Characterization of Voltage Fade in Lithium-ion Cells with Layered Oxides

Project ID: ES188

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Voltage Fade Team

Annual Merit Review
Washington DC, June 16-20, 2014

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Overview

Timeline
• Start: October 1, 2012
• End: Sept. 30, 2014
• Percent complete: 75%

Budget
• Voltage Fade project

Barriers
• Calendar/cycle life of lithium-ion cells being developed for PHEV and EV batteries that meet or exceed DOE/USABC goals

Partners
• ORNL
• NREL
• ARL
• JPL
Project Objectives - Relevance

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

- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing LMR-NMC based positive electrodes \( \text{LMR-NMC} = x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2 \) (\( M = \text{Ni, Mn, Co} \))
- To achieve the energy and power density targets these cells must be cycled to voltages that exceed 4.5 V vs. Li/Li⁺
- A continuous cycle-to-cycle decrease in positive electrode equilibrium voltage, termed voltage fade, reduces the cell’s energy and power output under these cycling conditions
- Mitigating voltage fade in LMR-NMC oxides is, therefore, critical to increasing longevity, thereby reducing lifetime cost, of these high-energy batteries
Approach - Voltage Fade Team

- 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

Suggest/implement approaches to mitigate voltage fade
Approach - Project

Electrochemical characterization is essential to evaluate and benchmark voltage fade characteristics of potential positive electrode materials

- Develop electrochemical protocols to track, quantify and characterize voltage fade in a reproducible and time-efficient manner
  - Disseminate protocols to partnering institutions and individuals to allow comparison of data generated at multiple laboratories
- Provide continuous feedback to team members for the development of electrochemical and atomistic models to explain voltage fade
  - Data from AC Impedance spectroscopy and galvanostatic intermittent titration experiments are used to develop models that explain diffusion and migration of lithium and transition metal atoms during oxide cycling
- Supply regular guidance to team members developing oxide materials to mitigate or minimize voltage fade during extended cycling
  - Electrochemical and material characterization data from cycling experiments form the basis for the selection of oxide synthesis techniques and oxide composition profiles that show reduced voltage fade
Established test protocol to measure and track voltage fade: use of an iR-corrected average voltage

- Cell configuration: oxide as positive, Li metal as negative
- Temperature: 30°C (also 55°C)
- Initial activation cycle: 2-4.7V @ 10 mA/g followed by 2-4.7V @ 20 mA/g cycles
- Number of cycles: 20; Test time: ~20 days
- 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 monitored rest.

1. Determine average charge and discharge voltages \( \frac{\text{Energy}_{\text{Energy}}}{\text{Capacity}_{\text{Q}}} \)
2. Obtain average charge and discharge resistances from the interrupts
3. Calculate resistance-corrected average voltages \( \frac{\text{Energy}}{\text{Q}} \pm \text{iR} \)
Summary of various studies
In general, voltage fade is greater at
- Higher test temperatures
- Higher upper cutoff voltage
- Longer aging periods
Also, voltage fade is greater for
- Charge cycle than discharge cycle
- Higher voltage hysteresis

Typical voltage fade results for 0.5Li$_2$MnO$_3$$\cdot$0.5LiNi$_{0.375}$Mn$_{0.375}$Co$_{0.25}$O$_2$

$V_{\text{avg}}-|\text{iR}|$

$\sim -10\text{mV/cycle}$
(-0.27% per cycle)

$\sim -6\text{mV/cycle}$
(-0.18% per cycle)

iR-corrected voltage gap
($\sim 250\text{mV}$)
Voltage fade in various Li- and Mn- rich oxides

All Li- and Mn- rich oxides studied display voltage fade and hysteresis.

Rate of fade depends on oxide composition.

Also see ES187 (Key), ES194 (Croy)
NCA & NCM333 oxide also display voltage fade (2-4.7V)

Fade rate is lower than for Li- and Mn-rich oxides

Li-stoichiometric
2-4.7V: 212 mAh/g (2nd Disch)
Fade rate < 1 mV/cycle

Li-excess (Li$_{1.05}$)
2-4.7V: 200 mAh/g (2nd Disch)
Fade rate < 2.6 mV/cycle

No measurable fade during 2-4.25V cycles

Bettge et al. JES 160 (2013) A2046
In 2-4.7 V cycling window $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$ shows highest energy density.

First (activation) cycle: 2-4.7V vs. Li, 10 mA/g, 30°C

In 2-4.25 V range $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ shows higher energy density.
No mitigation of voltage fade by select electrolyte additives or select oxide/electrode coatings (*tests vs. Li counter electrode*)

Relative change in average voltage in baseline cells and in cells containing an electrolyte additive or a coated cathode.

<table>
<thead>
<tr>
<th>Coating/additive</th>
<th>100 × rel. change in average voltage after 20 cycles (100 × s.e.)</th>
<th>100 × rel. change in average voltage after 50 cycles (100 × s.e.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Discharge</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>3.14 (0.10)</td>
<td>4.81</td>
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<tr>
<td>3-Hexylthiophene</td>
<td>2.88</td>
<td>4.52</td>
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<tr>
<td>LiDFOB</td>
<td>3.38</td>
<td></td>
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<tr>
<td>Al₂O₃ (5 ALD cycles)</td>
<td>3.40</td>
<td>5.30</td>
</tr>
<tr>
<td>Al₂O₃ (100 ALD cycles)</td>
<td>3.22</td>
<td>5.47</td>
</tr>
<tr>
<td>AlPO₄</td>
<td>3.68</td>
<td>5.48</td>
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<tr>
<td>LiAlO₂</td>
<td>3.32 (0.07)</td>
<td></td>
</tr>
<tr>
<td>TiO₂ (100 °C)</td>
<td>3.14 (0.04)</td>
<td></td>
</tr>
<tr>
<td>TiO₂ (150 °C)</td>
<td>3.20 (0.07)</td>
<td></td>
</tr>
<tr>
<td>ZrO₂ (100 °C)</td>
<td>3.17 (0.01)</td>
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<tr>
<td>ZrO₂ (150 °C)</td>
<td>3.26 (0.03)</td>
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<tr>
<td>LiPON (1 h)</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td>LiPON (2 h)</td>
<td>2.60</td>
<td></td>
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<tr>
<td>LiPON (3 h)</td>
<td>5.20</td>
<td></td>
</tr>
<tr>
<td><strong>Charge</strong></td>
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<td></td>
</tr>
<tr>
<td>Baseline</td>
<td>3.97 (0.49)</td>
<td>4.52</td>
</tr>
<tr>
<td>3-Hexylthiophene</td>
<td>3.16</td>
<td>4.20</td>
</tr>
<tr>
<td>LiDFOB</td>
<td>4.89</td>
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<tr>
<td>Al₂O₃ (5 ALD cycles)</td>
<td>3.52</td>
<td>5.15</td>
</tr>
<tr>
<td>Al₂O₃ (100 ALD cycles)</td>
<td>3.14</td>
<td>4.70</td>
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<td>AlPO₄</td>
<td>3.66</td>
<td>5.03</td>
</tr>
<tr>
<td>LiAlO₂</td>
<td>5.21 (0.05)</td>
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<tr>
<td>TiO₂ (100 °C)</td>
<td>4.39 (0.01)</td>
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<tr>
<td>TiO₂ (150 °C)</td>
<td>4.60 (0.01)</td>
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<td>ZrO₂ (100 °C)</td>
<td>4.62 (0.02)</td>
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<td>ZrO₂ (150 °C)</td>
<td>4.85 (0.03)</td>
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<td>LiPON (1 h)</td>
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<td>LiPON (2 h)</td>
<td>3.75</td>
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<tr>
<td>LiPON (3 h)</td>
<td>7.97</td>
<td></td>
</tr>
</tbody>
</table>

*Pol et al, JPS258 (2014) 46*

*Bloom et al., JPS 249 (2013) 509*
Impedance data affected by oxide voltage hysteresis
(in agreement with XAS, NMR and Neutron data)

Positive electrode data from a Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ //Graphite reference electrode cell
After formation cycling

3.75V vs. Li
13.4 mAh
2 mA current, 30°C

Impedance data differences indicate that Li atoms occupy different oxide sites during charge and discharge for same voltage and/or capacity

Also see ES187 (Key), ES194 (Croy), ES189 (Dees)
Slow voltage relaxation during current interrupts
Induces differences between data obtained by *ex situ* and *in situ* techniques

**Cycle 1 – activation cycle**

<table>
<thead>
<tr>
<th>Pulse No.</th>
<th>Capacity mAh/g</th>
<th>Before V vs. Li</th>
<th>After V vs. Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C_1</td>
<td>40</td>
<td>3.948</td>
<td>3.928</td>
</tr>
<tr>
<td>C_2</td>
<td>80</td>
<td>4.091</td>
<td>4.069</td>
</tr>
<tr>
<td>C_3</td>
<td>120</td>
<td>4.376</td>
<td>4.302</td>
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<tr>
<td>C_4</td>
<td>160</td>
<td>4.440</td>
<td>4.317</td>
</tr>
<tr>
<td>C_5</td>
<td>200</td>
<td>4.452</td>
<td>4.320</td>
</tr>
<tr>
<td>C_6</td>
<td>240</td>
<td>4.467</td>
<td>4.331</td>
</tr>
<tr>
<td>C_7</td>
<td>280</td>
<td>4.491</td>
<td>4.351</td>
</tr>
<tr>
<td>C_8</td>
<td>320</td>
<td>4.571</td>
<td>4.410</td>
</tr>
<tr>
<td>C_9</td>
<td>357</td>
<td>4.800</td>
<td>4.488</td>
</tr>
<tr>
<td>C_10</td>
<td>363</td>
<td>4.800</td>
<td>4.488</td>
</tr>
</tbody>
</table>

| D_1       | 323            | 3.927           | 4.031         |
| D_2       | 283            | 3.642           | 3.761         |
| D_3       | 243            | 3.460           | 3.612         |
| D_4       | 203            | 3.345           | 3.510         |
| D_5       | 163            | 3.265           | 3.424         |
| D_6       | 123            | 3.187           | 3.341         |
| D_7       | 83             | 3.071           | 3.226         |
| D_8       | 52             | 2               | 3.035         |
| D_9       | 47             | 2               | 2.995         |
| D_10      | 44             | 2               | 2.968         |

**Relaxation plot after 5th Charge**

Pulse (@200 mAh/g)

**Fit Equation**

\[ y = A1 \exp(-x/t1) + A2 \exp(-x/t2) + y0 \]

When \( t1 \) & \( t2 = \infty \)

\[ y = y0 \]

\[ y0 = 4.307 \]

**Relaxation plot after 4th Discharge**

Pulse (@203 mAh/g)

\[ y0 = 3.511 \]

Voltage continues to change even after 10 hours

**Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2** vs. Li.

Capacity limited charge (40 mAh/g), followed by 600 m rest at every step.

UCV = 4.8V; LCV = 2V; T = 30°C

**Details in adjacent table**

Also see ES189 (Dees), ES193 (Iddir)
Voltage Hysteresis observed in Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ vs. Li. One activation cycle (2-4.7V) followed by GITT cycling (0.1 mA/cm$^2$ current for 600s, followed by 6000s rest. Total time @ RT ~ 22 days/cycle ~ C/250 rate)

Voltage Hysteresis observed under all cycling conditions
Hysteresis decreases on cycling but does not disappear

Also see ES187 (Key), ES194 (Croy), ES189 (Dees)
Does oxide voltage stabilize after extended cycling?

Tests in $\text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2$//Li$_4$Ti$_5$O$_{12}$ cells; Li unsuitable for long-term cycling

500 cycles, 30°C, 0.75 - 3.15 V vs. LTO (2.3 - 4.7 V vs. Li/Li$^+$)

Also see ES187 (Key)

Negligible capacity loss even after 500 cycles – justifies capacity normalization
Voltage hysteresis decreases but persists even after 500 cycles
Voltage fade rate decreases and voltage profile stabilizes around 400 cycles
dQ/dV plot - voltage fade peaks stabilize around 400 cycles

Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$/Li$_4$Ti$_5$O$_{12}$ cells; 1000 cycles, 30°C, 0.75 - 3.15 V vs. LTO (2.3 - 4.7 V vs. Li/Li$^+$)

Changes on cycling
Continuous shift of 3.5V charge peak to 3.15 V
(corresponding peak on discharge shifts to 2.95 V)
Continuous decrease in 3.9 V charge (3.8 V discharge) peak
Gradual growth of 4.65 V charge peak

Also see previous slide
High-resolution electron microscopy of aged oxide samples (after 1000 cycles) show coexistence of multiple crystal structures including areas with layered, spinel, and Li$_2$MnO$_3$ characteristics.

- Particle-to-particle variations in structure
  - generally similar, but crystal structure fractions vary
- Electron diffraction patterns comprise
  - strong layered fundamental reflections
  - super reflections due to spinel ordering
  - super reflections from Li-TM ordering (Li$_2$MnO$_3$-like)

Miller, unpublished data
Neutron diffraction and magnetic property data on Li$_{1.2}$Ni$_{0.15}$Mn$_{0.55}$Co$_{0.1}$O$_2$ consistent with spinel ordering

Technical Accomplishments and Progress

Data from Oak Ridge National Laboratory
Also see Publications & Presentations

Lithium in tetrahedral (0 0 x) site
Shows better agreement parameter

This type of spin-glass behavior is observed only in cubic LiMn$_2$O$_4$ spinel (not in tetragonal Li$_2$Mn$_2$O$_4$ spinel)

3.2V-Discharged (after 26th cycle)

Mn in tetrahedral sites of Li layer
See ES193 (Iddir)
Responses to Previous Year Reviewers’ Comments

**Relevance**
Comments — “aligned with DOE objectives to reduce dependence on petroleum”, “project involves understanding voltage fade in LMR-NMC, a material of appreciable interest to reach EV goals”,
Response — positive comments, project direction maintained.

**Approach**
Comments — “quantifying and benchmarking electrochemical performance of LMR-NMC”, “focuses on definition of baseline and its characterization”
Response — This is not a stand-alone project but part of a team approach/effort to identify materials that have the potential to minimize or eliminate voltage fade

**Technical Accomplishments**
Comments — “project demonstrated that VF is unaffected by changes in electrode constitution and electrolyte additives”, “VF shown to not depend on electrode kinetics”, “unsure if resistance-corrected voltage approach is accurate because of voltage relaxation during current interruption”
Response — positive comments. Resistance-corrected voltage is one approach to examine voltage fade. The experimental conditions (current interrupt locations, relaxation times, voltage windows, etc.) need to be adjusted based on material tested to obtain reliable and consistent data.

**Future Research**
Comments — “test new LMR-NMC compositions, with dopants, from ANL and elsewhere”, “recommend that the team adopt impedance spectroscopy to gain more information”
Response — Examined 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$_2$, and other oxides. Impedance spectroscopy and GITT protocols applied to better understand voltage fade behavior.
Collaborations and Acknowledgment

Burrell, Anthony K.; Abouimrane, Ali; Abraham, Daniel; Amine, Khalil; Balasubramanian, Mahalingam; Barenco Garcia-Ontiveros, Javier; Belharouak, Ilias; Benedek, Roy; Bettge, Martin; Bloom, Ira D.; Long, Brandon R.; Chen, Zonghai; Croy, Jason R.; Dees, Dennis W.; Dogan, Fulya; Gallagher, Kevin G.; Henriksen, Gary L.; Iddir, Hakim; Ingram, Brian J.; Johnson, Christopher; Key, Baris; Li, Yan; Lu, Wenquan; Miller, Dean J.; Ren, Yang; Slater, Michael D.; Thackeray, Michael M.; Vaughey, John T.; Wu, Huiming; Wu, Qingliu; Zhu, Ye; Yang, Zhenzhen; Lee, Eungje; Aoun, Bachir; Vu, Anh D.; Lin, Chi-Kai; Rinaldo, Steven G.

The Team

- Tenant (NREL)
  - Nanda (ORNL)
  - Chen (LBNL)
  - Bugga (JPL)

- Abouimrane
- Belharouak
- Johnson
- Thackeray

- Synthesis

- Croy
- Ingram
- Chen

- Characterization

- Balasubramanian
- Miller
- Ren
- Vaughey

- Theory
- Benedek
- Iddir
- Persson (LBNL)

- Bloom
- Abraham
- Dees
- Gallagher
- Wu

- Electrochemistry, Modeling and Analysis

- Yang (BNL)

- Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
  - David Howell, Peter Faguy & Tien Duong

Also see Publications and Presentations
Publications and Presentations

   Title: Voltage Fade of Layered Oxides: Its Measurement and Impact on Energy Density
   Link: http://jes.ecsdll.org/content/160/11/A2046.full

   Title: Correlating Cation Ordering and Voltage Fade in a Lithium- Manganese-Rich Lithium-Ion Battery Cathode Oxide: a Joint Magnetic Susceptibility and TEM Study.
   Link: http://pubs.rsc.org/en/content/articlehtml/2013/cp/c3cp53658k

   Title: Effect of Interface Modifications on Voltage Fade in 0.5Li2MnO3•0.5LiNi0.375Mn0.375Co0.25O0.2 Cathode Materials

   Title: Neutron Diffraction and Magnetic Susceptibility Studies on a High-Voltage Li1.2Ni0.15Mn0.55Co0.1O2 lithium-ion Battery Cathode; an Insight to the Crystal Structure
   Link: http://pubs.acs.org/doi/full/10.1021/cm402278q

   Title: Correlating hysteresis and voltage fade in lithium- and manganese-rich layered transition-metal oxide electrodes

   Title: Investigating Phase Transformations in Li1.2Ni0.15Mn0.55Co0.1O2 lithium-ion battery cathodes during high-voltage hold (4.5V) via magnetic, X-ray diffraction and electron microscopy studies.
   Link: http://pubs.rsc.org/en/content/articlehtml/2013/ta/c3ta10304h
Future Work - FY 2014

- Initial electrochemistry experiments have indicated that gradual voltage fade during cycling is also observed in layered oxides that are not “activated”, i.e., in oxides cycled below the oxygen evolution plateau
  - Diffraction, spectroscopy, microscopy and atomistic modeling data from \( \text{Li}_{1.2}\text{Ni}_{0.15}\text{Mn}_{0.55}\text{Co}_{0.1}\text{O}_2 \) and \( \text{Li}_{1.2}\text{Co}_{0.4}\text{Mn}_{0.4}\text{O}_2 \) samples are being obtained and analyzed to determine reasons for this behavior

- Various electrochemistry experiments suggest that the high (>320 mAh/g) discharge capacities reported for LMR-NMC oxides are a consequence of testing in Li-metal counter electrode cells
  - LMR-NMC charge compensation mechanisms will be re-examined because tests in \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) counter electrode cells show discharge capacities less than 275 mAh/g

- “Wrap up” studies exclusively associated with voltage fade
  - Document data in reports and share information with the battery community to enable development of advanced high-energy and high-power PEV and EV battery chemistries
Summary

- Investigated Voltage Fade in various lithium– and manganese– rich, and lithium– stoichiometric oxides, with the iR-corrected voltage protocol
  - All Li- and Mn-rich layered oxides display voltage fade and voltage hysteresis
  - Li–stoichiometric oxides, cycled to 4.7V, also show fade but at a much lower rate
  - In general, voltage fade rate is greater at higher temperatures, at higher upper cutoff voltages and at longer aging periods
- Voltage Fade is not mitigated by surface coatings and additives that form passivation films on the oxide particles
  - This fade arises from crystal structure changes in the oxide
- AC impedance data are strongly affected by voltage hysteresis
  - For the same oxide potential and/or Li-content, observed differences indicate that Li atoms occupy different sites during the charge and discharge cycles
- Extended cycling data from Li$_4$Ti$_5$O$_{12}$ counter electrode cells indicate that the voltage profile stabilizes around 400 cycles
  - Voltage hysteresis decreases but persists even after 1000 cycles
  - High-resolution electron microscopy of oxides from aged cells show co-existence of multiple crystal structures including areas with spinel-ordering
  - Neutron diffraction and magnetic property data are also consistent with presence of spinel structures
Technical Back-Up Slides
Advantages & disadvantages of tracking the iR-corrected avg. voltage

+ Advantages of this 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

  *This protocol allows us to evaluate strategies that tackle voltage fade*

- Limitations of this 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

  *Tracking average voltage does not capture mechanistic details*
Voltage fade decreases as upper cut-off voltage is lowered

But there is a corresponding reduction in capacity/energy density

No discernible voltage fade for cells cycled between 2 and 4.25V vs. Li

Bettge et al., JPS 233 (2013) 346