Electrochemical Characterization of Voltage Fade in LMR-NMC cells

Project Id: ES188

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In Collaboration with the Voltage Fade Team

DOE Vehicle Technologies Program Annual Merit Review
Arlington, VA May 13 - 17, 2013

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Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2013
- Percent complete: 50%

Budget

- FY13: $300K

(part of Voltage Fade project)

Barriers

- Calendar/cycle life of lithium-ion cells

Partners

- Voltage Fade Team at Argonne
- Researchers at Brookhaven, Oak Ridge and Lawrence Berkeley National Labs

Project Objectives - Relevance

Voltage Fade in lithium and manganese rich (LMR-NMC) oxides reduces energy density of lithium-ion cells on calendar–life and cycle–life aging

- Mitigating voltage fade will enable the use of these high–energy NMC composite oxides {xLi_2MnO_3 •$(1-x)LiMO_2$ (M=Ni, Mn, Co)} for PHEV and EV applications

Milestones

- Establish baseline material and test protocols to determine the extent of Voltage Fade — December 2012
- Establish baseline data on standard materials to facilitate comparison of various datasets — March 2013
- Obtain data to determine effect of electrode formulation, temperature, electrolyte additives, electrode coatings, etc. on the extent of Voltage Fade — September 2013

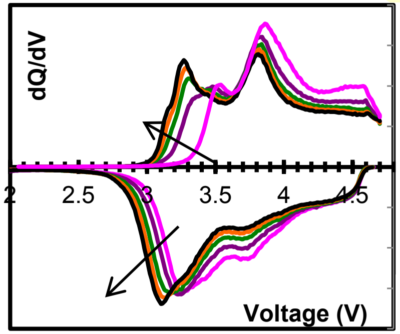
Approach

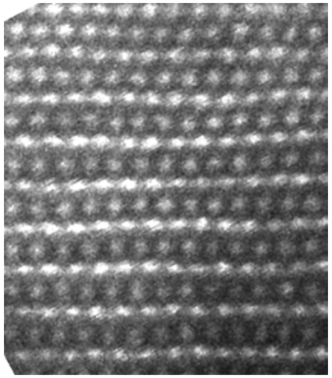
- **Multi-institution effort to identify factors that contribute to voltage fade in lithium– and manganese– rich NMC oxides (LMR-NMC)**

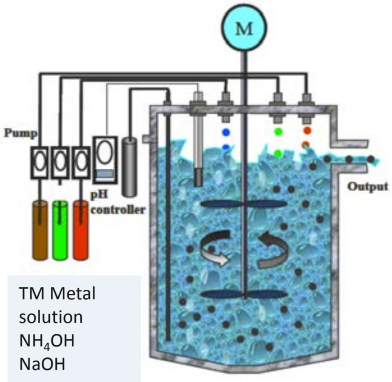
Electrochemical Characterization & Modeling

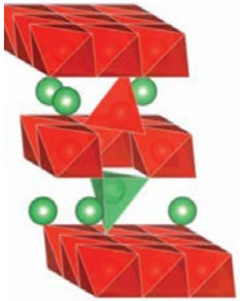
Physicochemical Characterization & Atomistic Modeling

Oxide Synthesis & Surface Modification









E: Dumbbell Defect

Suggest/implement approaches to mitigate voltage fade

Technical Accomplishments and Progress

- **Established baseline material and test protocols to determine extent of Voltage Fade** (met milestone)
  - Selected $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ ($0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$) as the baseline oxide to study voltage fade
  - Showed that voltage fade is accelerated by temperature. Cells cycled at 55°C show greater fade than those cycled at 30°C
  - Determined that the extent of voltage fade depends on upper cutoff voltage (UCV) for cycling: UCV = 4.7 > 4.6 > 4.5 > 4.4 > 4.3. Verified that voltage fade is minimal in cells cycled at 4.3V vs. Li/Li^+
  - Demonstrated that voltage fade is unaffected by changes in electrode constitution (oxide : carbon : binder ratios)
  - Established that voltage fade is unaffected by select electrolyte additives and by select ALD-based electrode coatings
  - Confirmed that voltage fade is less dramatic in lithium-stoichiometric (i.e., not over-lithiated) oxides, such as $Li_{1.0}Ni_{0.80}Co_{0.15}Al_{0.05}O_2$
  - Concluded that voltage fade is present even in cells cycled at very slow rates (~C/250), i.e., it's unaffected by electrode kinetics.

Baseline cell chemistry

Positive Electrode (made by Saft):

86 %wt $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$

($0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$)

8%wt Solvay Solef® 5130 PVDF binder

4%wt Timcal Timrex® SFG-6 graphite

2 %wt Timcal Super P®

6.64 mg/cm^2 oxide loading density

37.1% electrode porosity

35-µm-thick coating

15-µm-thick Al current collector

Negative Electrode:

Li metal

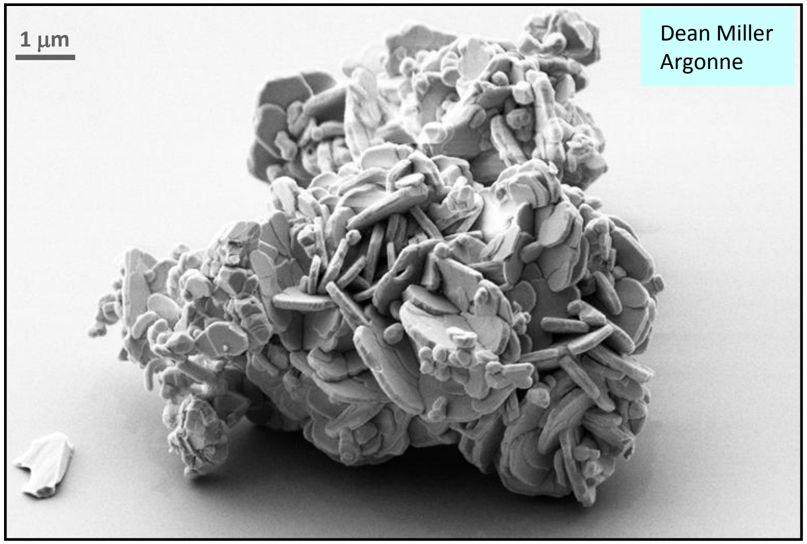
Electrolyte:

EC:EMC (3:7 by wt.) + 1.2M $LiPF_6$

Cells:

coin cells, 1.6 cm^2 electrodes

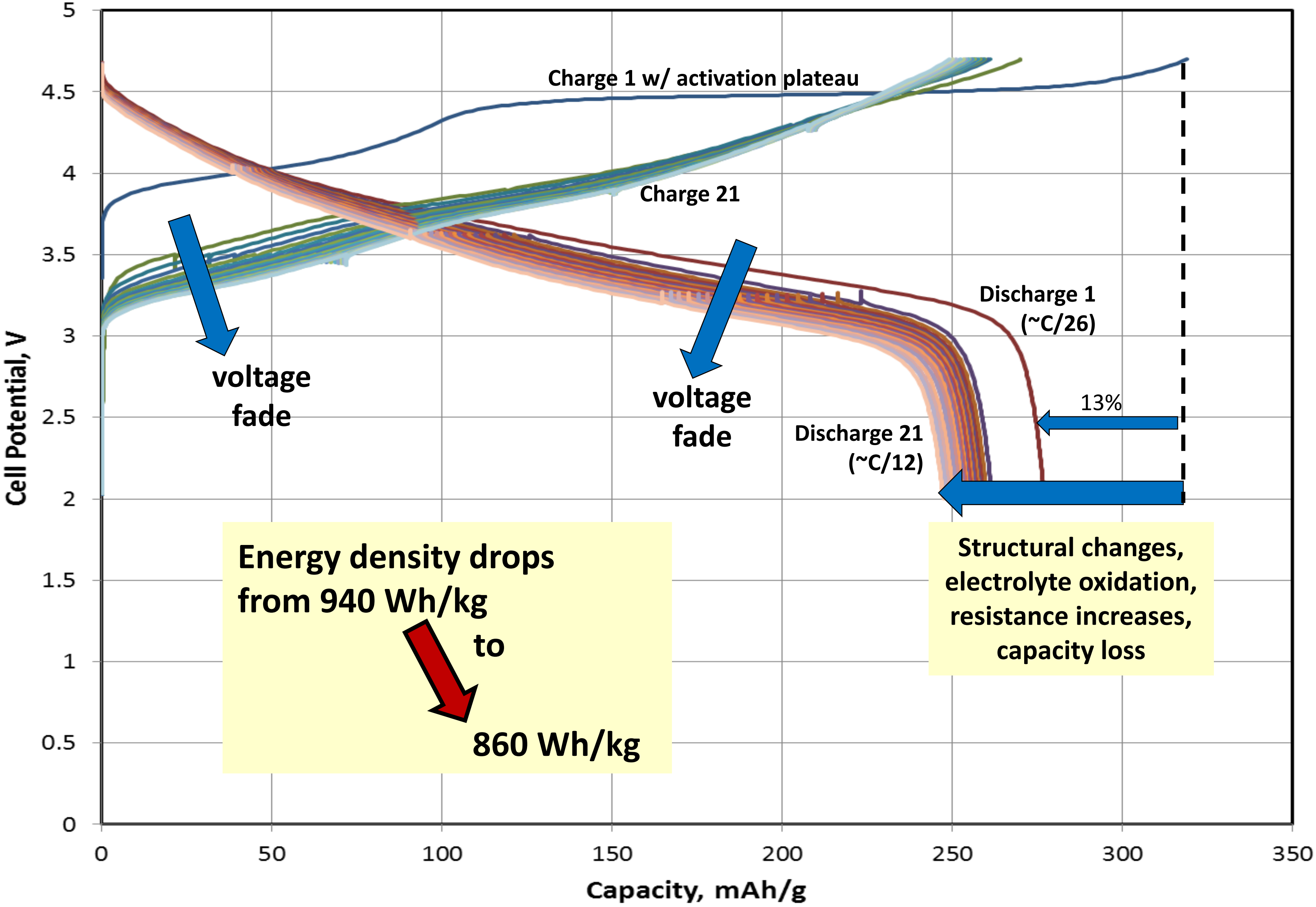
& Celgard® 2325 separator



Dean Miller
Argonne

Oxide primary particles consist of randomly oriented plate-like grains

Cycle performance of $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ baseline



Energy density drops from 940 Wh/kg to 860 Wh/kg

Structural changes, electrolyte oxidation, resistance increases, capacity loss

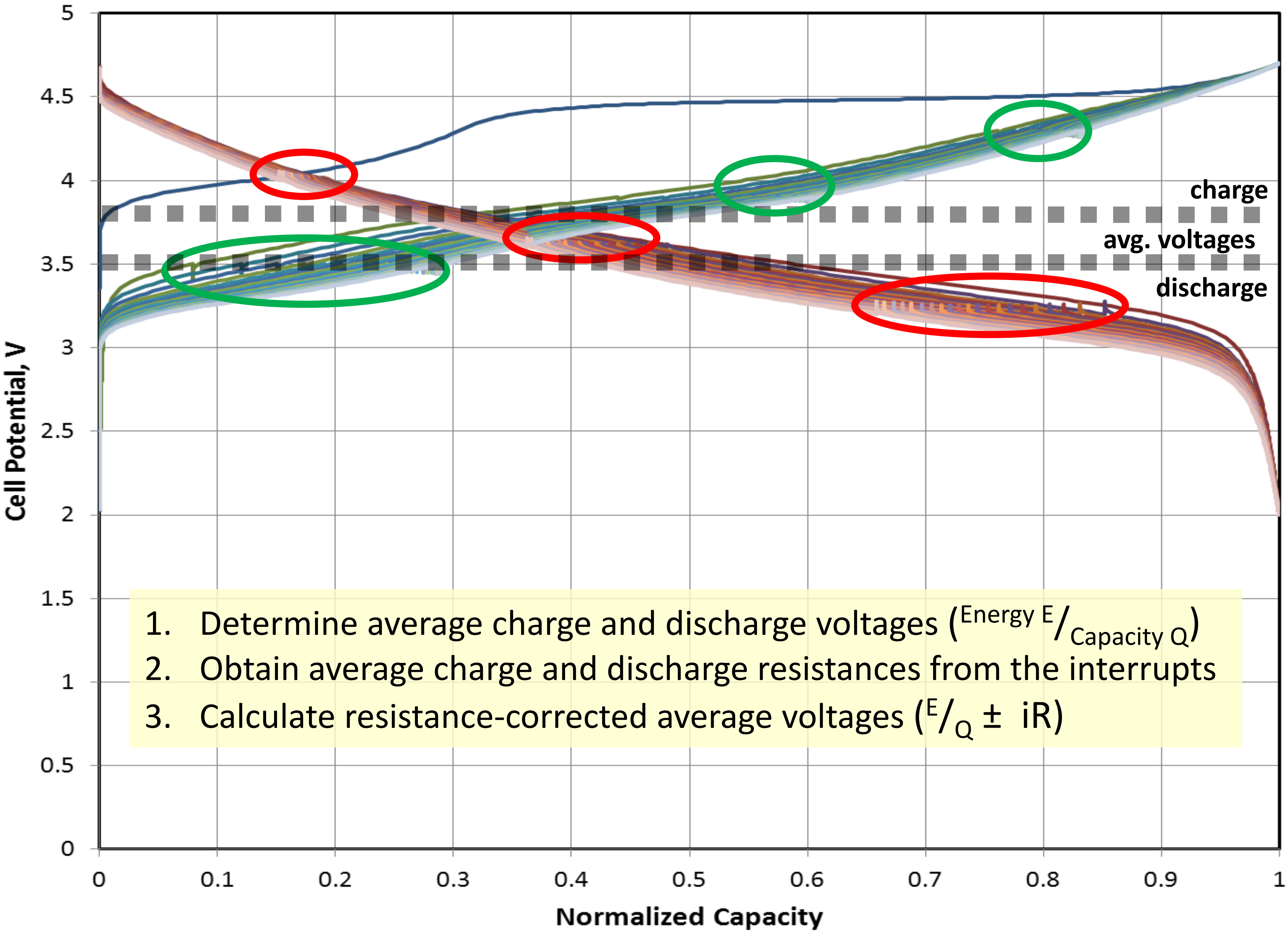
Voltage Fade Baseline Material and Test Protocol

- Team chose a baseline material: **$0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$**
  (well characterized positive electrode, available in large quantities)
- Cell configuration: oxide as positive, Li metal as negative

- Temperature: RT (also 30°C and 55°C)
- Initial activation cycle: 2-4.7V @ 10 mA/g
- Following cycling procedure: 2-4.7V @ 20 mA/g
- Total of 6 current interrupts implemented to obtain quasi-OCVs & DC cell resistances during charge at 3.5V, 3.9V, 4.3V, and during discharge at 4.0V, 3.6V, 3.2V.
  Each interrupt is a 10 minute rest.

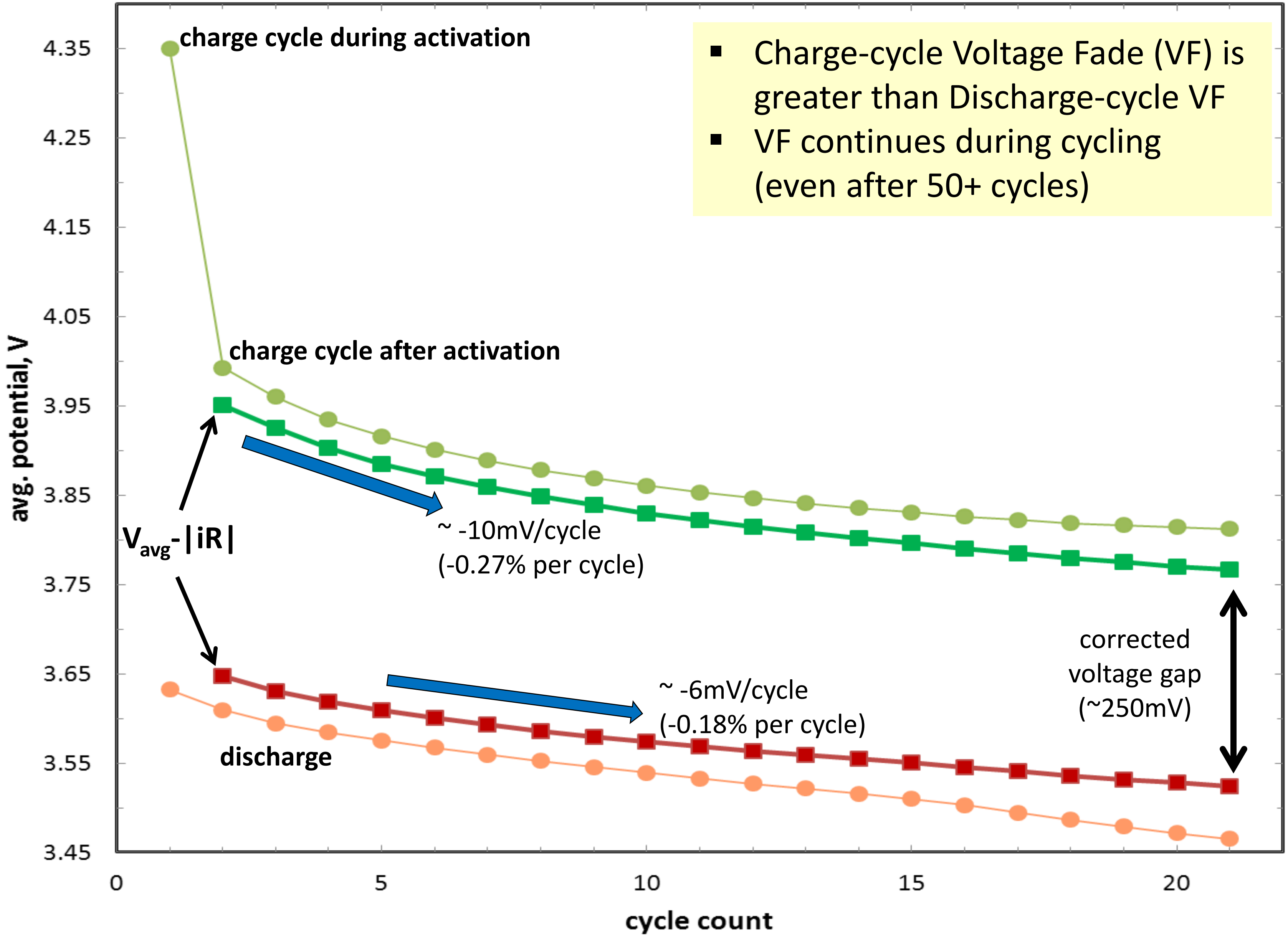
- Number of cycles: 20
- Total test time (days): ~20
- Excel macro processes acquired data, collection in database (Ira Bloom, Argonne)

iR-corrected average voltage is used to track voltage fade



1. Determine average charge and discharge voltages (${}^{\text{Energy E}}/_{\text{Capacity Q}}$)
2. Obtain average charge and discharge resistances from the interrupts
3. Calculate resistance-corrected average voltages (${}^{E}/_{Q} \pm iR$)

Voltage fade for $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ baseline



- Charge-cycle Voltage Fade (VF) is greater than Discharge-cycle VF
- VF continues during cycling (even after 50+ cycles)

Advantages & Disadvantages of our Methodology

Advantages of our methodology

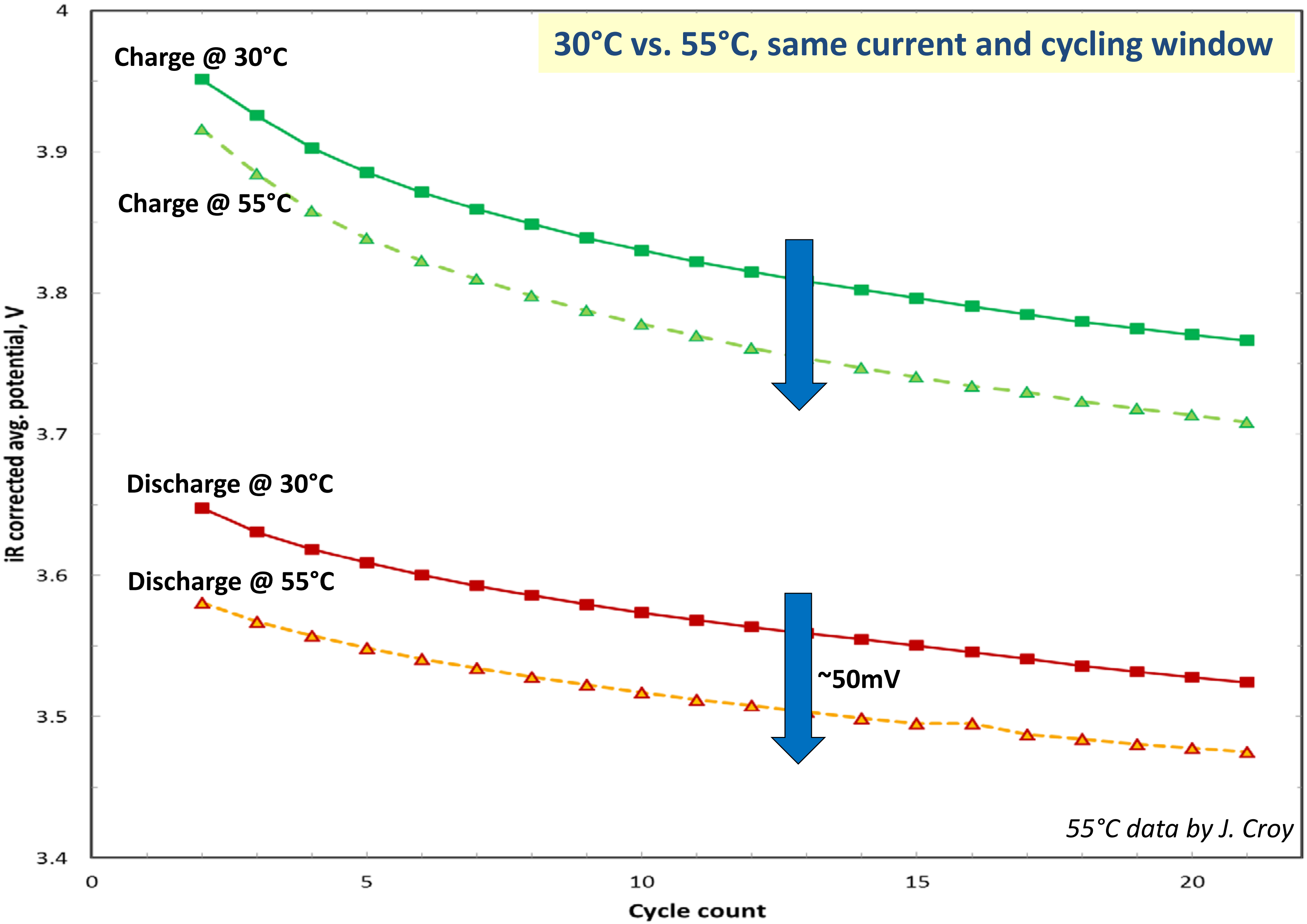
- Eases comparison between similar materials under similar testing conditions
- Good & reasonably fast tracking of an "average quasi-OCV" during cycling
- Tracking of other materials-related properties: capacities, and energy densities
- Measurement of the average cell resistance

Limitations of our methodology

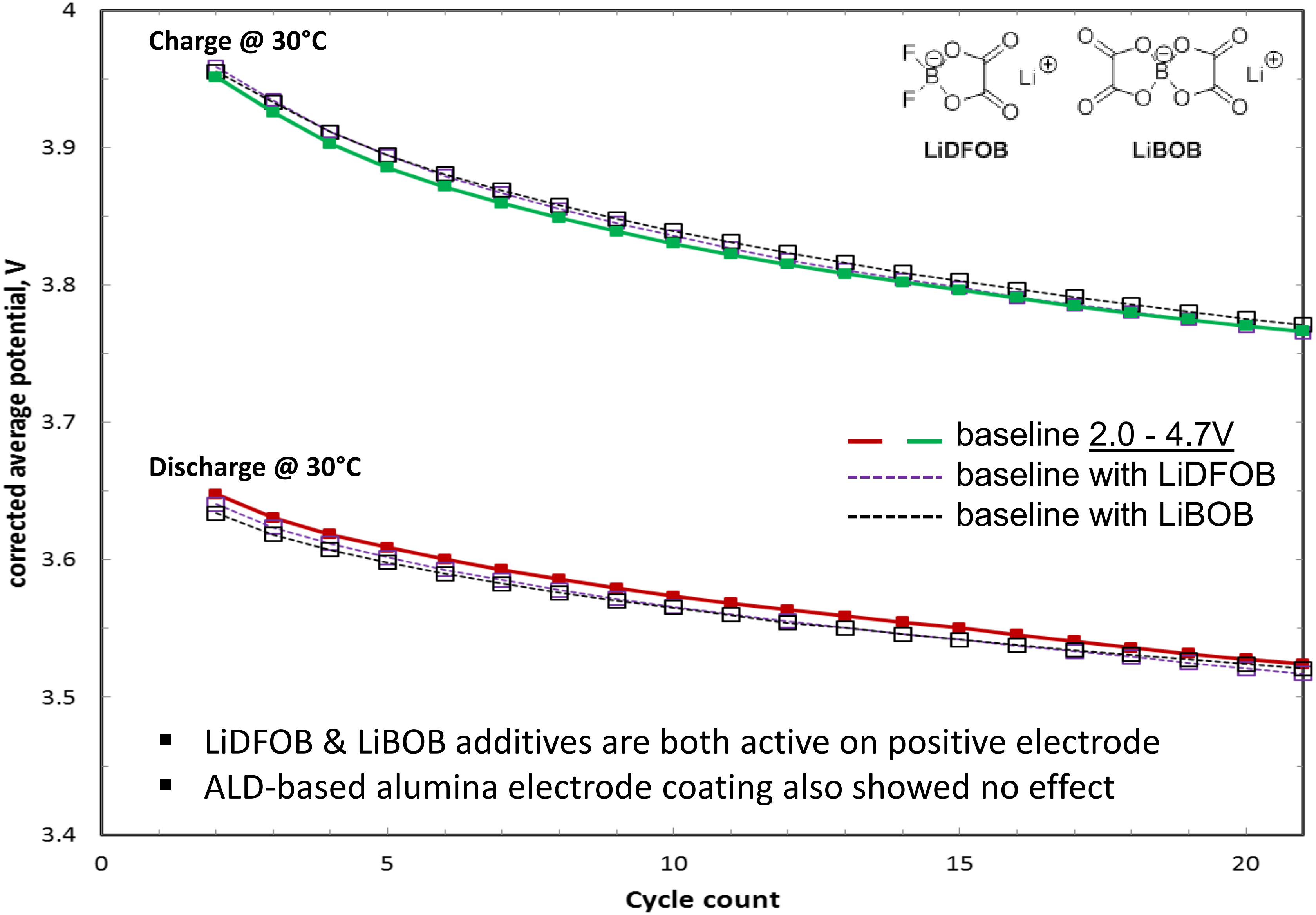
- Only approximation of the "true" average voltage
  (averaging effects, changes in SOC, long relaxation times)
- Exp. conditions need to be carefully adjusted depending on material & cycling conditions (interrupts & window & rate & holds)
- Sensitive to temperature effects

- **Concept of average voltage does not capture mechanistic details**
  Information on mechanisms will be provided in presentations by Baris Key, Mali Balasubramanian, Dean Miller and Chris Johnson

Voltage Fade is more pronounced at higher temperatures

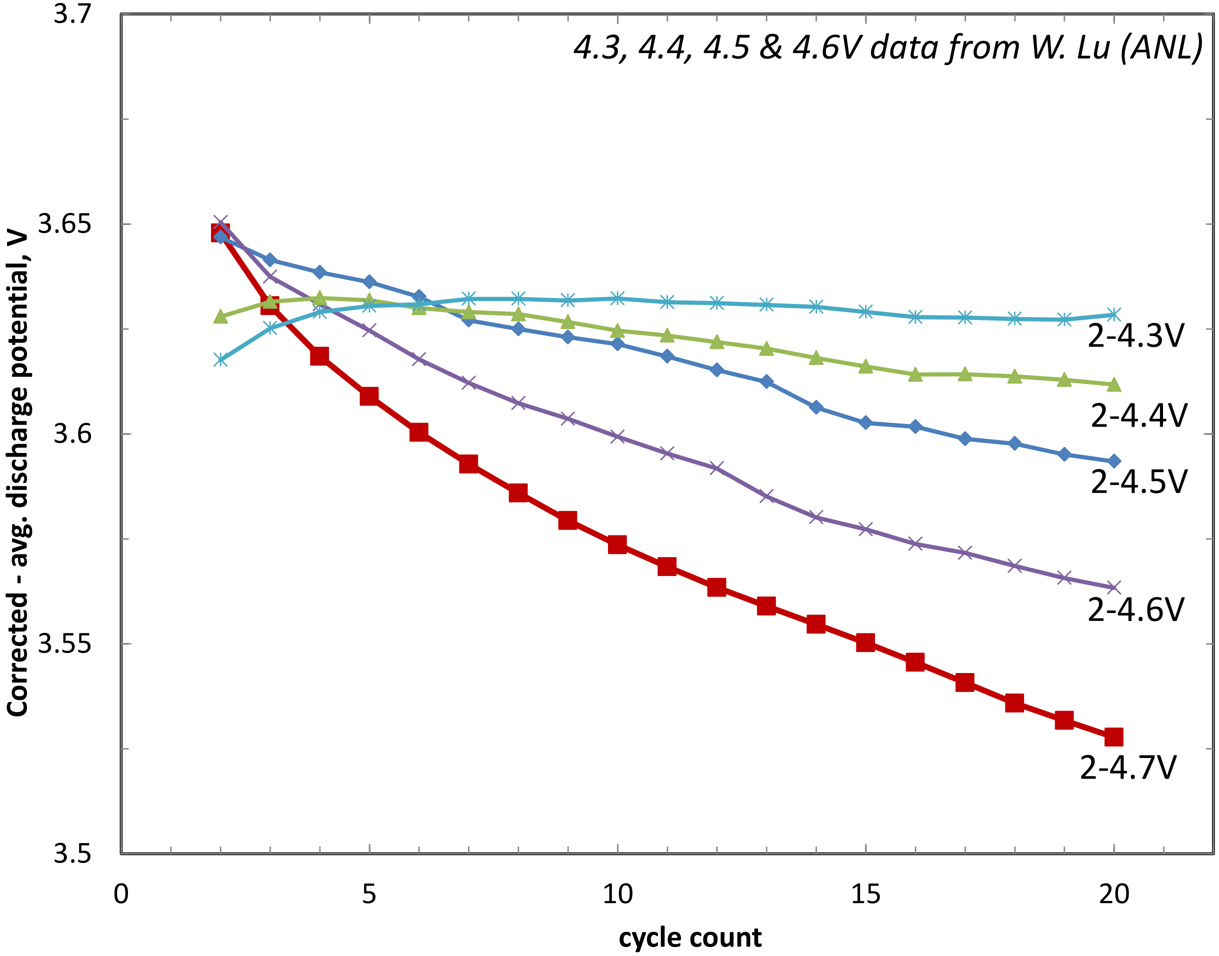


No mitigation of voltage fade by select electrolyte additives or select ALD-based electrode coatings (more information from synthesis subgroup)



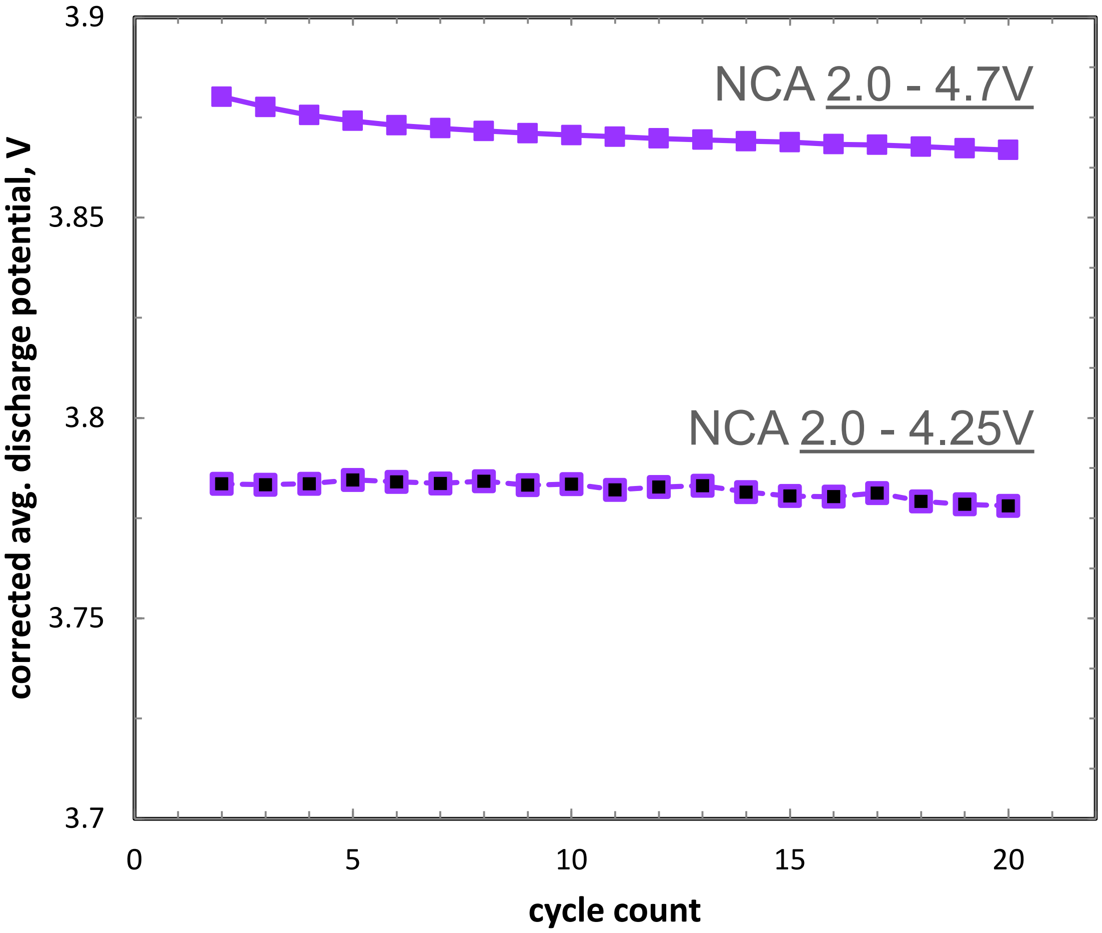
- LiDFOB & LiBOB additives are both active on positive electrode
- ALD-based alumina electrode coating also showed no effect

Voltage fade decreases as upper cut-off voltage is lowered



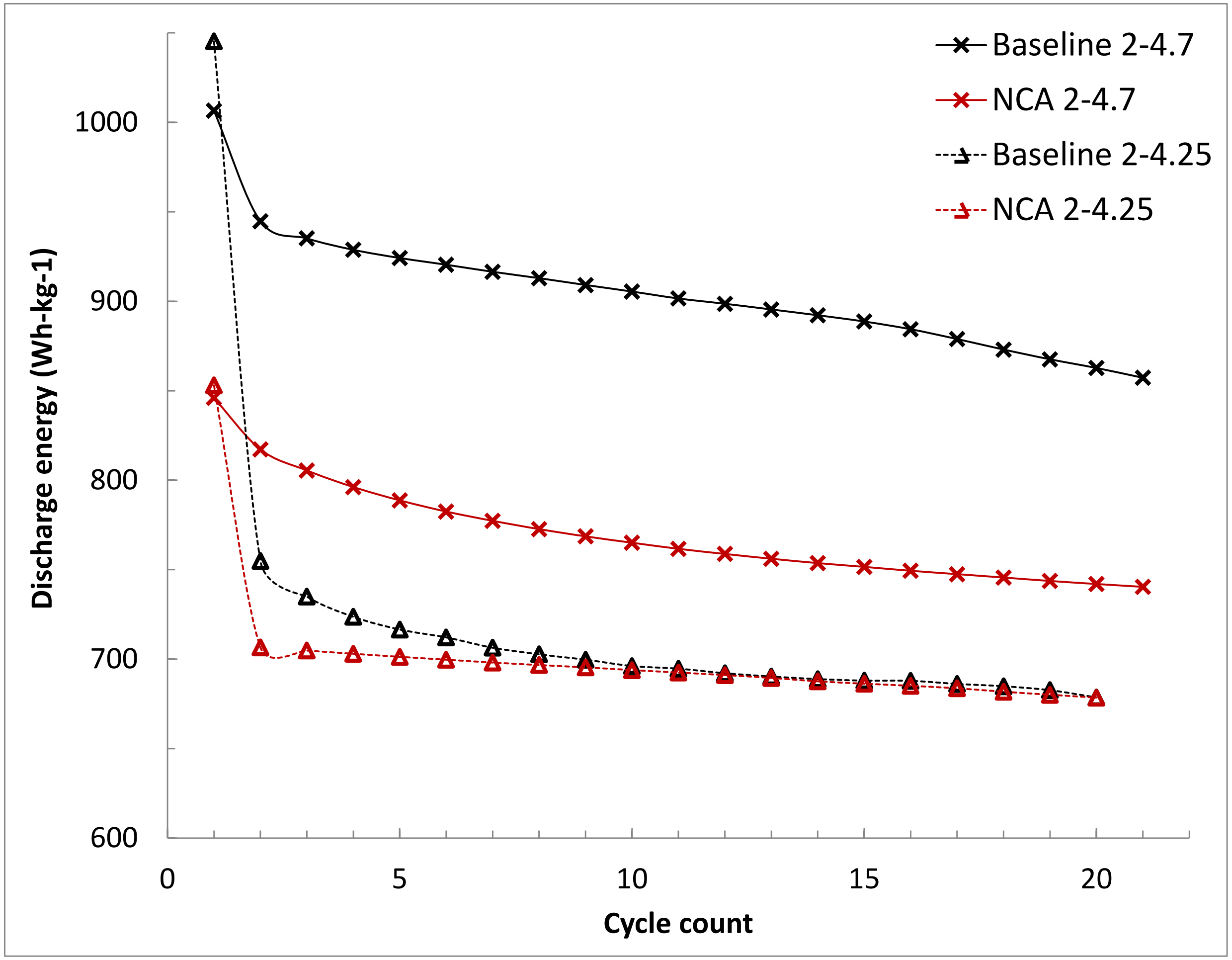
- First (activation) cycle between 2 – 4.7V vs. Li
- No voltage fade when cell is cycled between 2 – 4.25V

Voltage fade is less dramatic in lithium-stoichiometric oxides, such as $Li_{1.0}Ni_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA)



- No VF is observed for NCA cycled up to 4.25V vs. Li/Li^+
- Minor fade exists when cycled up to 4.7V vs. Li/Li^+

Energy density: $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ vs. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)



For all cells, first "activation" cycle: 2 – 4.7V vs. Li/Li^+

In the 2 – 4.7 V vs. Li cycling window, the baseline oxide has a higher energy density than NCA (940 Wh/kg vs. 810 Wh/kg, 2nd cycle). Energy densities in the 2 – 4.25 V vs. Li cycling window are similar.

Improved cell chemistry

Positive Electrode (made by ANL's CFF, no graphite):

92% wt. $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$

($0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$)

4.1%wt Solvay Solef® 5130 PVDF binder

4%wt Timcal Super P®

6.57 mg/cm^2 oxide loading density

42-µm-thick coating

20-µm-thick Al current collector

Negative Electrode:

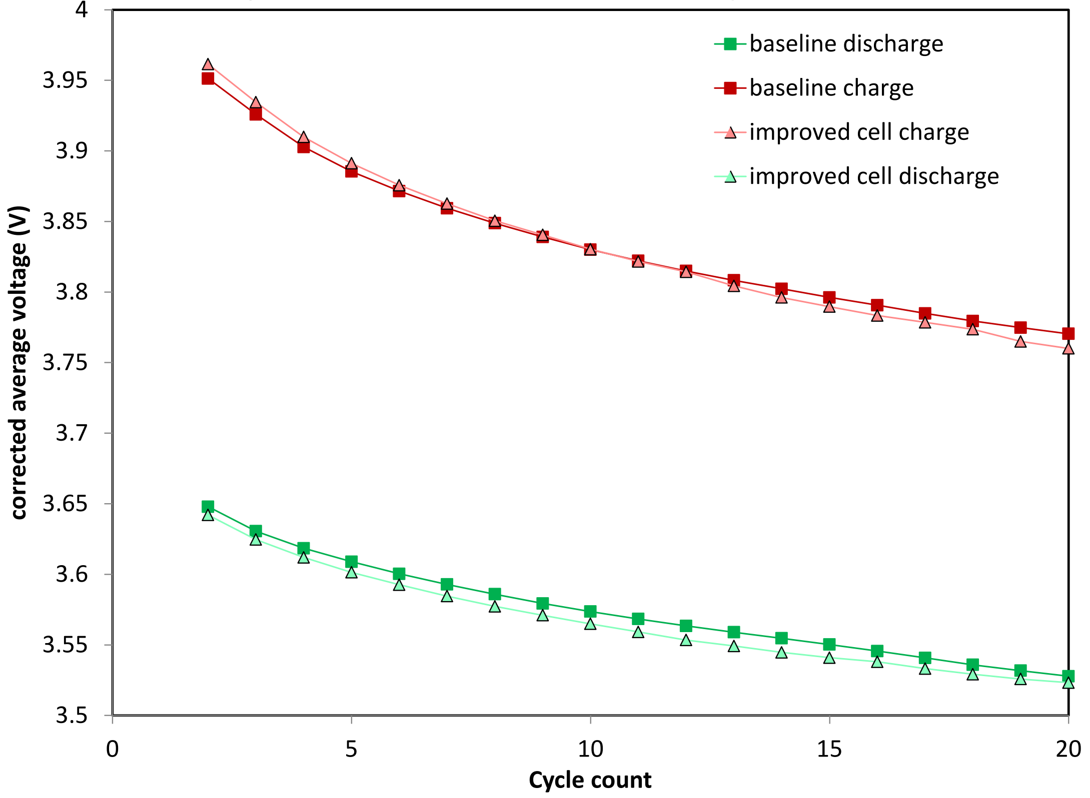
Li metal

Electrolyte/Additive:

EC:EMC (3:7 by wt.) + 1.2M $LiPF_6$

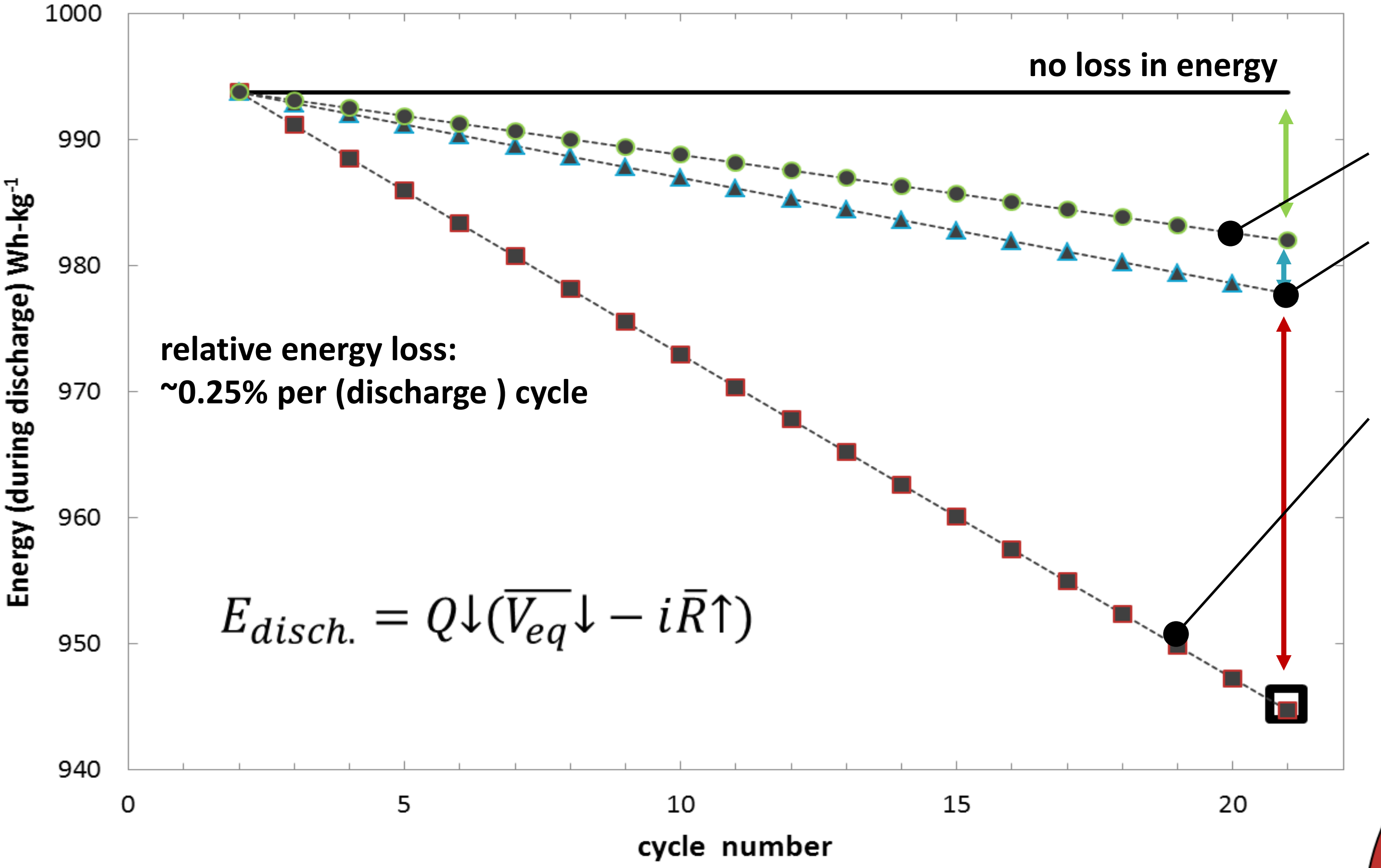
+ 2 wt. % LiDFOB

Data from cells with baseline and improved chemistries



By modifying electrode constitution and by using electrode additives we can dramatically reduce cell impedance rise and capacity fade. However, voltage fade characteristics are unaffected.

Energy output (discharge) for $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$ *vs.* Li



relative energy loss:
~0.25% per (discharge) cycle

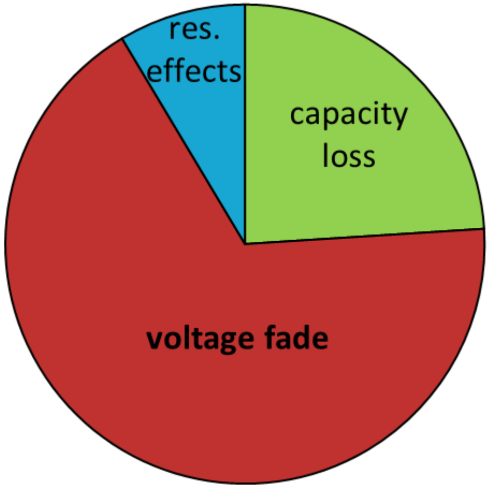
$$E_{disch.} = Q\downarrow(\overline{V_{eq}}\downarrow - i\bar{R}\uparrow)$$

capacity loss of active oxide

resistance effects +
capacity loss

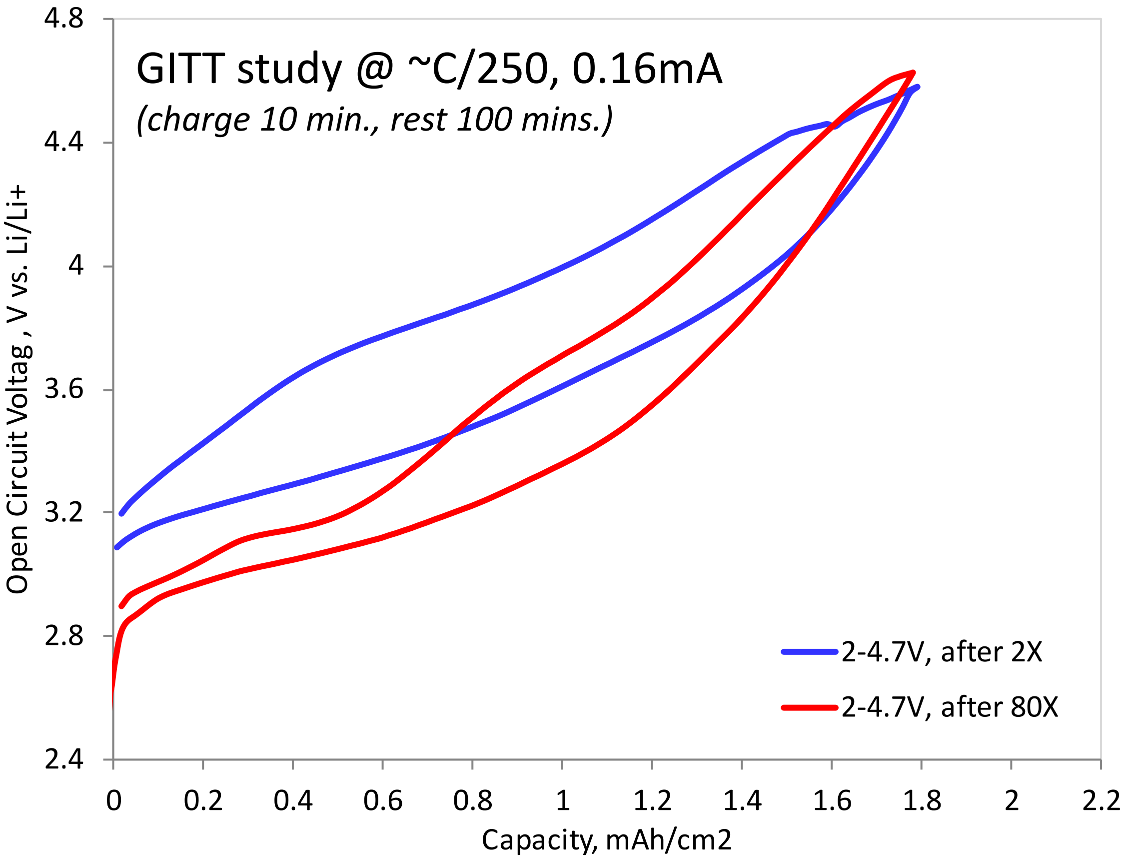
incl. also voltage fade

contributions to energy loss after 20 cycles



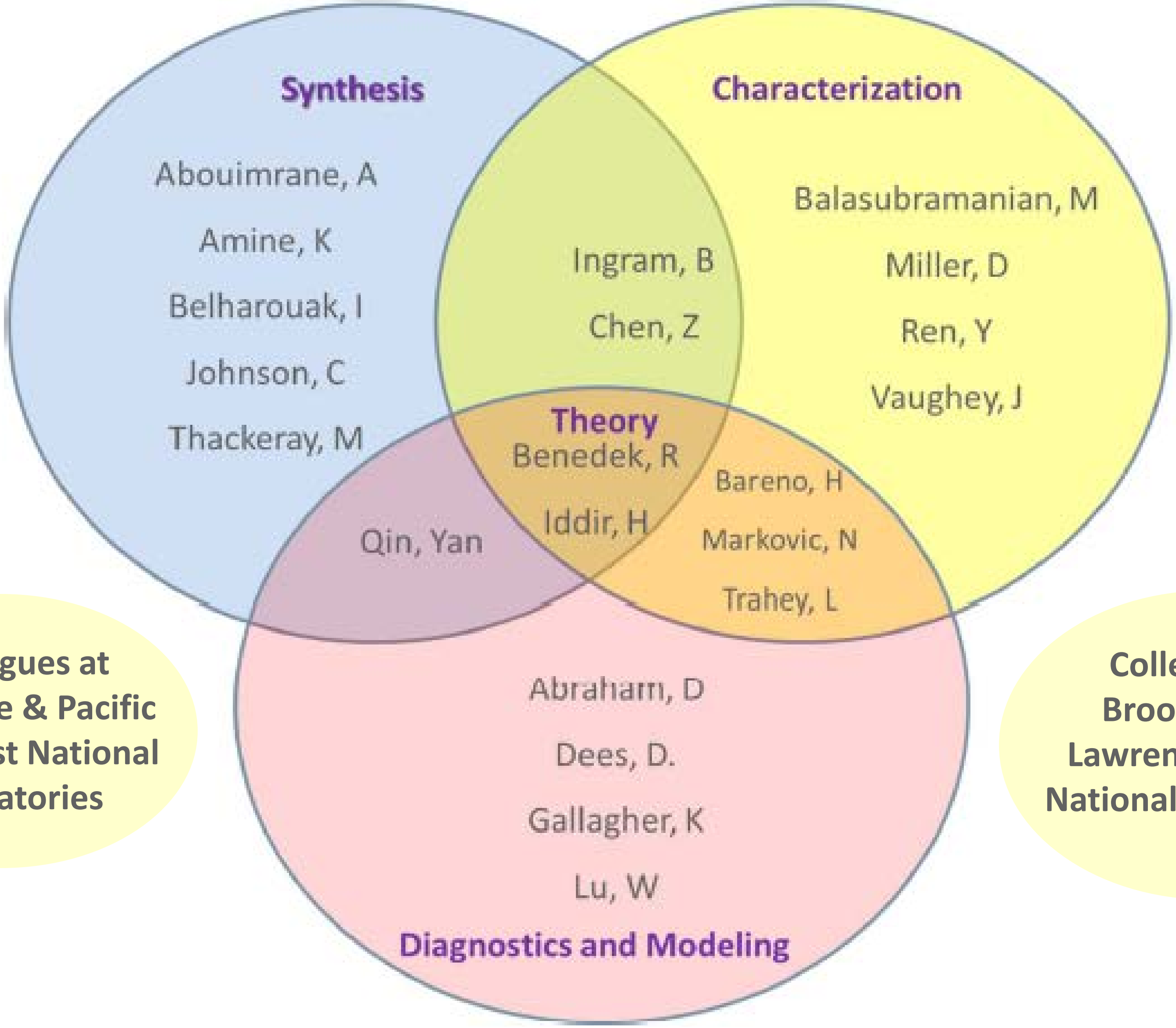
Mitigating impedance rise and capacity fade of the positive electrodes through use of electrode coatings and electrolyte additives makes Voltage Fade the dominant contributor to cell energy fade.

Voltage Fade - persists even at very slow cycling rates



- Equilibrium potentials drop throughout cycling
- Voltage Fade (VF) is non-uniform
- Lower potentials drop from >3.2V to ~3V
- VF on charge is greater than that on discharge
- Materials also show large hysteresis (this becomes less during cycling, K. Gallagher)

Collaborations



Synthesis

Abouimrane, A

Amine, K

Belharouak, I

Johnson, C

Thackeray, M

Characterization

Balasubramanian, M

Miller, D

Ren, Y

Vaughey, J

Ingram, B

Chen, Z

Theory

Benedek, R

Iddir, H

Qin, Yan

Bareno, H

Markovic, N

Trahey, L

Abraham, D

Dees, D.

Gallagher, K

Lu, W

Diagnostics and Modeling

Colleagues at Oak Ridge & Pacific Northwest National Laboratories

Colleagues at Brookhaven & Lawrence Berkeley National Laboratories

Work in Progress/Future Work

- Investigate Voltage Fade in various lithium– and manganese– rich and lithium–stoichiometric oxides and compare data with baseline oxide
  - Data from $Li_{1.2}Ni_{0.4}Mn_{0.4}O_2$, $Li_{1.2}Co_{0.4}Mn_{0.4}O_2$, $Li_{1.2}Cr_{0.4}Mn_{0.4}O_2$, $Li_{1.2}Fe_{0.4}Mn_{0.4}O_2$ and $Li_{1.04}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{0.96}O_2$, are being analyzed to correlate type of transition metal (Ni, Co, Cr, Fe) with voltage fade characteristics
- Examine effect of formation cycling and other cell test conditions (such as temperature) on voltage fade behavior
  - Initial data show that “step-wise formation cycling” significantly increases the measured discharged capacity. Other data show that temperature and cycling window affect discharge capacity and voltage hysteresis of the oxides, which may also affect voltage fade behavior
- Coordinate characterization/diagnostic studies and work with materials synthesis team members to mitigate voltage fade
  - Recommend solutions to mitigate crucial challenges that may hinder commercialization, which include first cycle irreversibility, structural stability, and power delivery capability

Summary

Voltage Fade in general

- .. is not a cell-kinetic phenomenon; originates from structural changes of the cathode material
- .. proceeds at a rate of few mV per cycle
- .. is a problem common to many layered materials when cycled to high voltages (>4.4 vs. Li)
- .. lowers theoretical energy output throughout cycling
- .. can be tracked through the resistance-corrected average voltages as a function of cycle number

The VF team established a protocol to track voltage fade during cycling. This protocol allows us to evaluate strategies that tackle voltage fade.