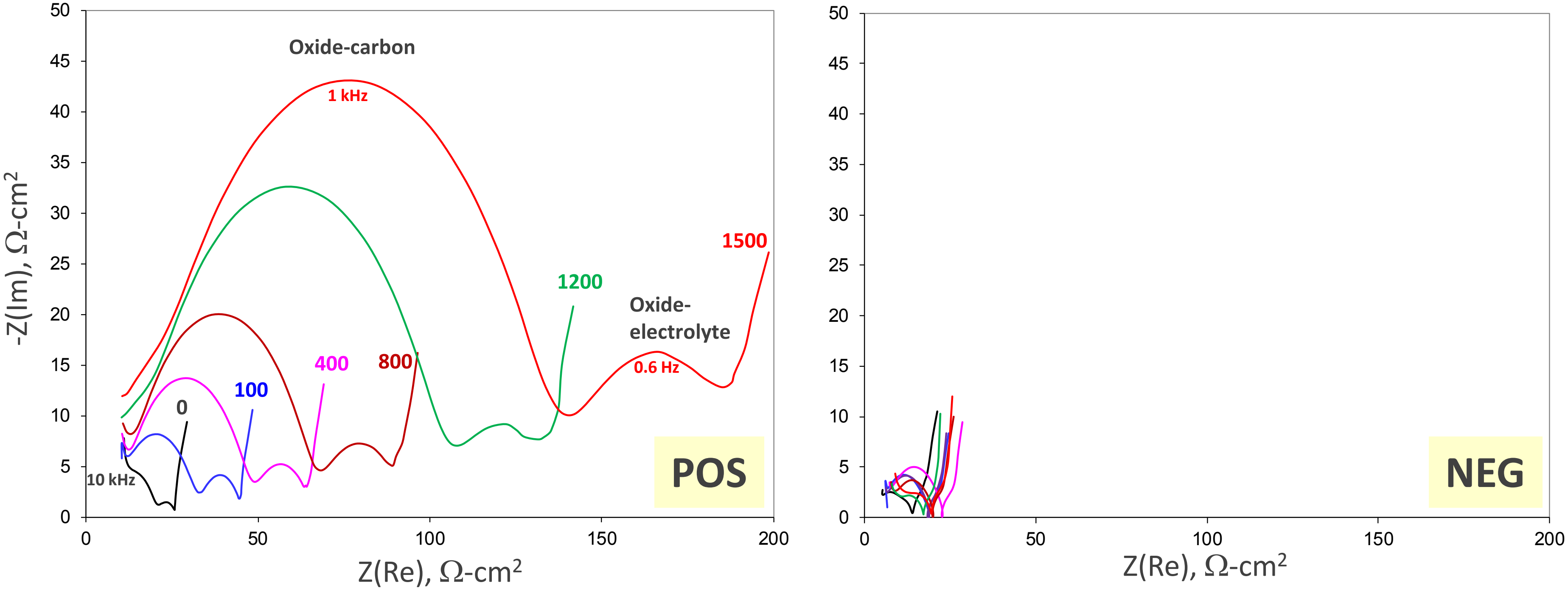


Performance degradation is greater at higher upper-cutoff voltages, at higher temperatures, and for wider voltage cycling windows (i.e., when a larger proportion of the Li⁺ inventory is shuttled between the electrodes.)

Full cell impedance increase is mainly from the positive electrode

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

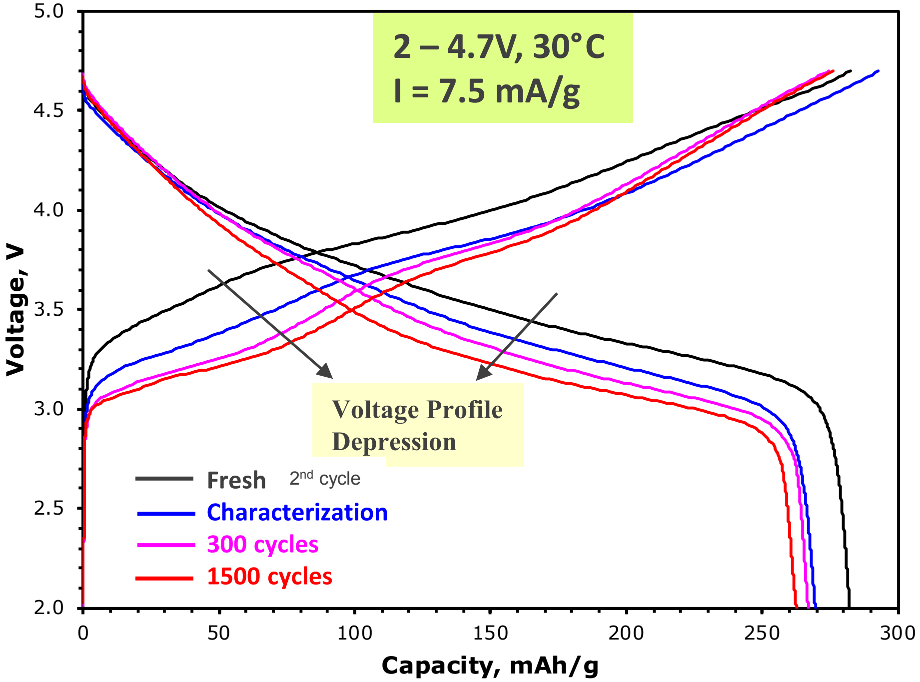
EIS data at 3.75V Full cell voltage, 30°C, 100kHz-0.01Hz



Data from cells with a Li-Sn reference electrode show that the negative electrode contribution to cell impedance increase is small. The impedance rise arises mainly at the positive electrode, and can be attributed to processes at the oxide-carbon (high-frequency arc) and oxide-electrolyte (mid-frequency arc) interfaces.

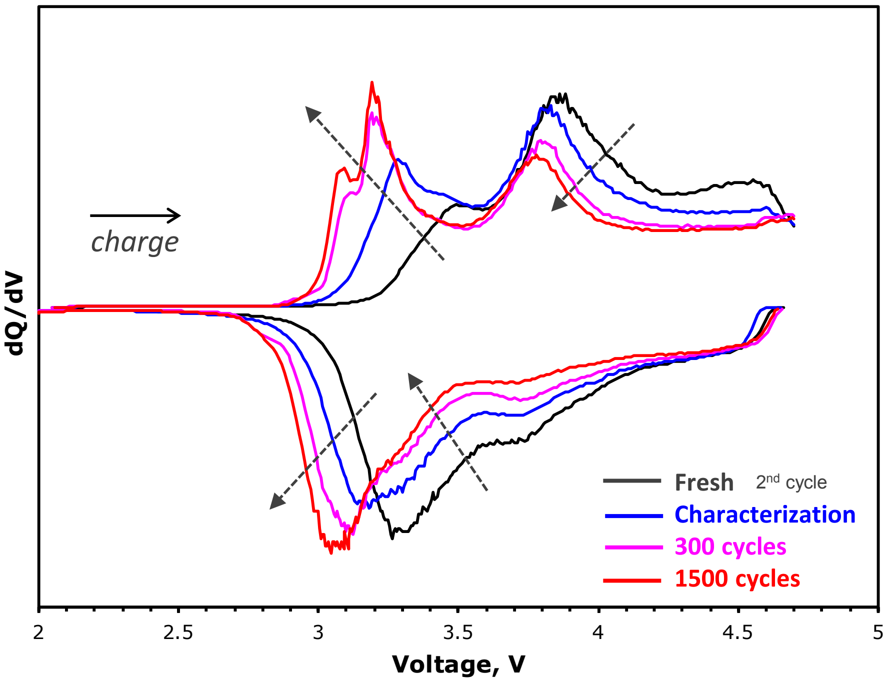
Electrochemistry on harvested electrodes shows that positive electrode contribution to "true" capacity fade is small

Data from coin cells with fresh and "harvested" positive electrodes, Li metal and Gen2 electrolyte



2 – 4.7V, 30°C
I = 7.5 mA/g

Voltage Profile Depression

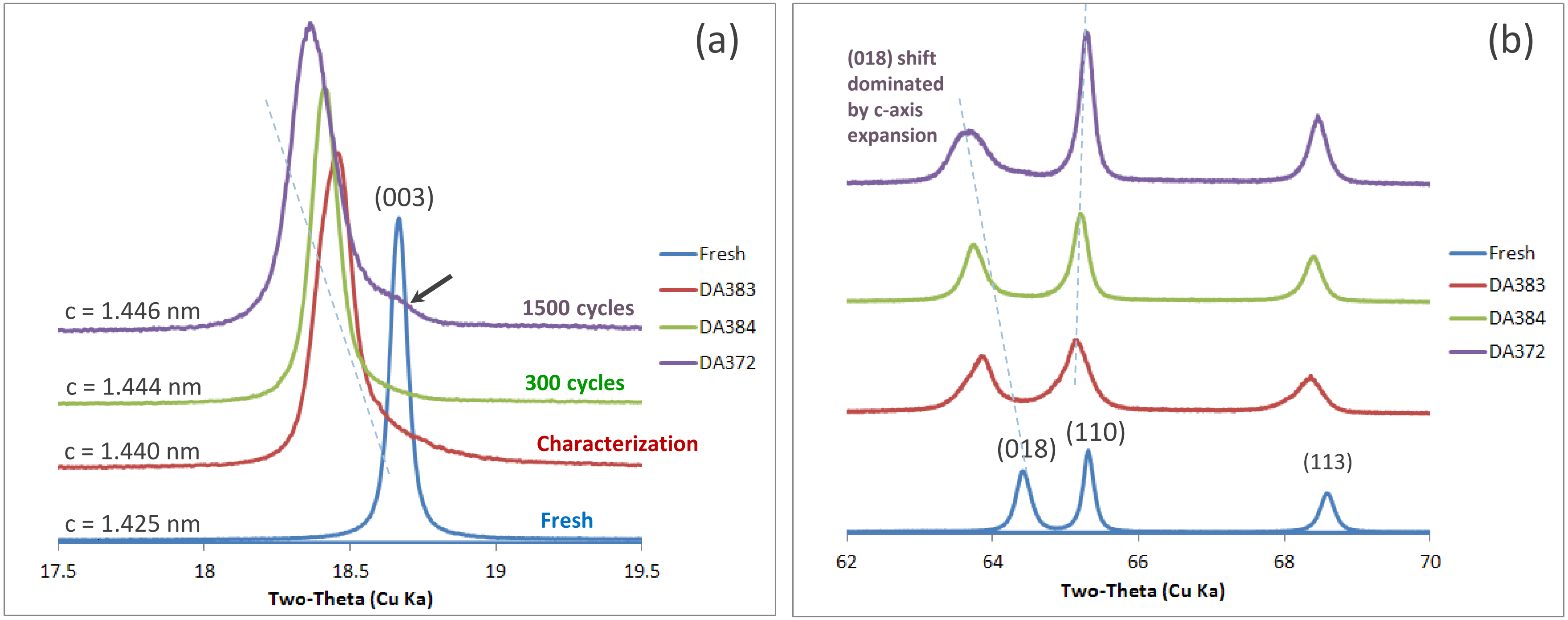


charge

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 electronic connectivity (loss of oxide-carbon contact) or ionic connectivity (particle surface films or surface structure changes)

The voltage profile changes are reflected in the dQ/dV plots – the "3V region" appears to grow at the expense of the "4V region". The double-peak in the charge profile indicates distinct new crystal structures in the highly-cycled samples.

X-ray diffraction (XRD) data show differences between the fresh and harvested positive electrodes



Peak shifts indicate c-axis expansion

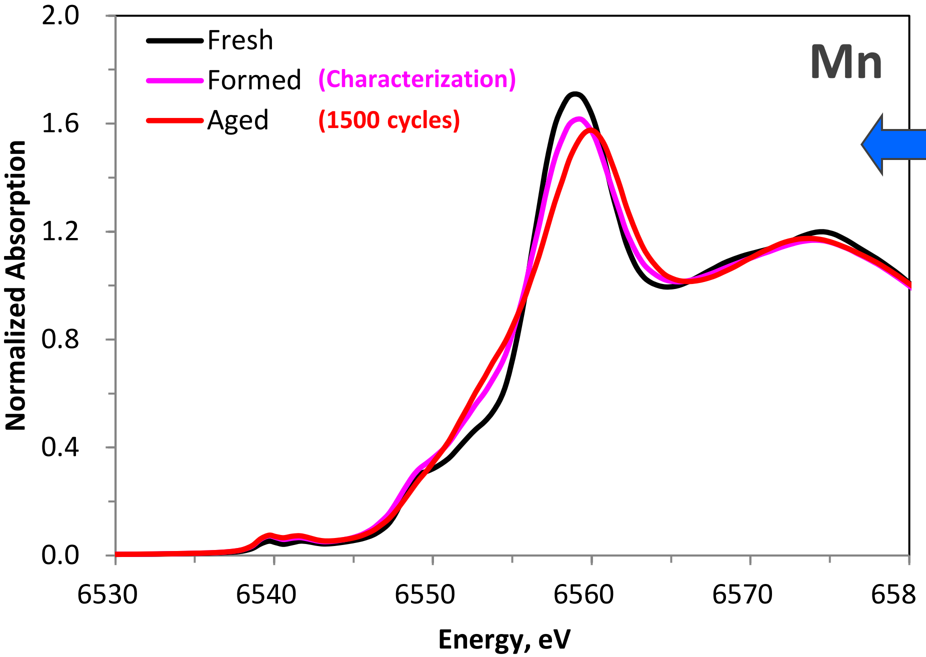
because cycled/aged samples contain lithium deficient oxides. The arrow indicates presence of another layered phase – this suggests inhomogeneity during lithiation. That is, different oxide particles may show different levels of lithiation.

Peak shifts indicate complex behavior in TM-plane behavior

The (110) peak arises from changes within the transition metal plane. A closer examination shows that the peak moves to smaller 2-Theta values initially (increasing a), and then to larger to 2-Theta values (decreasing a) on cycling/aging

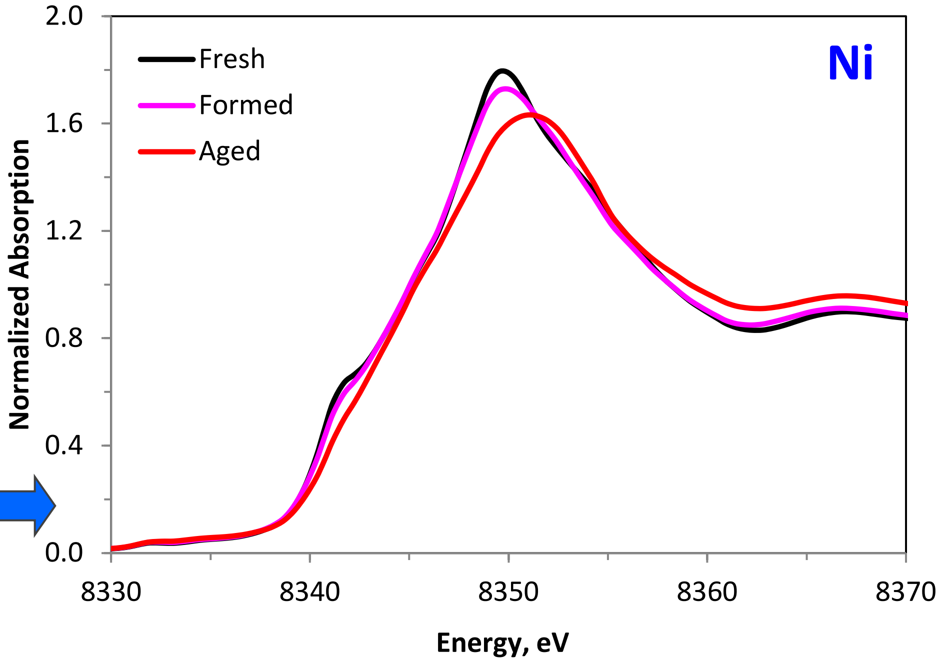
X-ray Absorption Spectroscopy - $Li(Li_{0.2}Ni_{0.15}Mn_{0.55}Co_{0.1})O_2$

XANES data provides information on transition metal (TM) oxidation states

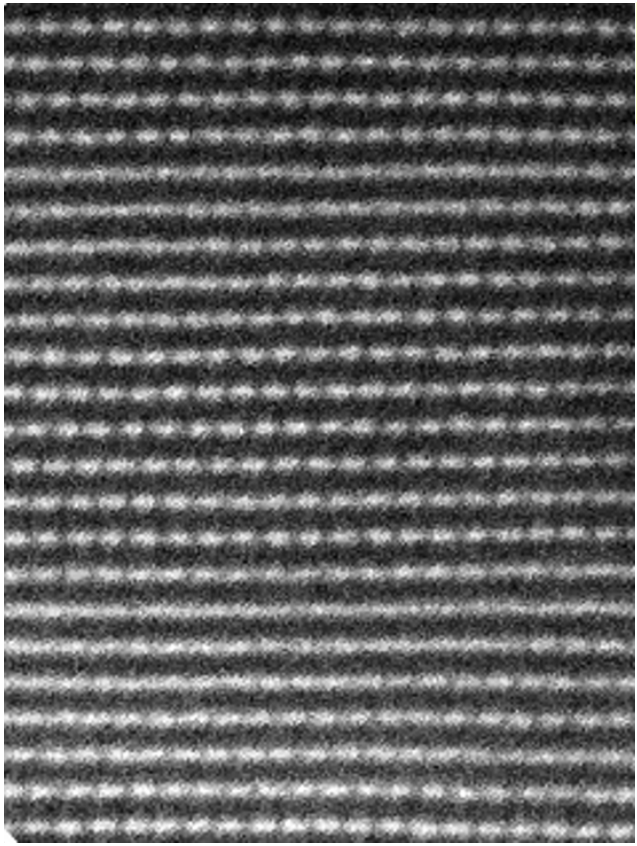


Formation cycling induces the biggest change; changes on further cycling are relatively small. The Mn-oxidation state appears unchanged from 4+ on aging. Changes seen in the FORMED sample are probably associated with loss of oxygen , which may preferentially occur around the Mn atoms.

The average Ni oxidation state in the FRESH sample is slightly higher than 2+. A slight increase in oxidation state is seen for the FORMED sample. More Ni 3+ is present in the AGED sample. This shift is a result of Li-loss from the oxide; charge compensation is achieved through Ni oxidation.



Voltage profile changes on cycling caused by intermixing of Li and TM atoms

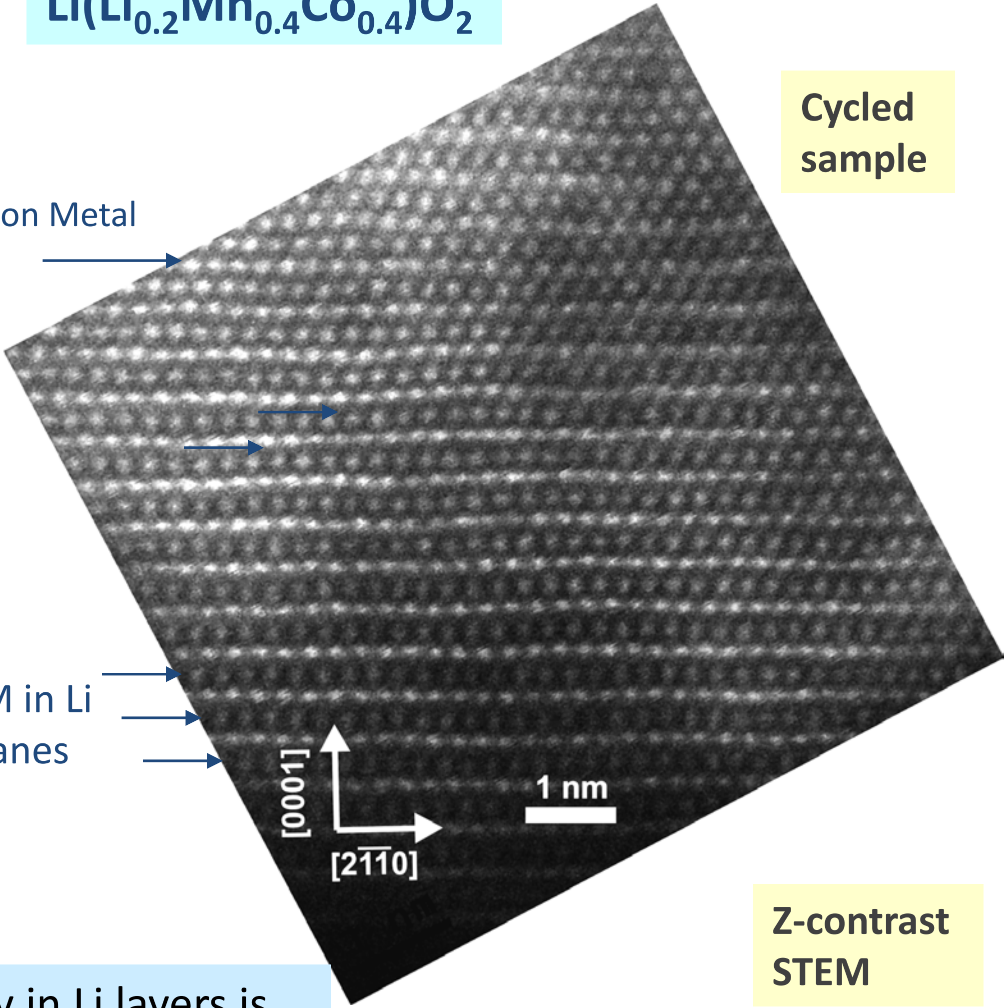


Fresh sample

Li-Mn ordering in TM planes results in Li_2MnO_3-like and $LiCoO_2$-like areas

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

Transition Metal planes



Cycled sample

TM in Li planes

Z-contrast STEM

Periodic intensity in Li layers is characteristic of spinel structure

J. Bareno, Argonne; JG Wen, I. Petrov – CMM-Illinois

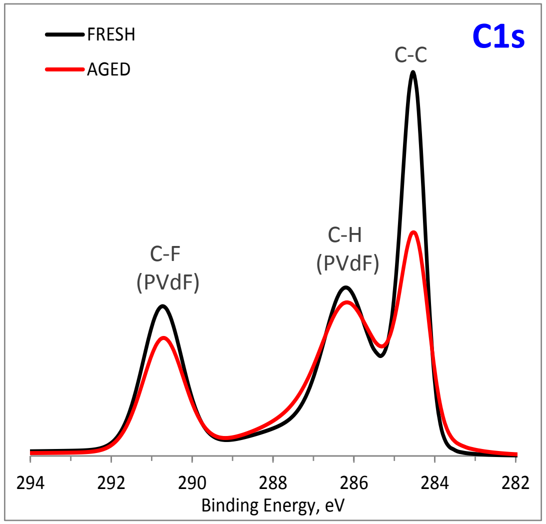
X-ray Photoelectron Spectroscopy - Cathode

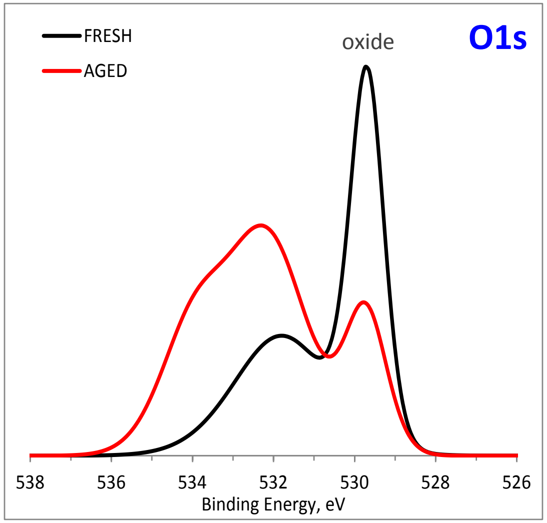
Spectra show changes in electrode surface as cell ages

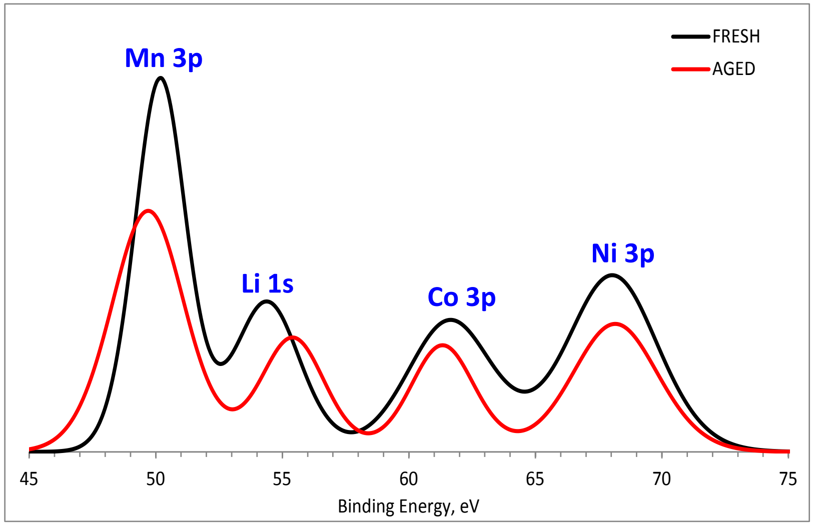
EMC-rinsed samples. Y-axis (counts) scale is different for each plot

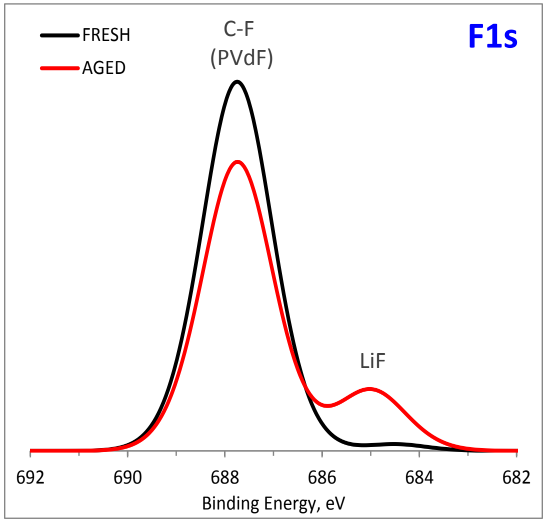
Composition, at%

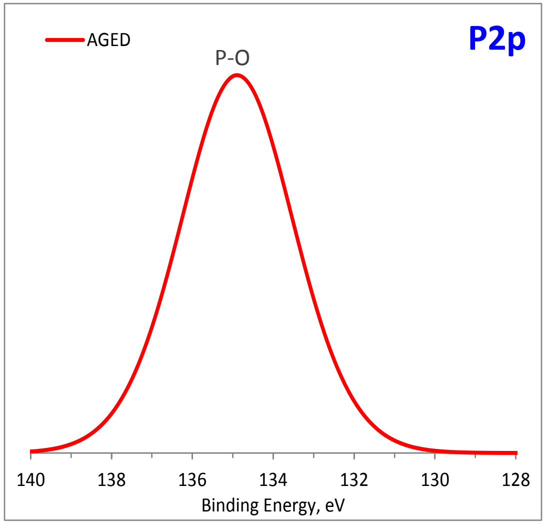
Sample	F	O	C	P	Ni	Co	Mn
FRESH	14.8	5.0	30.3	0.0	2.5	2.4	6.6
AGED	15.3	7.2	29.3	0.9	2.2	1.9	7.6







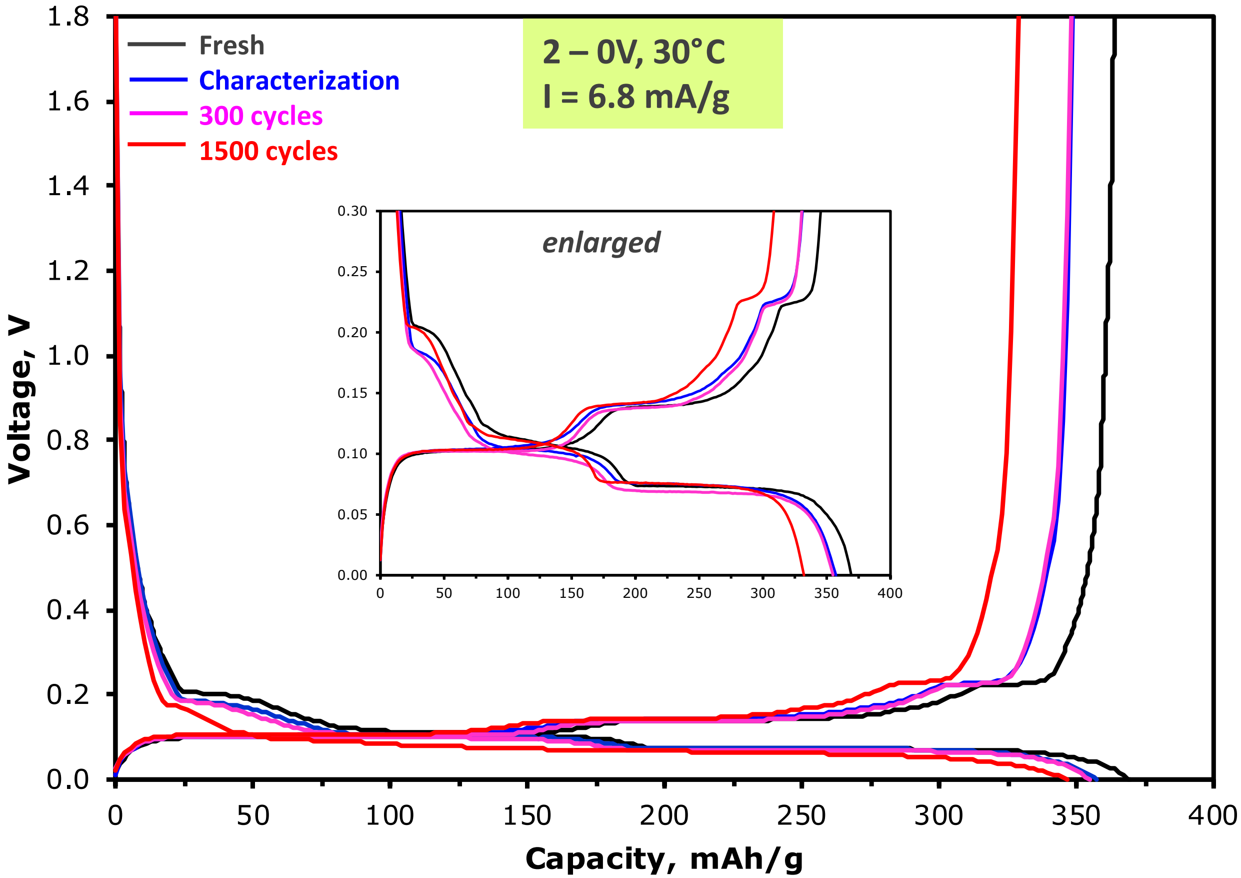




FRESH electrode data showed peaks from oxide, carbons and PVdF binder.
AGED electrode data suggests that surface films are non-uniform. Partial coverage of binder and carbons seen. Oxide peak is visible but has lower intensity . AGED spectra suggests alkoxides (ROLi), LiF and $Li_xPF_yO_z$. Mn, Co and Ni-bearing species may also be present in surface films.

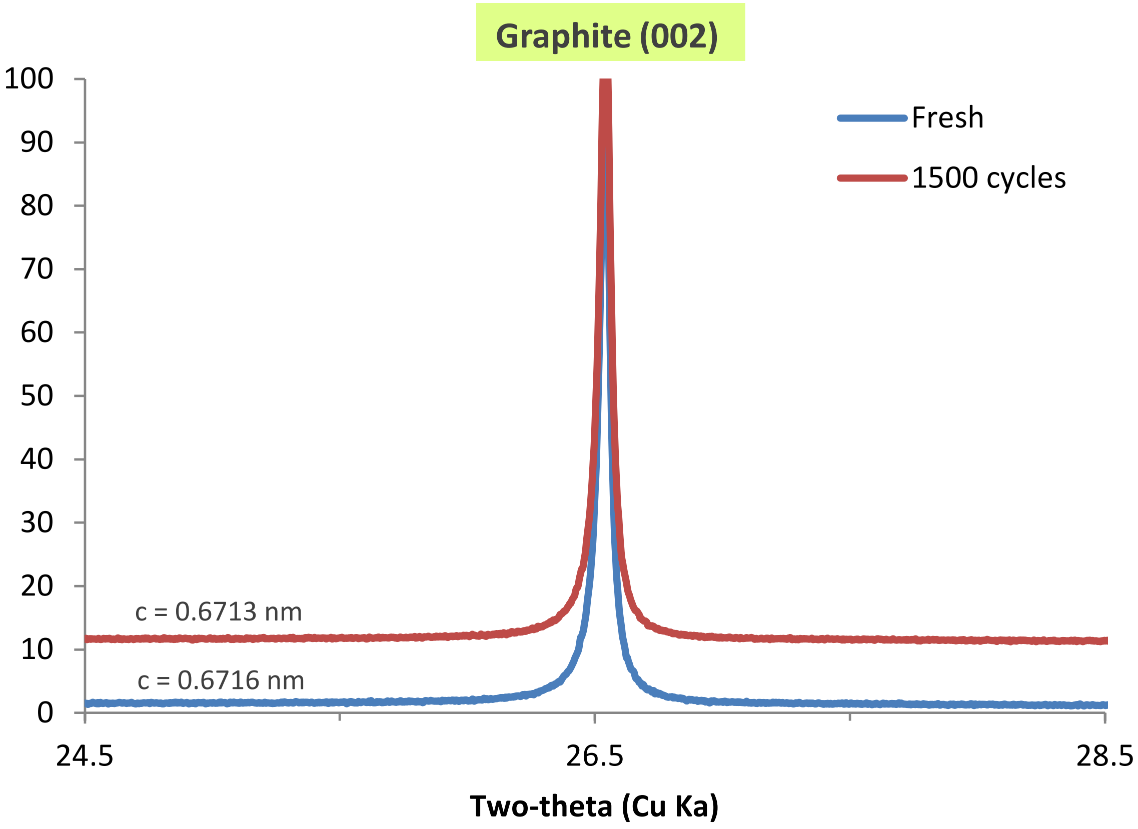
Electrochemical studies on harvested negative electrodes shows that the graphite bulk is not damaged by cycling/aging

Data from coin cells with fresh and "harvested" negative electrodes, Li and Gen2 electrolyte



Capacity (Fresh electrode): 366 mAh/g; Capacity (1500 cycle electrode): 341 mAh/g.
The capacity data includes contributions of the graphite and SuperP carbons.
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.

X-ray diffraction (XRD) data from fresh and harvested negative electrodes are very similar



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

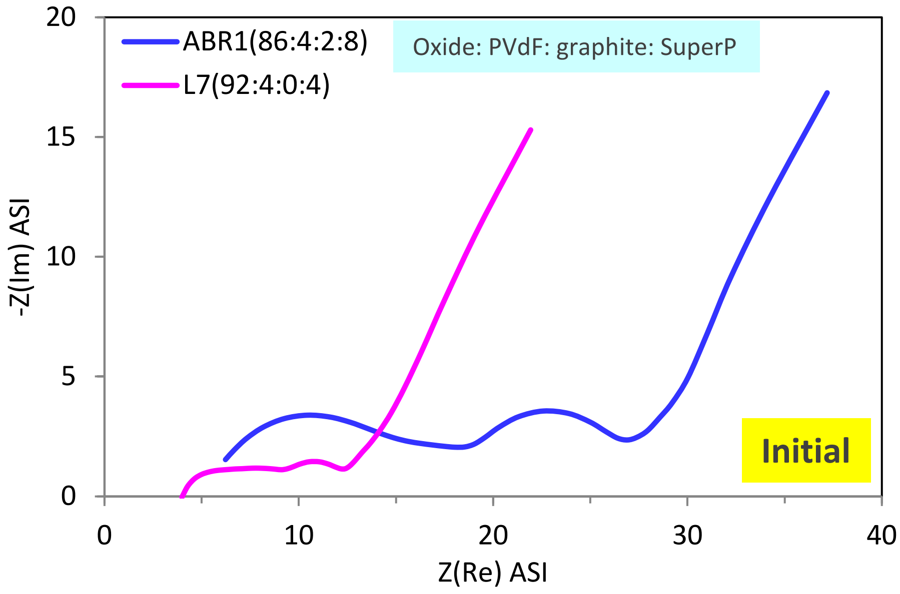
Li^+ trapped in the negative electrode SEI is the main contributor to cell capacity fade: *Negative electrode SEI changes are apparent in XPS data.*

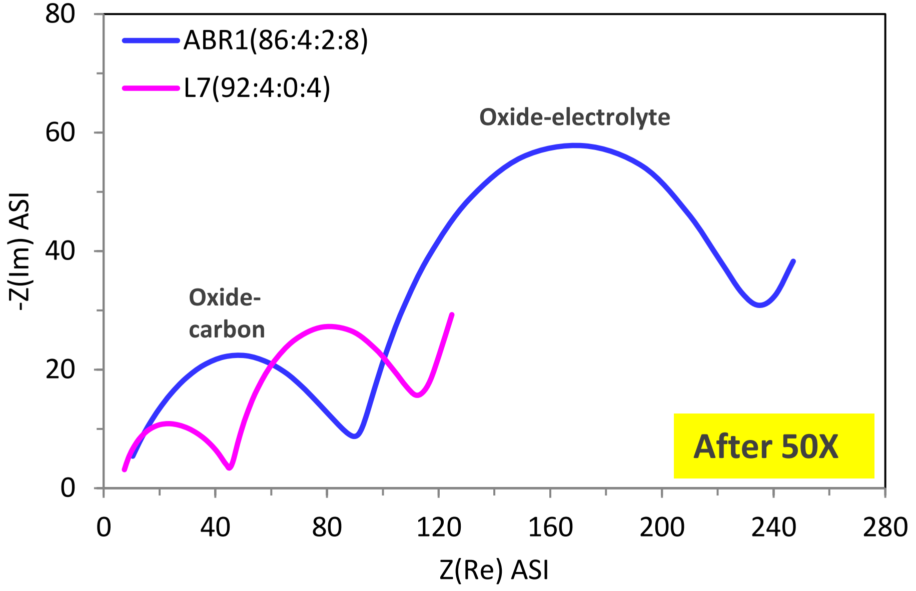
Solutions

Modifying electrode constitution improves cell performance

Full Cell with ABR-1S(-), EIS data, 30 C, 100 kHz-0.01Hz

Before and after 50 cycles at 30 C in the 2.2 – 4.6V voltage window



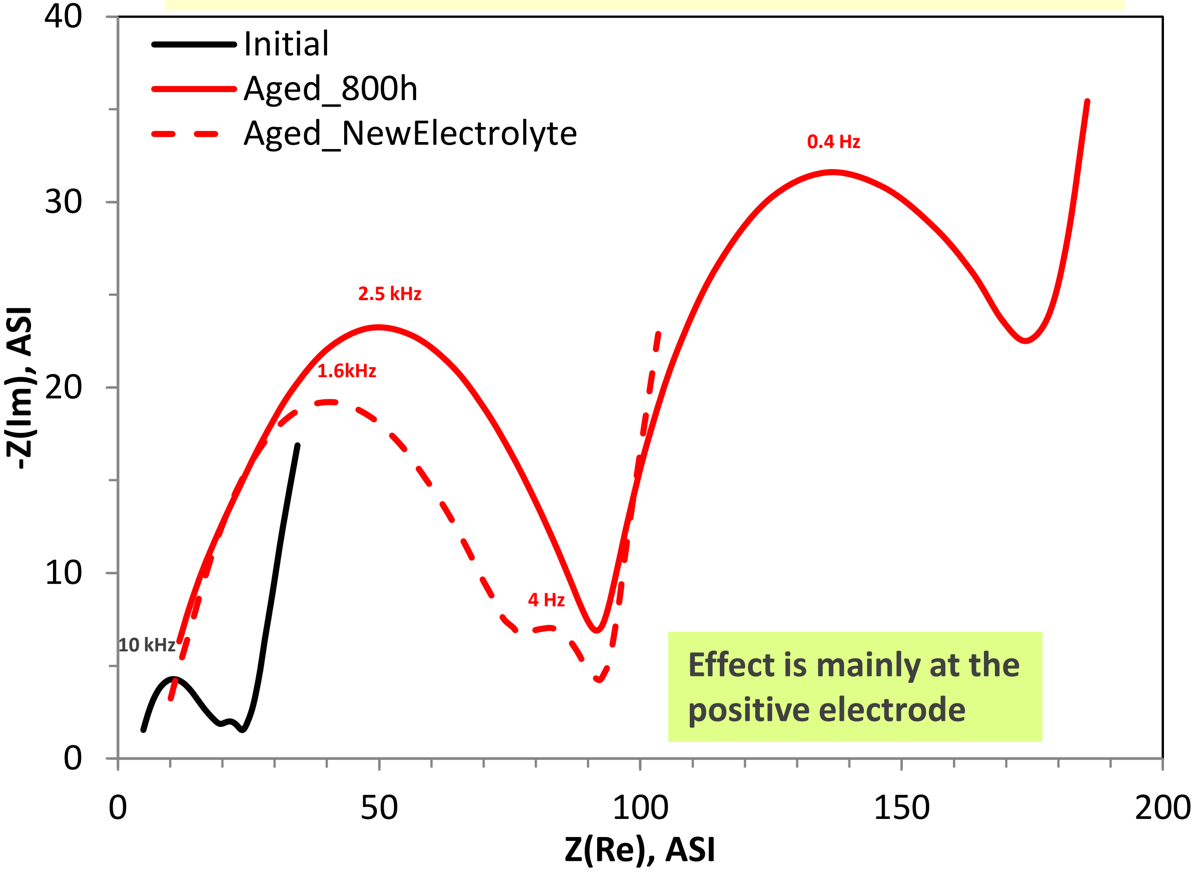


By altering carbon and binder contents, mixing procedures, and calendaring conditions the impedance associated with the high-frequency arc (oxide-carbon interface) can be reduced, which lowers the full cell impedance.

L7, the "modified positive electrode" cell shows a lower impedance rise. The impedance increases associated with the high-frequency arc (oxide-carbon interface) and the mid-frequency arc (oxide-electrolyte interface) are smaller.

Adding FRESH electrolyte (and reassembling cell - all other components stay the same) **reduces the mid-frequency arc observed in the AGED cell**

Data from full cells prepared from electrodes harvested from 4.5V calendar-life aged cell: EIS, 30°C, 100 kHz-0.01Hz, 3.75V



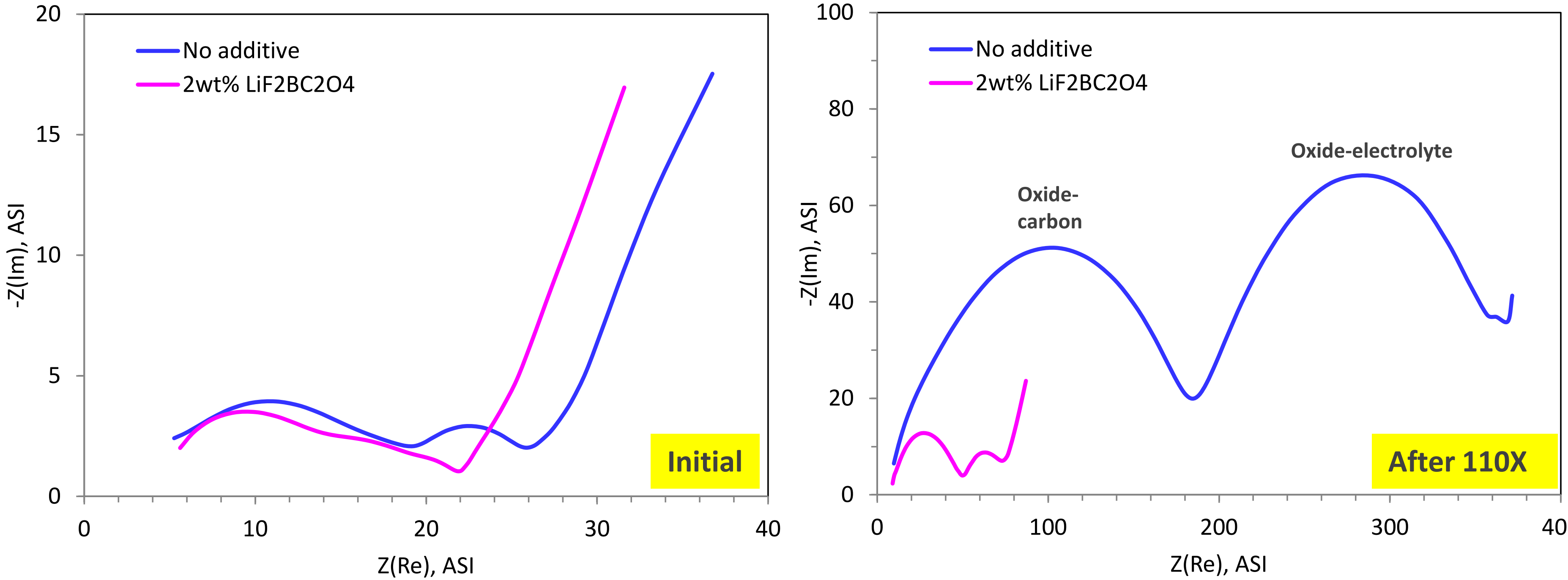
Effect is mainly at the positive electrode

Electrolyte oxidation at voltages > 4.6V vs. Li/Li^+ is a significant contributor to cell impedance rise

Electrolyte additives improve cell performance

Full Cell with ABR-1S(-), EIS data, 30℃, 100 kHz-0.01Hz

Before and after 110 cycles at 30°C in the 2.2 – 4.6V voltage window



Initial impedances of cells with and without the 2 wt% $LiF_2BC_2O_4$ additive are similar.

After 110 cycles, impedance rise of $LiF_2BC_2O_4$ -bearing cell is lower than that of the control cell. Note, however, that the electrolyte additive does not prevent impedance rise.

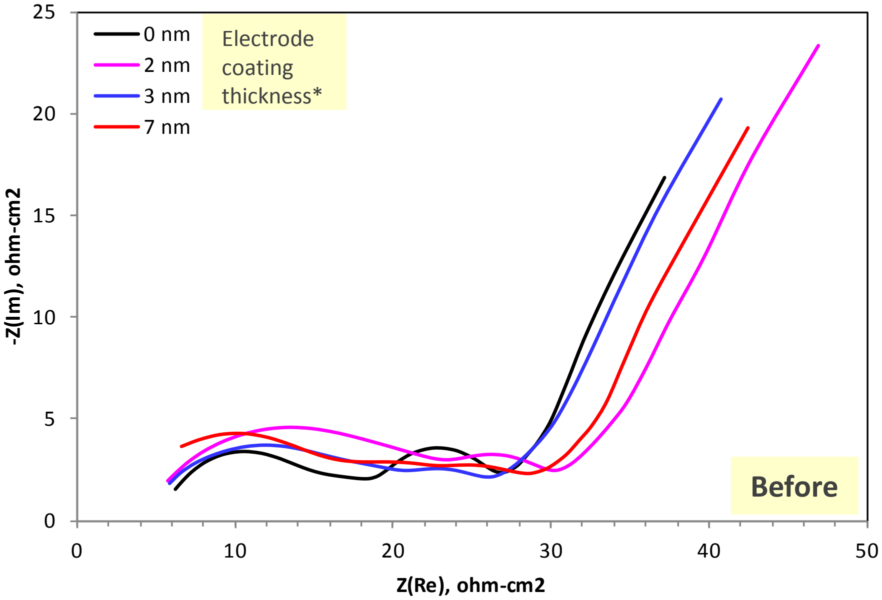
The EM1 additive (WildCat Discovery Technologies) appears better than $LiF_2BC_2O_4$
Cells with EM1 show 87% capacity retention after 210 cycles (C/3, 30 C)

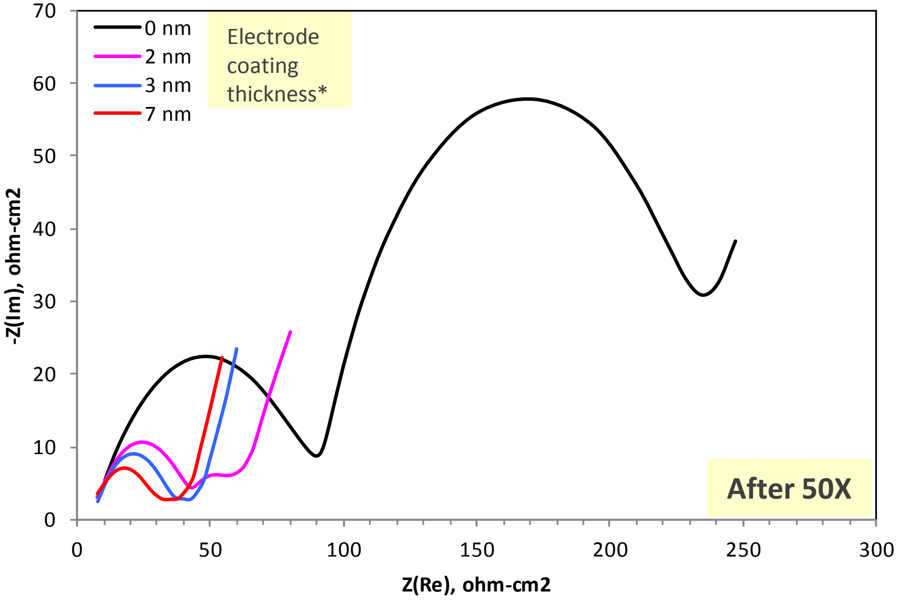
Positive electrode coating by Al_2O_3 improves cell performance

Full Cell, EIS data, 30°C, 100 kHz-0.01Hz

Before and after 50 cycles at 30°C in the 2.2 – 4.6V voltage window

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





The initial impedances of the as-prepared and ALD-coated samples are quite similar.

After 50 cycles, the as-prepared electrode shows the highest impedance. The impedance decreases with coating thickness -- the 7 nm coated electrode shows the lowest impedance.

The positive electrode coating also reduces cell capacity loss; capacity fade of the 7nm coated positive electrode cell was 0.5% after 50 cycles (C/5, 30°C).

Collaborations

- **Argonne Colleagues** (M. Balasubramanian, D. Miller, Cell Fabrication Facility {B. Polzin}, Post-Test Facility {N. Dietz}, D. Dees, A. Jansen, W. Lu, K. Gallagher, etc.)
  - Better electrode formulations, advanced diagnostic techniques, electrode and cell performance degradation modeling
- **University of Illinois** (B. Sankaran, R. Haasch, 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
- **WildCat Discovery Technologies** (G. Cheng et al.)
  - Improve cell performance through electrolyte additives
- **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

- “Wrap up” studies on ABR-1 electrochemical couple and cell constituents
  - Document data in reports; share information with interested colleagues
  - Incorporate “degradation mitigation solutions” into cells and determine mechanisms that lead to improvement in performance
- Coordinate “voltage fade in LMR-NMC oxides” characterization/diagnostic study and work with materials synthesis team to solve problem
  - Identify causes and recommend solutions to mitigate crucial challenges that may hinder commercialization, which include first cycle irreversibility, structural stability, and power delivery capability
- Initiate characterization and aging experiments on electrodes and electrode constituents identified for the next set of ABR couples
  - 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 cells, and recommend solutions to improve performance

Summary

- The objective of this study is to identify factors that contribute to cell performance and performance degradation characteristics (capacity fade, impedance rise, voltage fade) 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 LMR-NMC based cathodes and graphite based anodes.
  - Our data show that cell impedance rise on aging arises at the positive electrode, and can be attributed to processes that include electrolyte oxidation especially at cell voltages that exceed 4.5V vs. Li/Li+.
  - Cell capacity loss can be attributed to a variety of factors that include (i) lithium trapping in the negative electrode SEI; (ii) active material isolation in the electrodes; (iii) transition metal dissolution into the electrolyte; and (iv) positive electrode impedance rise that hinders lithium-ion transport at practical rates of operation.
- We've been studying the structure and structural rearrangements in layered $Li_{1+x}Ni_aMn_bM'_cO_2$ compounds using X-ray, electron beam, and electrochemical techniques.
  - Our data indicate that the biggest changes in atomic rearrangements occur during formation cycling; changes on further cycling are relatively small.
  - We conclude that a fundamental understanding of oxide structural changes during formation cycling is required in order to solve the voltage-fade problem.