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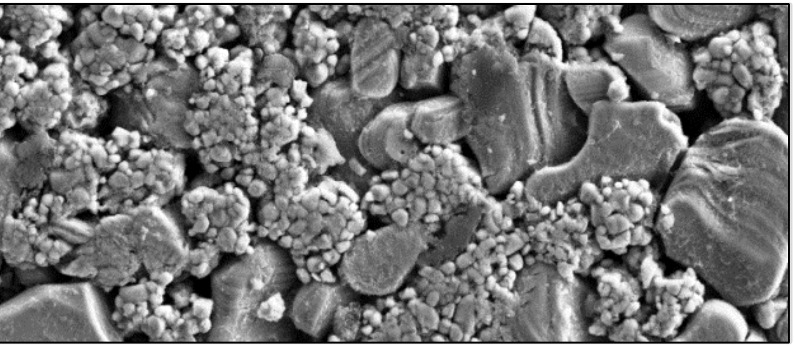
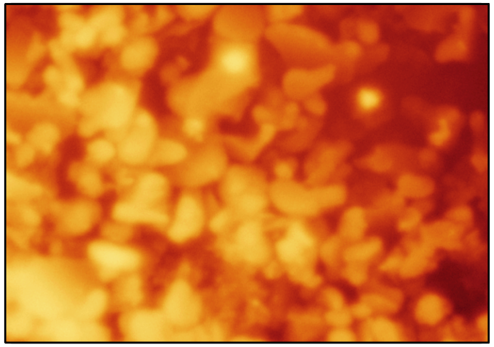


Ph.D. Graduate Work

The Rate Dependency of Li-ion Battery Degradation Mechanisms

Chelsea Snyder

KAPL Interview - March 16th, 2016

Rensselaer

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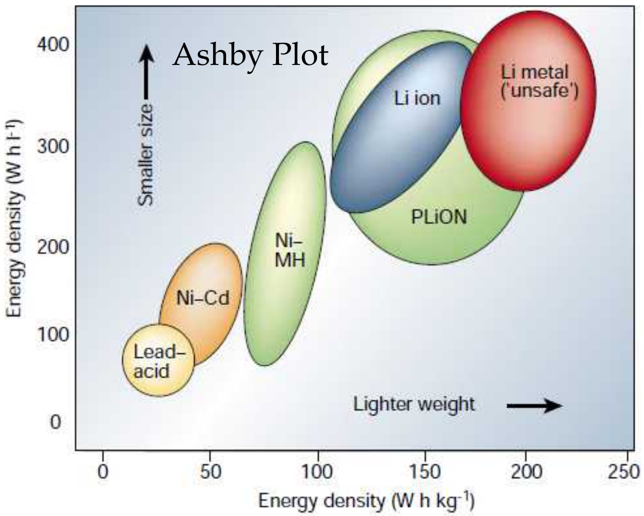
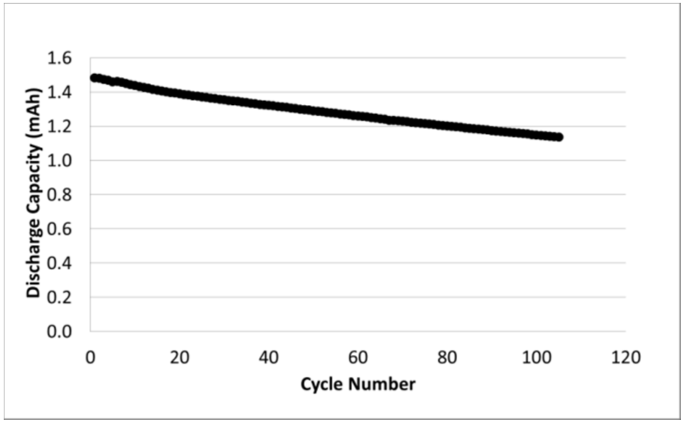
Sandia National Laboratories

Motivation

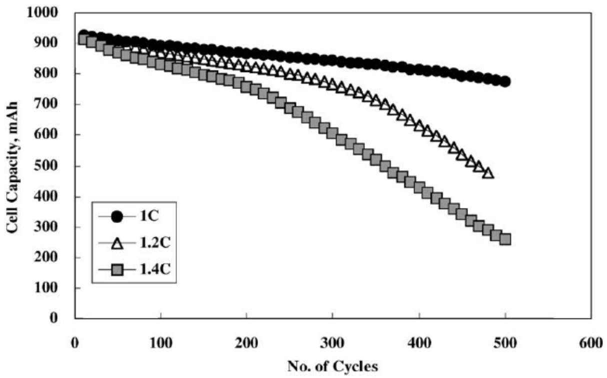


J. Tarascon and M. Armand *Nature* 414 (2001) 359-367

Capacity Fade



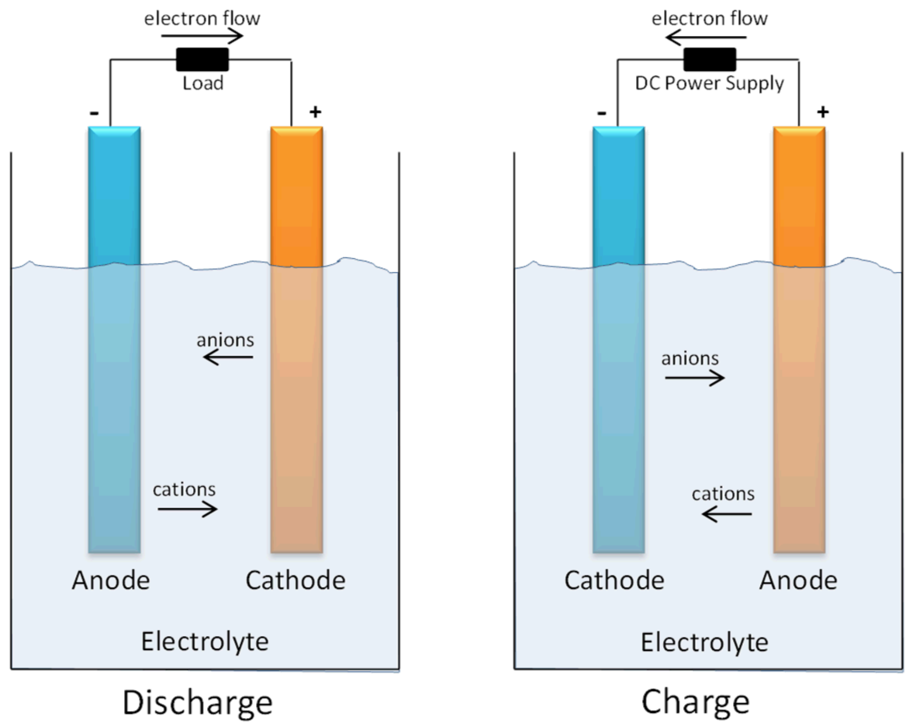
Rate Effects

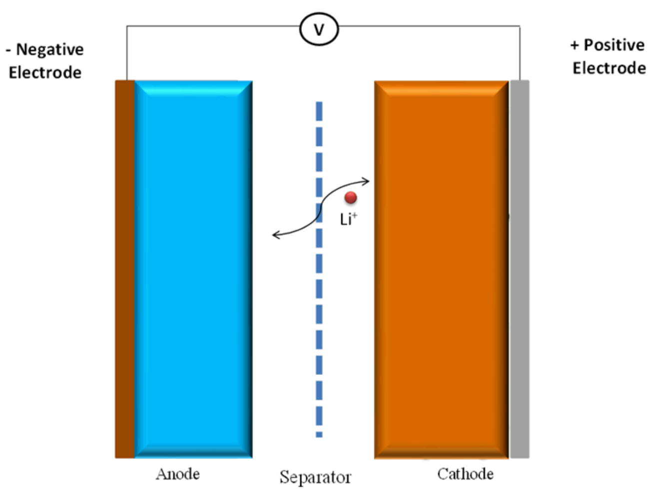


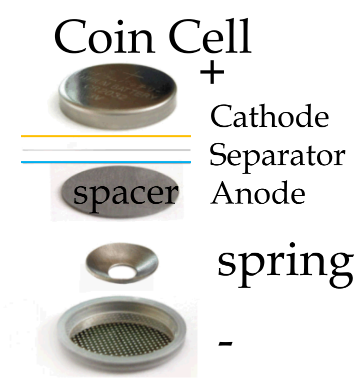
Choi et al. *Journal of Power Sources* 111 (2002) 130-136

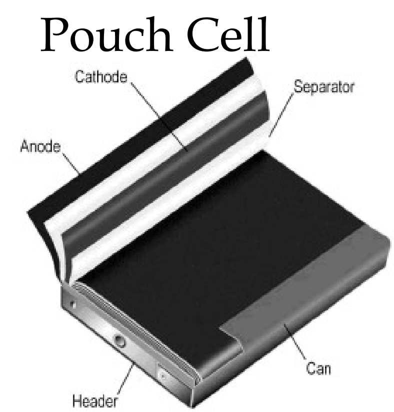
Batteries

- A battery converts stored chemical energy into electrical energy through an electrochemical oxidation-reduction reaction
- Anode: oxidized species
- Cathode: reduced species



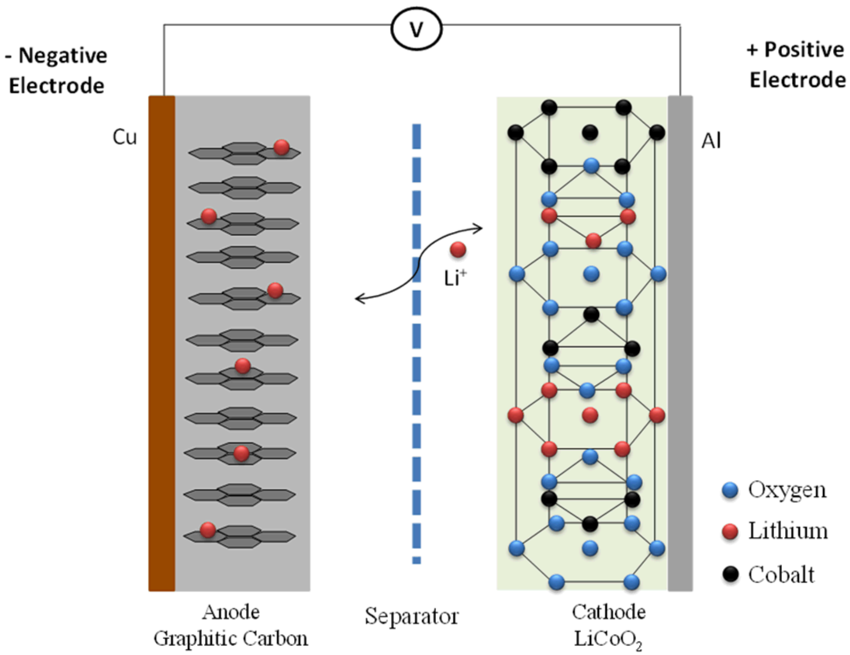






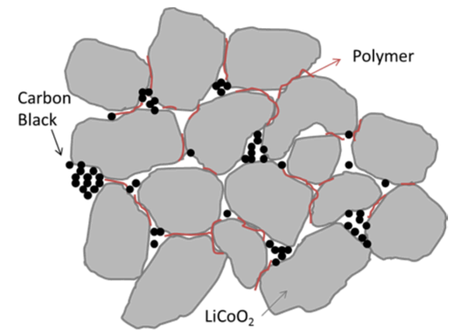
Linden, D., *Linden's Handbook of Batteries*. Fourth ed. 2011: The McGraw-Hill Companies, Inc.
J. Goodenough and K. Park *Journal of American Chemical Society* 135 (2013) 1167-1176

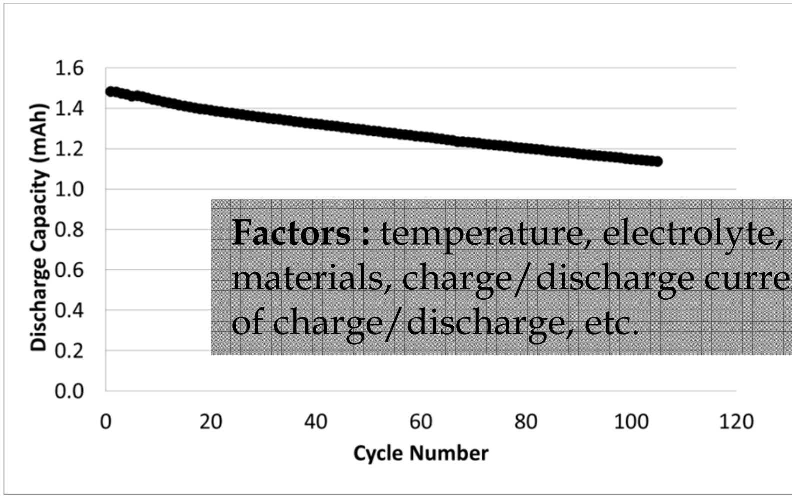
Lithium-ion Batteries



"Rocking Chair"

$$LiCoO_2 + \frac{x}{y}C \underset{discharge}{\overset{charge}{\rightleftarrows}} \frac{x}{y}Li_yC + Li_{1-x}CoO_2$$





Factors : temperature, electrolyte, electrode materials, charge/discharge currents, depth of charge/discharge, etc.

Electrolyte: 1.2 M $LiPF_6$ EC:EMC (3:7)
Cycle Rate: C/10
Voltages: 3.0-4.2 V
Room Temp (25°C)

Linden, D., *Linden's Handbook of Batteries*. Fourth ed. 2011: The McGraw-Hill Companies, Inc.
J. Goodenough and K. Park *Journal of American Chemical Society* 135 (2013) 1167-1176
L.S. Kanevskii and V.S. Dubasova *Russian Journal of Electrochemistry* 41 (2005) 1-16

Degradation Mechanisms

1. Loss of Primary Active Material (Li^+ ion Inventory)
2. Loss of Secondary Active Material ($LiCoO_2$)
3. Loss of Secondary Active Material (Graphite)
4. Increased Impedance of Cell and Electrodes

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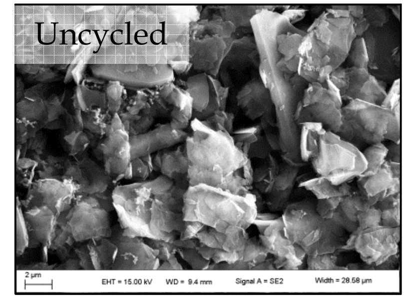
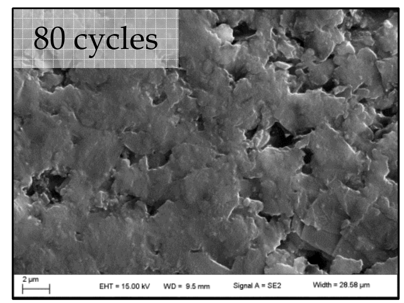
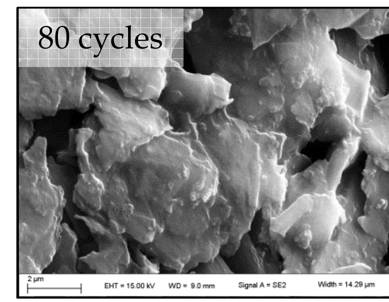
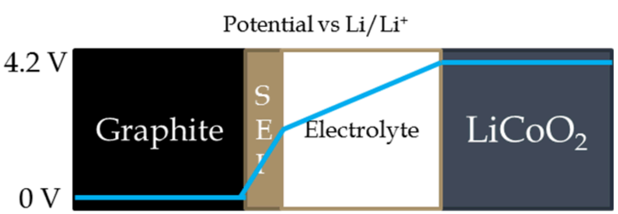


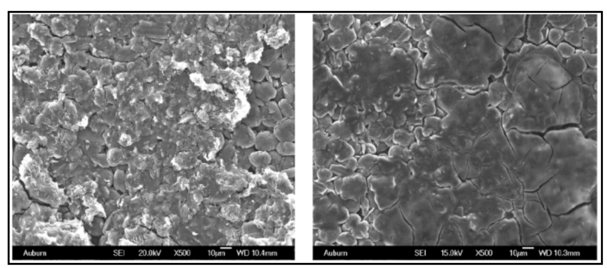




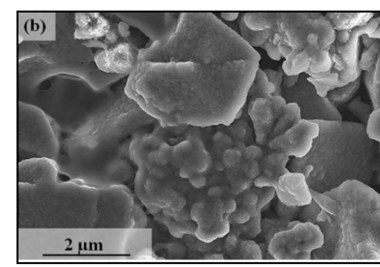
Solid Electrolyte Interphase (SEI) formation

- Reduction of electrolyte to form passive surface film
- Largest impact during first few cycles
- Increases impedance and charge transfer resistance





V. Agubra and J. Fergus *Materials* 6 (2013) 1310-1325



J. Lee et al. *Carbon* 52 (2013) 388-397

Degradation Mechanisms

1. Loss of Primary Active Material (Li^+ ion Inventory)
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3. Loss of Secondary Active Material (Graphite)
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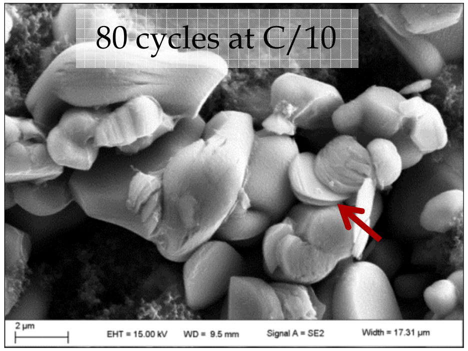
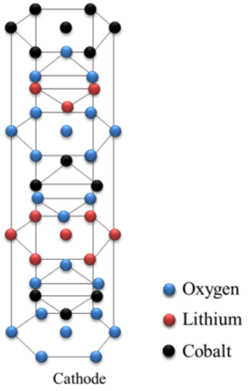
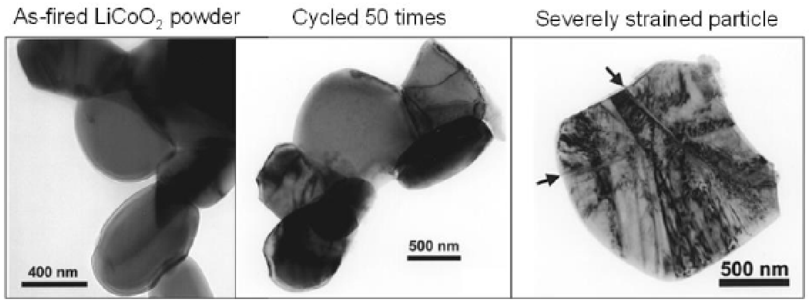


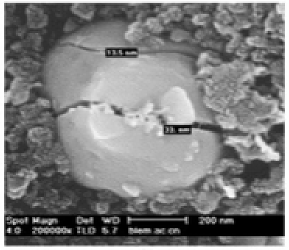


Anisotropic expansion/contraction
- Internal strains and dislocation defects
- Fracture of particles
- Contact loss between electrically conductive components

Electrode disordering
- Deactivation of Li ions, cracks, pores
- Triggered by strain caused by volumetric changes



W. Haifeng et al. *Journal of the Electrochemical Society* 146 (1999) 473-480



D. Wang et al. *Journal of Power Sources* 140 (2005) 125-128

Degradation Mechanisms

1. Loss of Primary Active Material (Li^+ ion Inventory)
2. Loss of Secondary Active Material ($LiCoO_2$)
3. Loss of Secondary Active Material (Graphite)
4. Increased Impedance of Cell and Electrodes

Exfoliation of particles

- Solvent molecules intercalate between graphene layers and lead to particle cracking and loss of active material

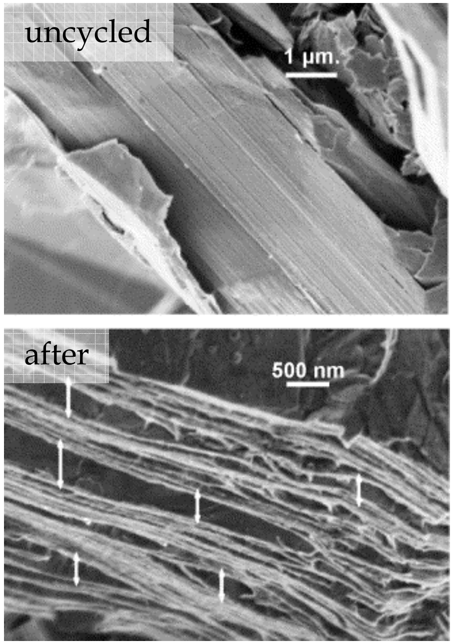
Structural disorder and damage

- Triggered by volumetric expansion

Contact Loss in composite material

- Due to expansion of graphite (10% linear expansion at full charge)

Exfoliation of Graphite



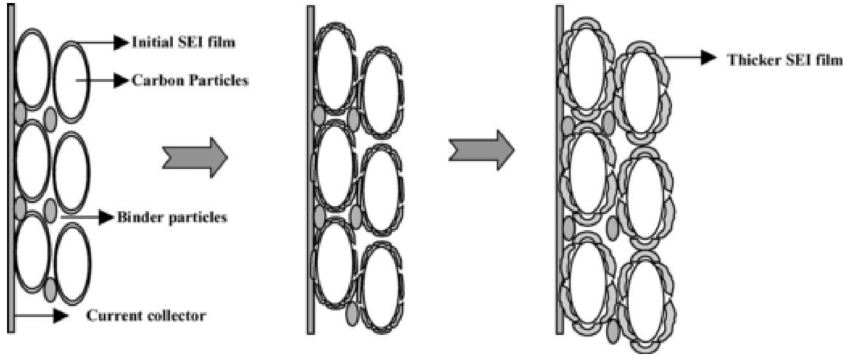
H. Buqa et al. *Journal of Power Sources* 153 (2006) 385-390

Degradation Mechanisms

1. Loss of Primary Active Material (Li^+ ion Inventory)
2. Loss of Secondary Active Material ($LiCoO_2$)
3. Loss of Secondary Active Material (Graphite)
4. Increased Impedance of Cell and Electrodes

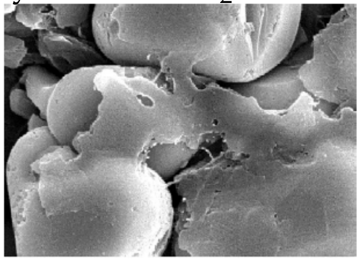
Film formation and thickening
- SEI on graphite anode
- Electrolyte oxidation at $LiCoO_2$ electrode

Increased Cell Resistance
Degradation of binder conductivity



G. Ning et al. *Journal of Power Sources* 117 (2003) 160-169

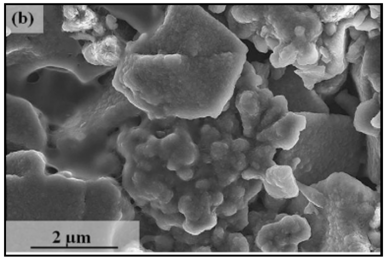
Cycled $LiCoO_2$ Electrode



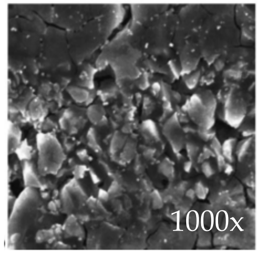
Scale: 9 mm=1 micron

D. Aurbach et al., *Electrochimica Acta* 00 (2002) 1-13

Cycled Graphite Electrode



J. Lee et al. *Carbon* 52 (2013) 388-397



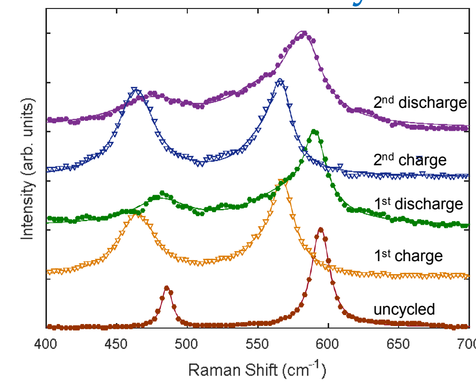
G. Ning et al. *Journal of Power Sources* 117 (2003) 160-169

Degradation Mechanisms

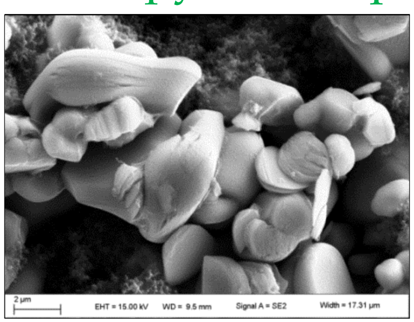
Relative contributions depend on physical and chemical nature of the system, temperature, and **c-rate**

1. Loss of Primary Active Material (Li^+ ion Inventory) → Raman Analysis
2. Loss of Secondary Active Material ($LiCoO_2$)
3. Loss of Secondary Active Material (Graphite)
4. Increased Impedance of Cell and Electrodes

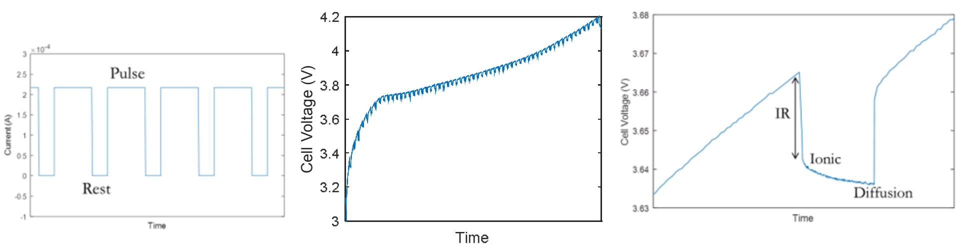
Raman Analysis



Electrochemical Testing
Microscopy Techniques



Current Interrupt (CI) Methods

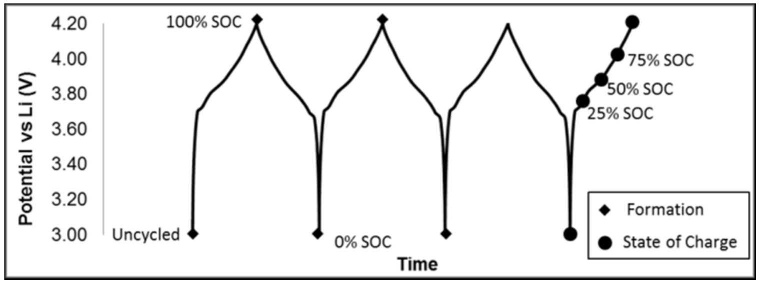


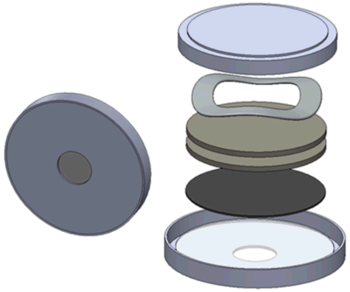
Hypothesis: Chemical mechanisms of degradation in a Li-ion battery dominate capacity loss at low strain rates, whereas, mechanical degradation dominates at high strain rates.

Develop Model to Estimate Lithiation State

Develop Model:
1. Formation Cycle Test (Cycle 1 and 2)
2. State of Charge Test (Cycle 4)

Implement:
3. Long Term Cycle Test (Cycle 10, 20, 40, 80)





Cell Information

$LiCoO_2$/Graphite/1.2 M $LiPF_6$ EC:EMC (3:7 w/w)

C-rate : C/10

Temperature: 25 °C

Disassembled within Argon filled glove box

Raman Analysis Information

System: Witec Alpha 200R

Laser : Nd:YAG at 532 nm

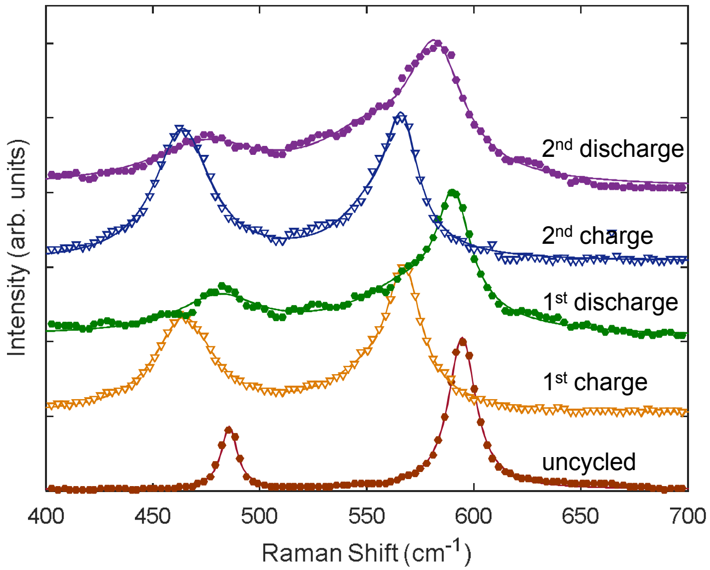
Objective: 50 x , 0.55 NA (600 nm spot size)

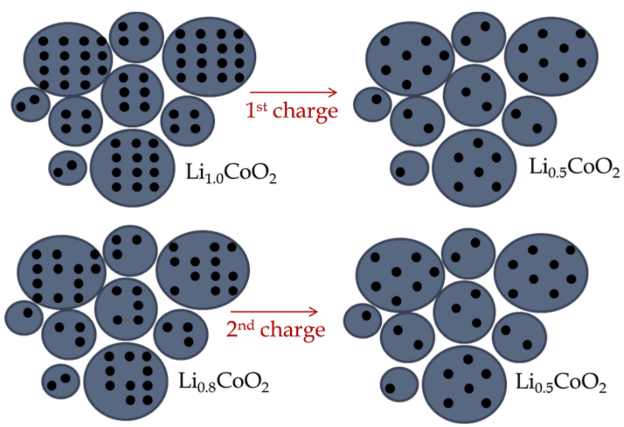
Power : 250 μW

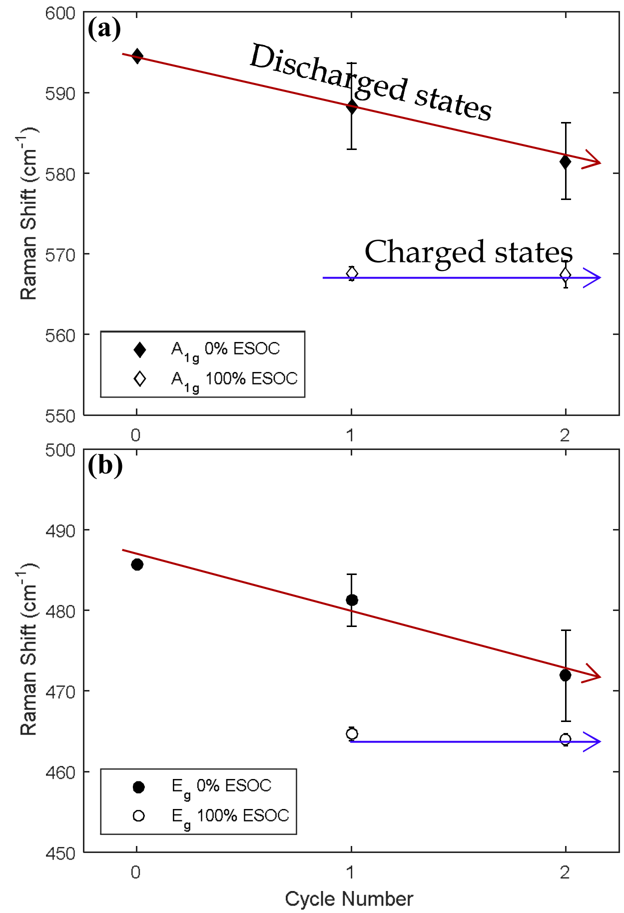
Integration time : 300 s per particle

Snyder et al. *Journal of The Electrochemical Society* (accepted March 2016)

Formation Study







Li_xCoO_2

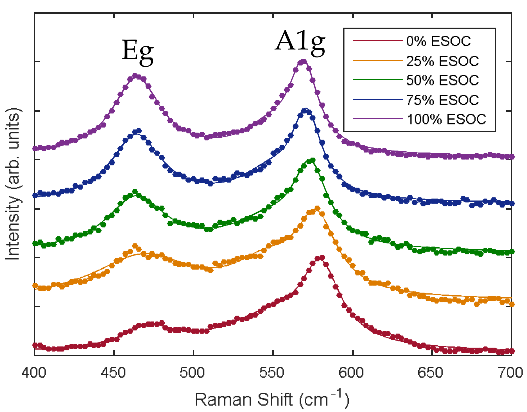
$Li_{0.5}CoO_2$

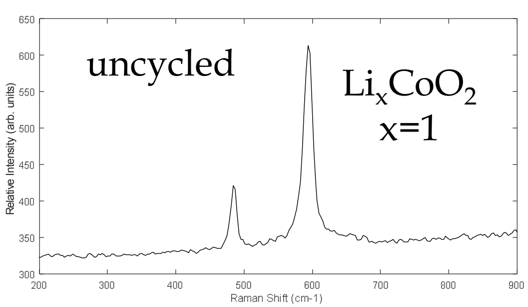
*Each data point represents the averaged peak position from ten particles randomly selected on the electrode

Snyder et al. *Journal of The Electrochemical Society* (accepted March 2016)

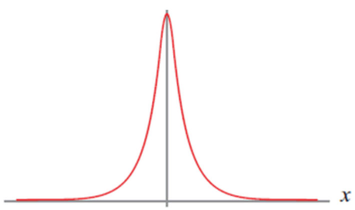
Raman Analysis

SOC Study → Assign x in Li_xCoO_2 → Fit Particle Spectrum → Determine Average State → Validate Model → Compare to Capacity Loss Data





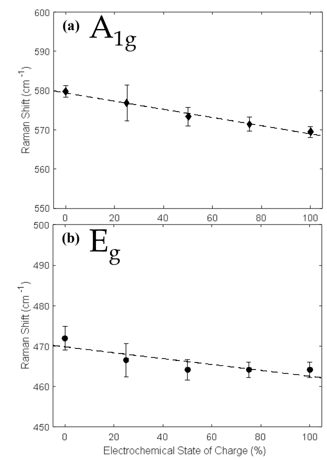
Lorentz Function

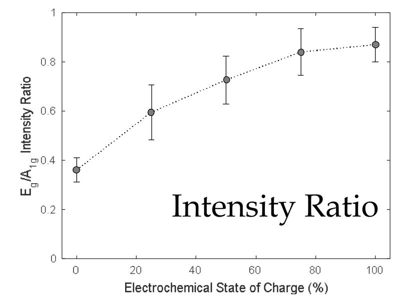


$$L(x) = A * \frac{1}{1 + \frac{(x-p)^2}{w^2}}$$

A ~ Amplitude
w ~ line width
p ~ peak position

Peak positions

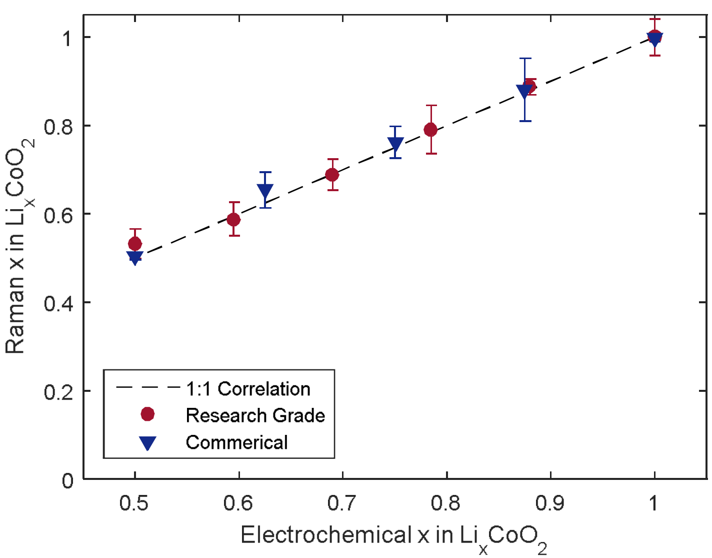




Raman Analysis

SOC Study → Assign x in Li_xCoO_2 → Fit particle Spectrum → Determine Average State → **Validate Model** → Compare to Capacity Loss Data

Raman vs Electrochemical



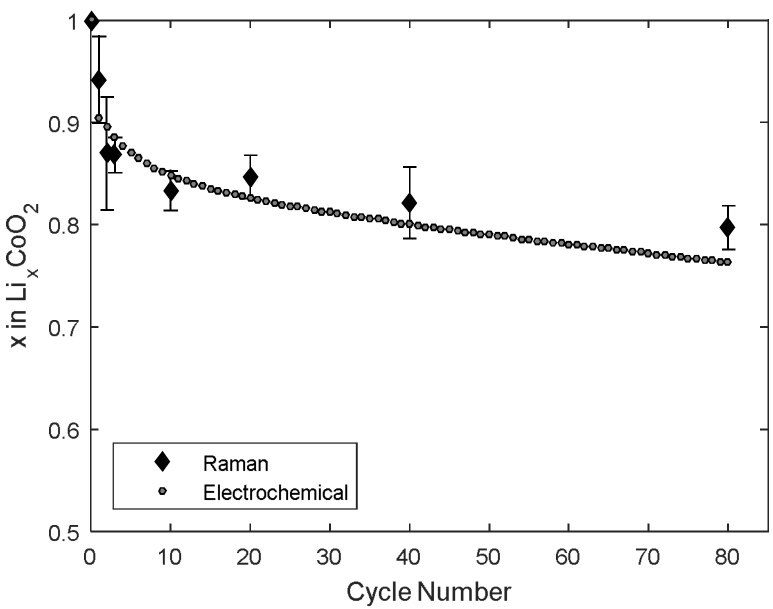
Research Grade
- SOC Samples

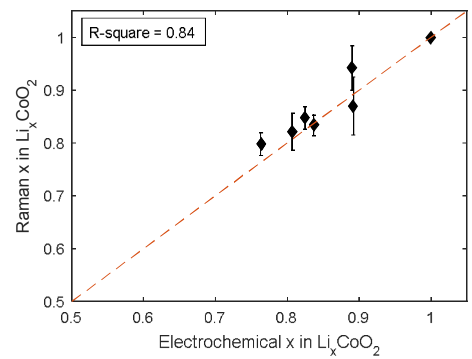
Commercial Electrodes
- Refreshed electrolyte (excess Li^+)

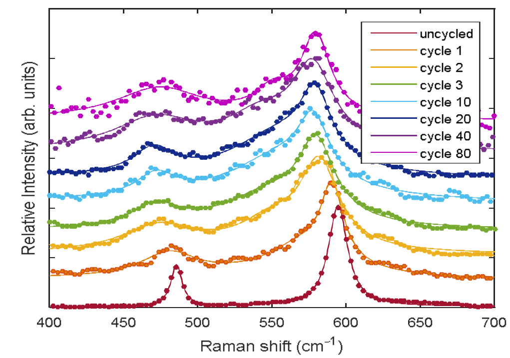
Snyder et al. *Journal of The Electrochemical Society* (accepted March 2016)

Raman Analysis

SOC Study → Assign x in Li_xCoO_2 → Fit particle Spectrum → Determine Average State → Validate Model → Compare to Capacity Loss Data



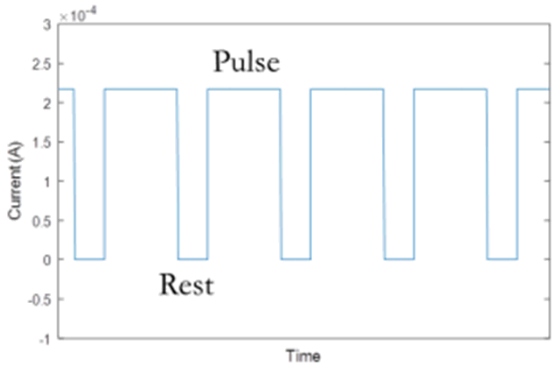


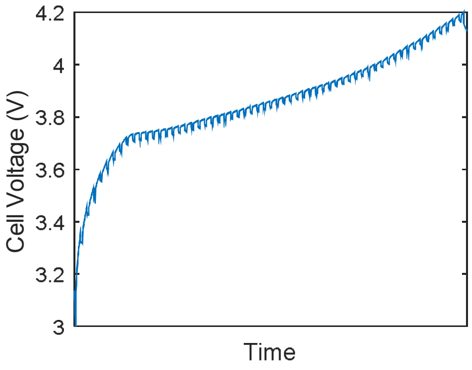


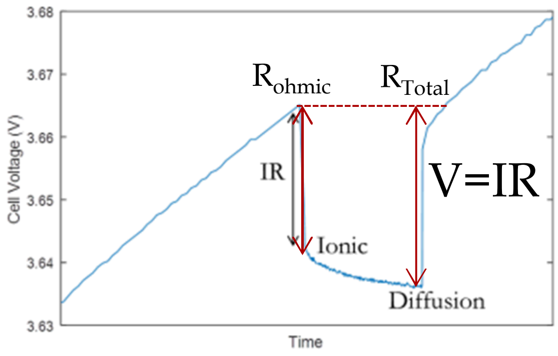
1. Raman microscopy is capable of estimating the lithiation state within individual $LiCoO_2$ particles
2. At these slow rates, Capacity loss is exclusively caused by a loss of cycleable Li+
3. No "inactive" particles of LCO were found on the surface of the electrode
4. All particles were in a relatively homogenous state of lithiation at the slow rates (C/10)

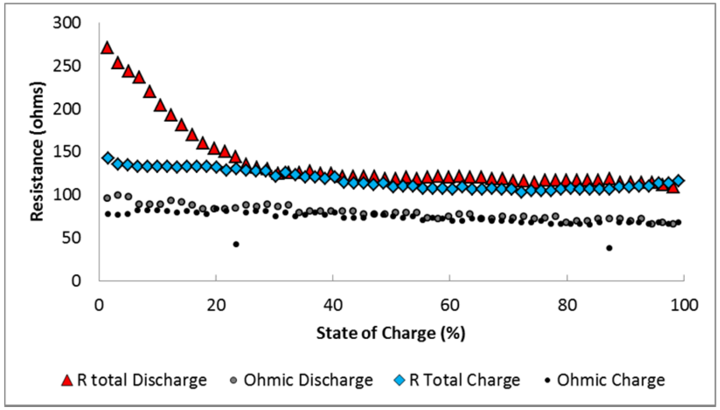
Snyder et al. *Journal of The Electrochemical Society* (accepted)

Current Interrupt Testing





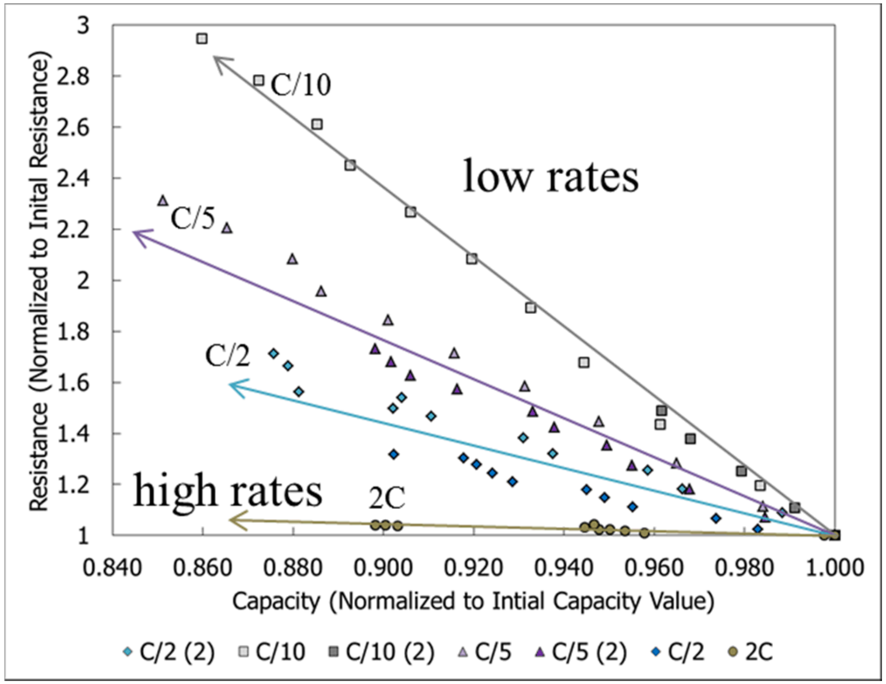


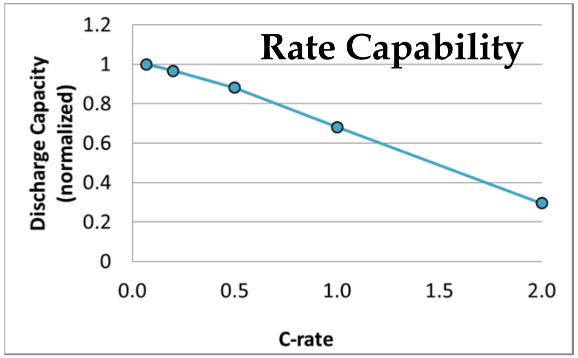


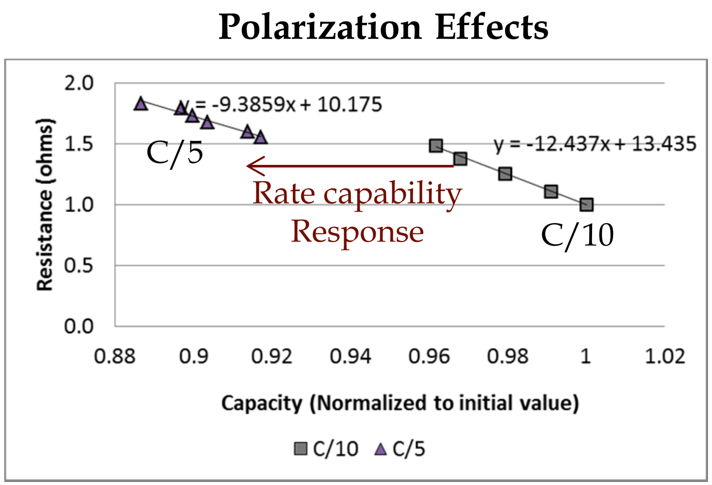
What we looked at

- Ohmic resistance as a function of cycle number and c-rate
- Total resistance as a function of cycle number and c-rate
- Relate to measured capacity loss

Rate Dependency



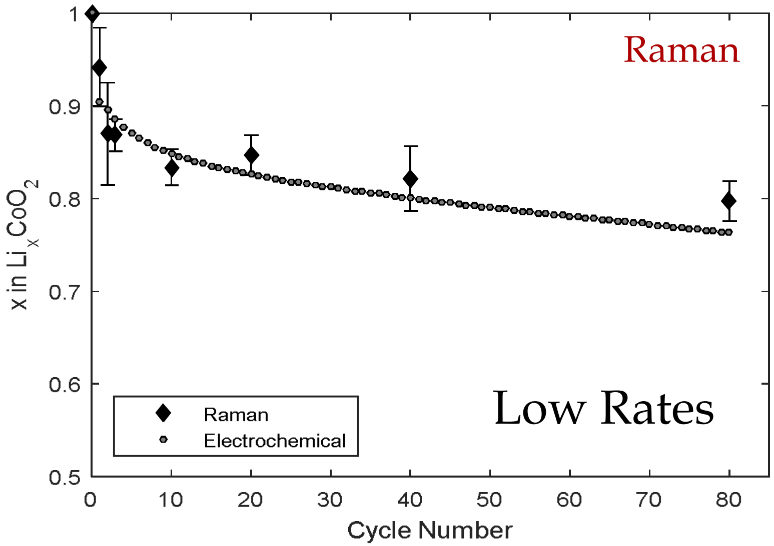




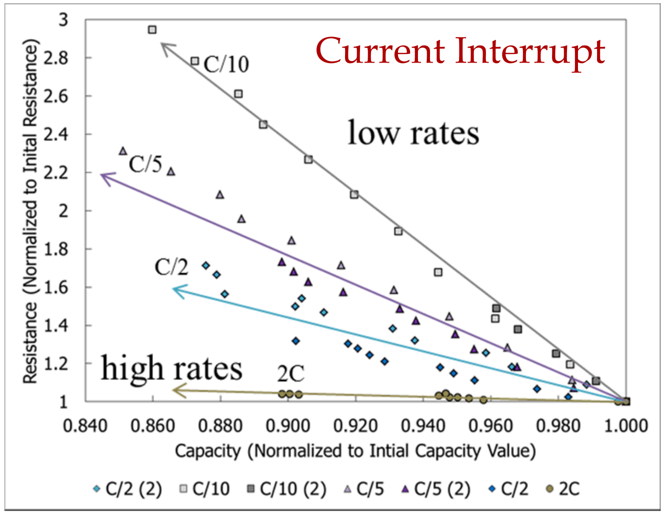
- Under fast rates, mechanical degradation dominates capacity loss - thus results in insignificant changes to resistance. Meanwhile at slow rates, chemical mechanisms dominate which result in increased measured resistance. At moderate rates, a combination of mechanical and chemical mechanisms contribute to capacity fade.
- Considerations: cell to cell variability, rate capability, polarization effects, and repeatability
- Testing for physical evidence is underway (thickening of SEI, fracture of particles, etc.)

Thesis Statement

- Chemical mechanisms of degradation in a Li-ion battery dominate capacity loss at low strain rates, whereas, mechanical degradation dominates at high strain rates.



Loss of Li^+ inventory due to SEI thickening and other side reactions is the primary mechanism responsible for capacity fade.



At low rates an increased cell impedance is responsible a larger portion of capacity loss compared to at high rates where other mechanisms begin to dominate.

Acknowledgements

- Dr. Christopher Apblett and Dr. Anne Grillet for project mentorship
- Professor Duquette for project oversight and advisement

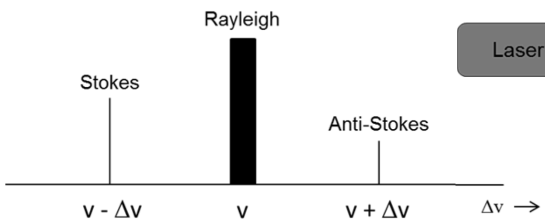
Other Contributors: Dr. Thomas Beechem, Anthony McDonald, Dr. Scott Roberts, Dr. Farid El Gabaly, Dr. Kyle Fenton, Dr. Mani Nagasubramanian, Dr. Brian Perdue, Jon Coleman, Lorie Davis, Bonnie McKenzie

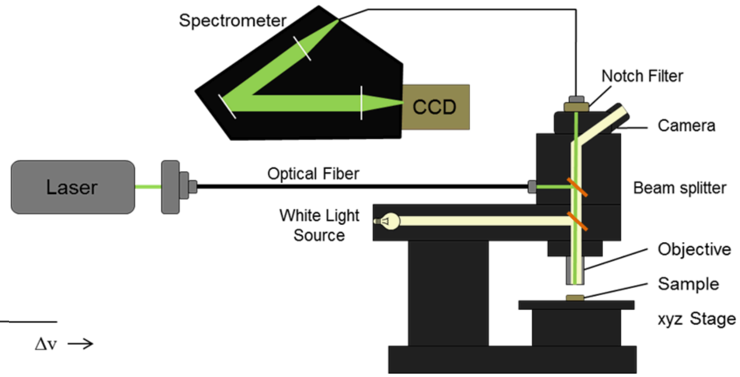
Related Technical Talks/Publications

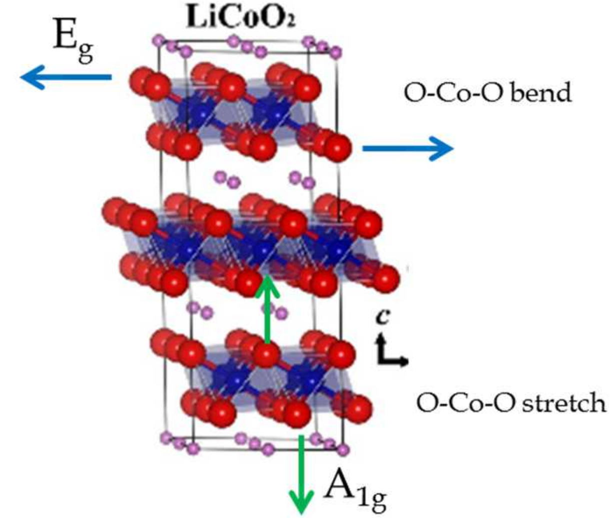
- "Measuring Li^+ Inventory Losses in $LiCoO_2$/Graphite Cells using Raman Microscopy". Chelsea Snyder, Christopher Apblett, Thomas Beechem, Anne Grillet, David Duquette, Journal of The Electrochemical Society (accepted March 2016).
- "Measuring Li^+ Inventory Losses in $LiCoO_2$/C Cells Using Ex-Situ Raman Spectroscopy", Chelsea Snyder, Christopher Apblett, Anne Grillet, Thomas Beechem, David Duquette, 229th Electrochemical Society Meeting, San Diego, CA, May 29– June 3, 2016.
- "Steps Towards In-Situ Studies of the Mechanical Degradation of Lithium Ion Batteries using Fluorescence Confocal Microscopy", Chelsea Snyder, Christopher Apblett, David Duquette, Anne Grillet, 227th Electrochemical Society Meeting, Chicago, IL May 24-28, 2015.

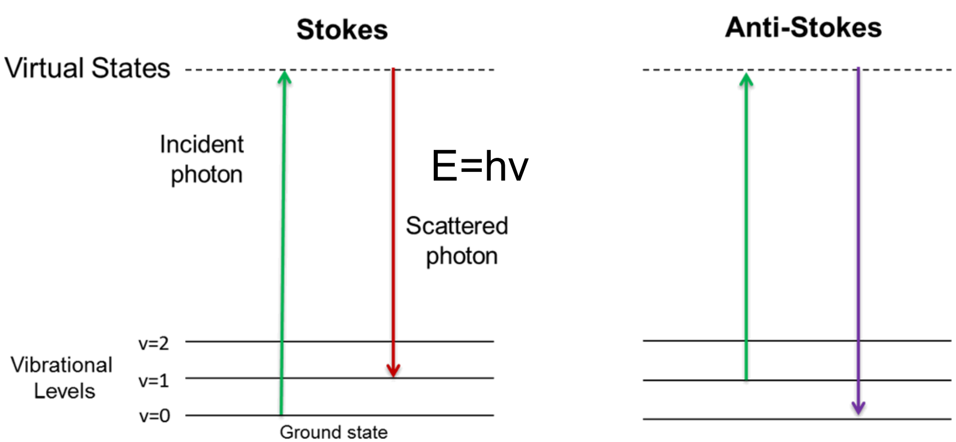
Back up slides

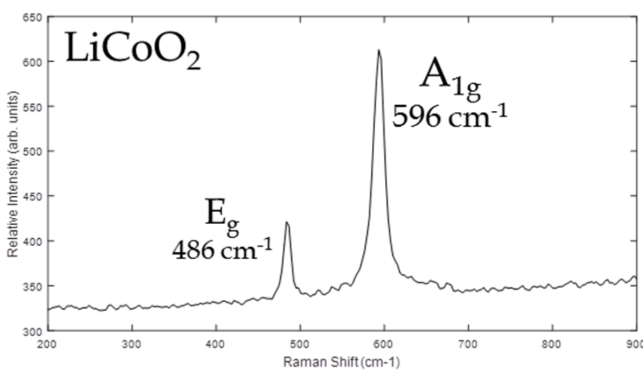
Raman Spectroscopy







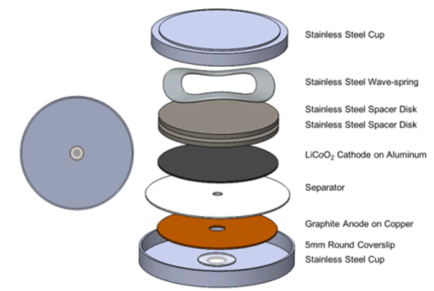


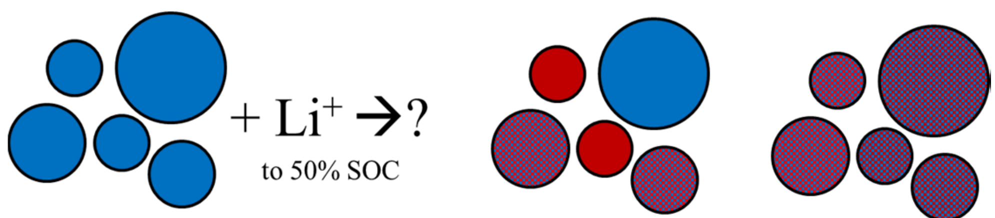


Upcoming Raman work

- Loss of Li^+ Inventory in Commercial Cell (1C for 500+ cycles)
- In-situ studies
  - Kinetic limitations at accelerated c-rates
  - Electrode SOC homogeneity

In-situ Cell

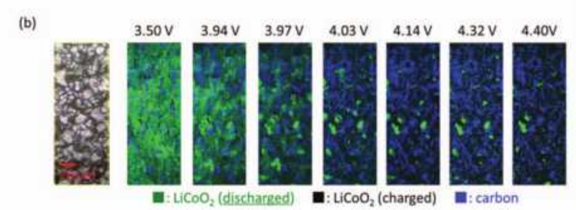




1C

C/10

Non-uniform charge/discharge
Inhomogeneous SOC distribution

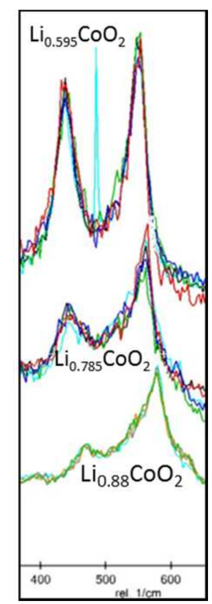


Nishi et al. *Journal of the Electrochemical Society* 160 (2013) A1785-A1788

Uniform charge/discharge
Homogenous SOC distribution

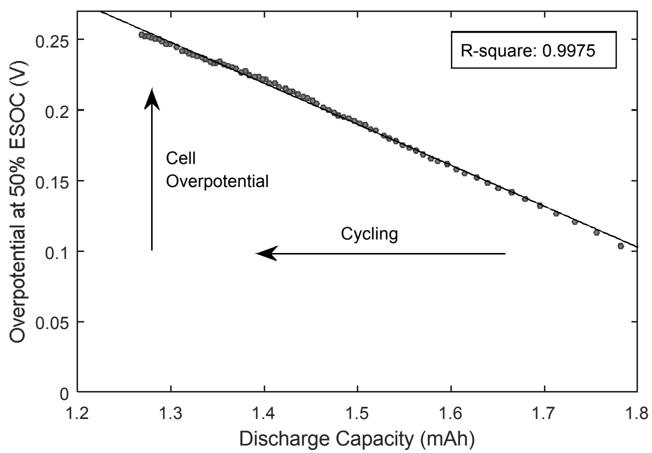
Snyder et al. *Journal of the Electrochemical Society* (submitted)

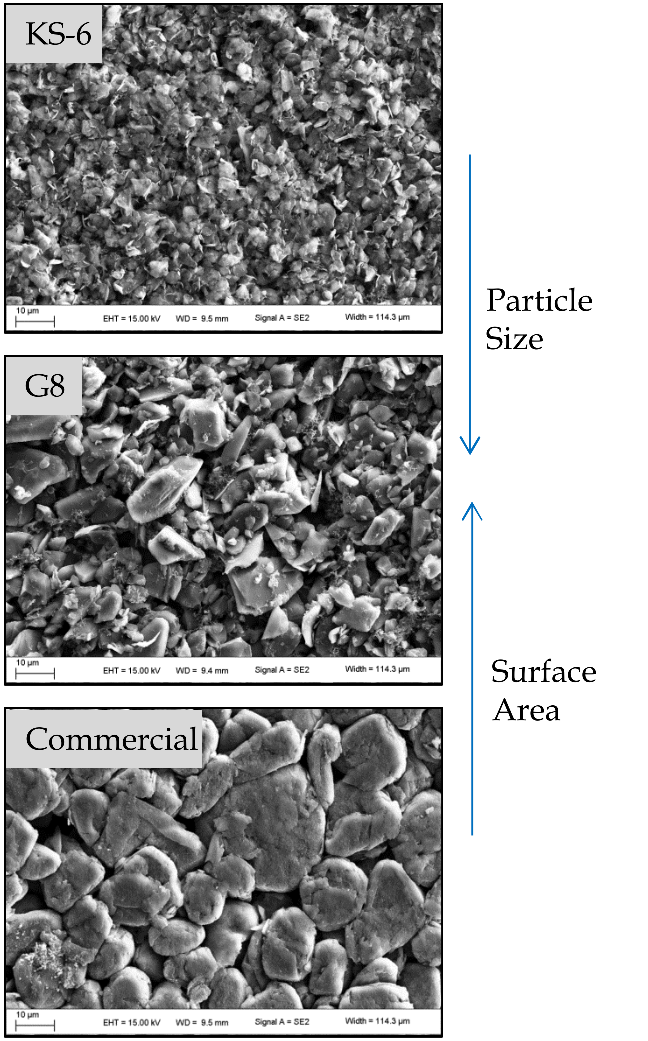
Raw Raman Data



Accelerated Loss of Li^+ Inventory

- No Electrolyte Additives to form more stable SEI
  - Unstable SEI = more cracks/reforming and consumption of Li^+
- High surface area Graphite anodes (using KS-6) compared to commercial anodes
  - High surface area = more SEI growth more initial consumption of Li and more SEI area
- Will use G8 anodes (graphite optimized for anode use) in future testing

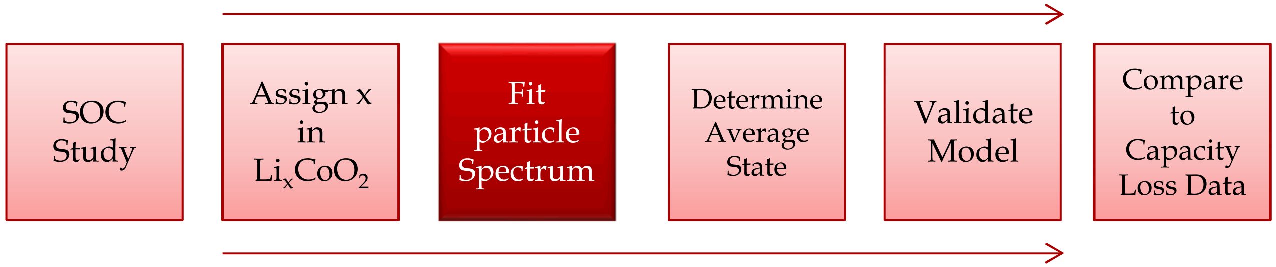




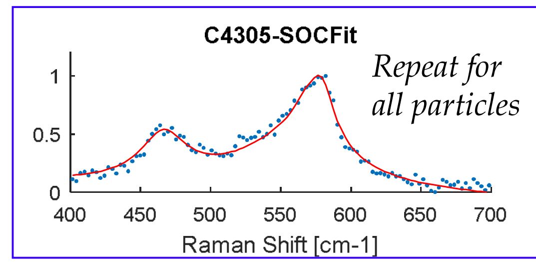
Snyder et al. *Journal of The Electrochemical Society* (submitted)

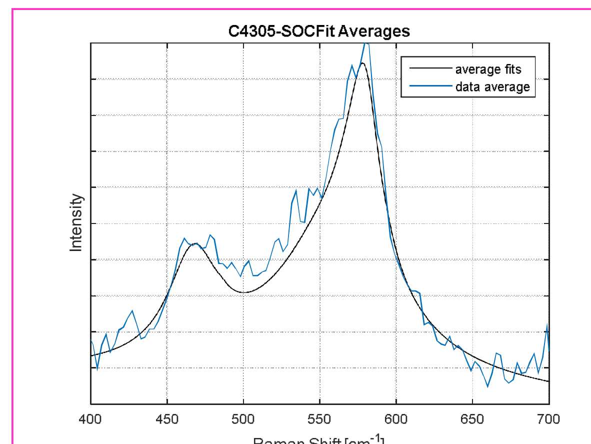
LG ICR18650C2

Raman Analysis



1. Preprocessing
   - Exclude data outside 400-700 cm^{-1}
   - Linear Background Removal
   - Cosmic Ray Removal
   - Normalize Intensity
2. Fit to Linear Combination of SOC spectra - use weights in peak regions to maximize fit
3. Compare Average Fit to Average Data – ensure fits represent the data well
4. Export coefficients and R^2 fit value

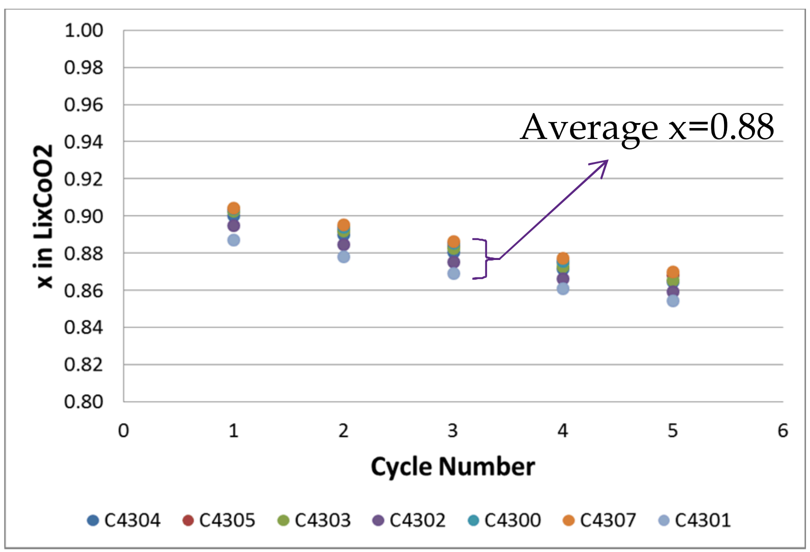




Raman Analysis

SOC Study → Assign x in Li_xCoO_2 → Fit particle Spectrum → Determine Average State → Validate Model → Compare to Capacity Loss Data

Discharge Capacity Normalized to Theoretical Capacity



Assignment of lithiation state

ESOC (%)	x in Li_xCoO_2	PSOC (%)
0	0.88	24
25	0.785	43
50	0.69	62
75	0.595	81
100	0.5	100

Raman Analysis

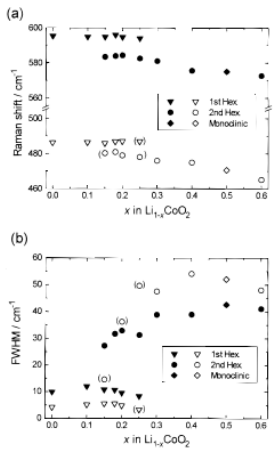
SOC Study → Assign x in Li_xCoO_2 → Fit particle Spectrum → **Determine Average State** → Validate Model → Compare to Capacity Loss Data

Example Fit Output

Particle	x=1	x=0.88	x=0.785	x=0.69	x=0.595	x=0.5	Net State, x
1	0	0.5	0.5	0	0	0	0.83
2	0	0.6	0.4	0	0	0	0.84
3	0	0.4	0.6	0	0	0	0.82
4	0.2	0.8	0	0	0	0	0.90
5	0	0.8	0.2	0	0	0	0.86
6	0	0.1	0.8	0.1	0	0	0.79
7	0	0.7	0.3	0	0	0	0.85
8	0	0.9	0.1	0	0	0	0.87
9	0	0.8	0.1	0.1	0	0	0.85
10	0	0.8	0.2	0	0	0	0.86

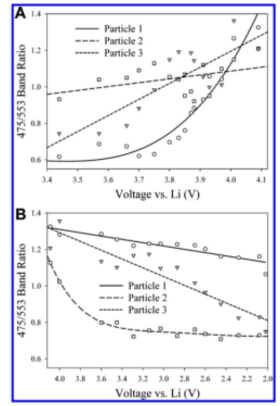
Average Lithiation State:
$x=0.8482 \pm 0.0314$

Raman Spectroscopy



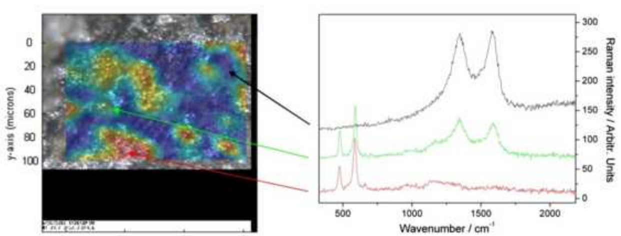
Inaba et al. *Journal of Raman Spectroscopy* 28 (1997) 613-617

- First report on Raman of $LiCoO_2$ throughout deintercalation
- Li Half Cell



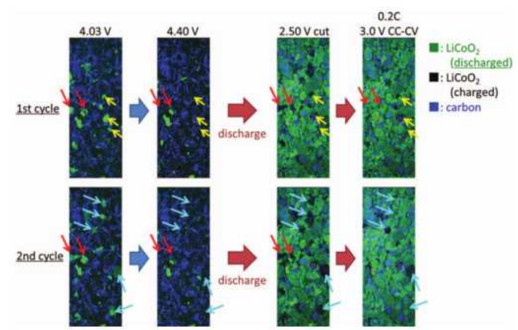
Lei et al. *J. Phys. Chem. B 109* (2005) 952-957

- In-situ monitor of SOC of individual $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ particles
- In-situ
- Half Cell (C/5)



Gross and Hess *Journal of Power Sources 256* (2014) 220-225

- Compositional mapping of $LiCoO_2$ cathode – binder and active material

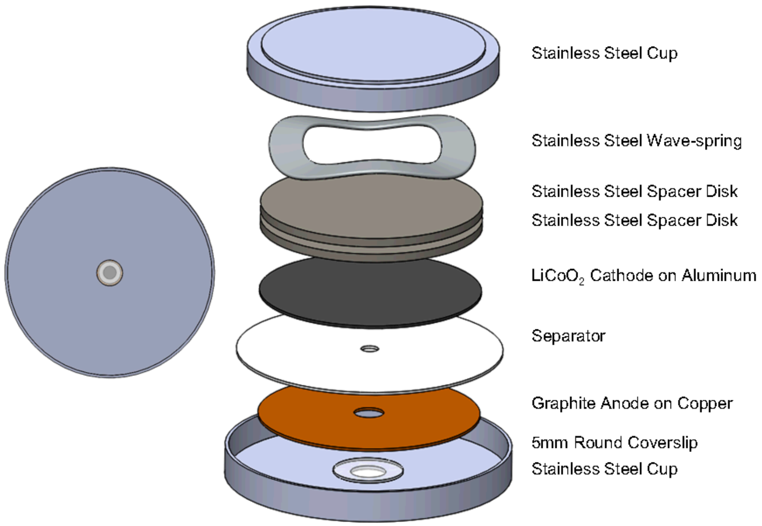


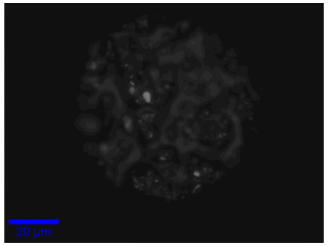
Nishi et al. *Journal of The Electrochemical Society* 160 (2013) A1785-A1788

- LiCoO2/Li Half Cell (1C)
- In-situ Analysis
- Electrode mapping
- Inhomogeneous SOC distribution

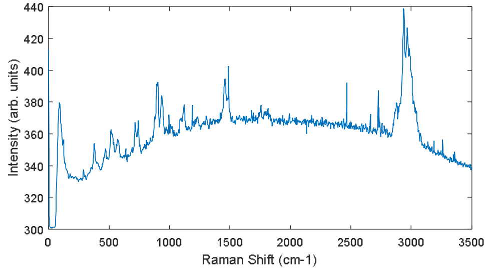
Backup

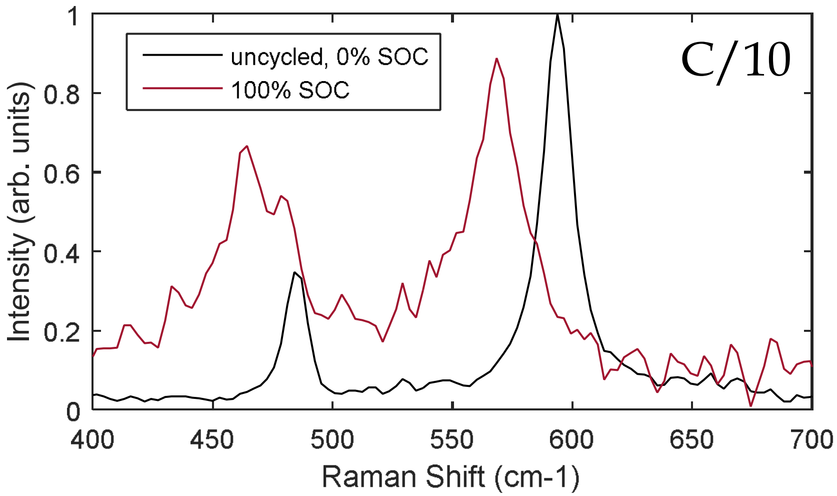
In-situ Raman Analysis



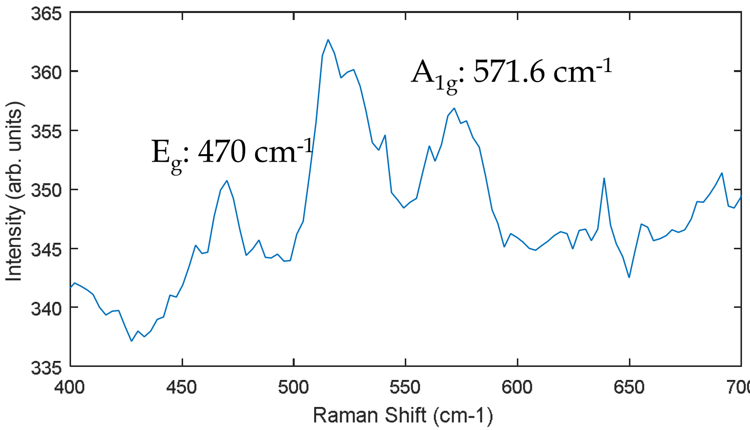


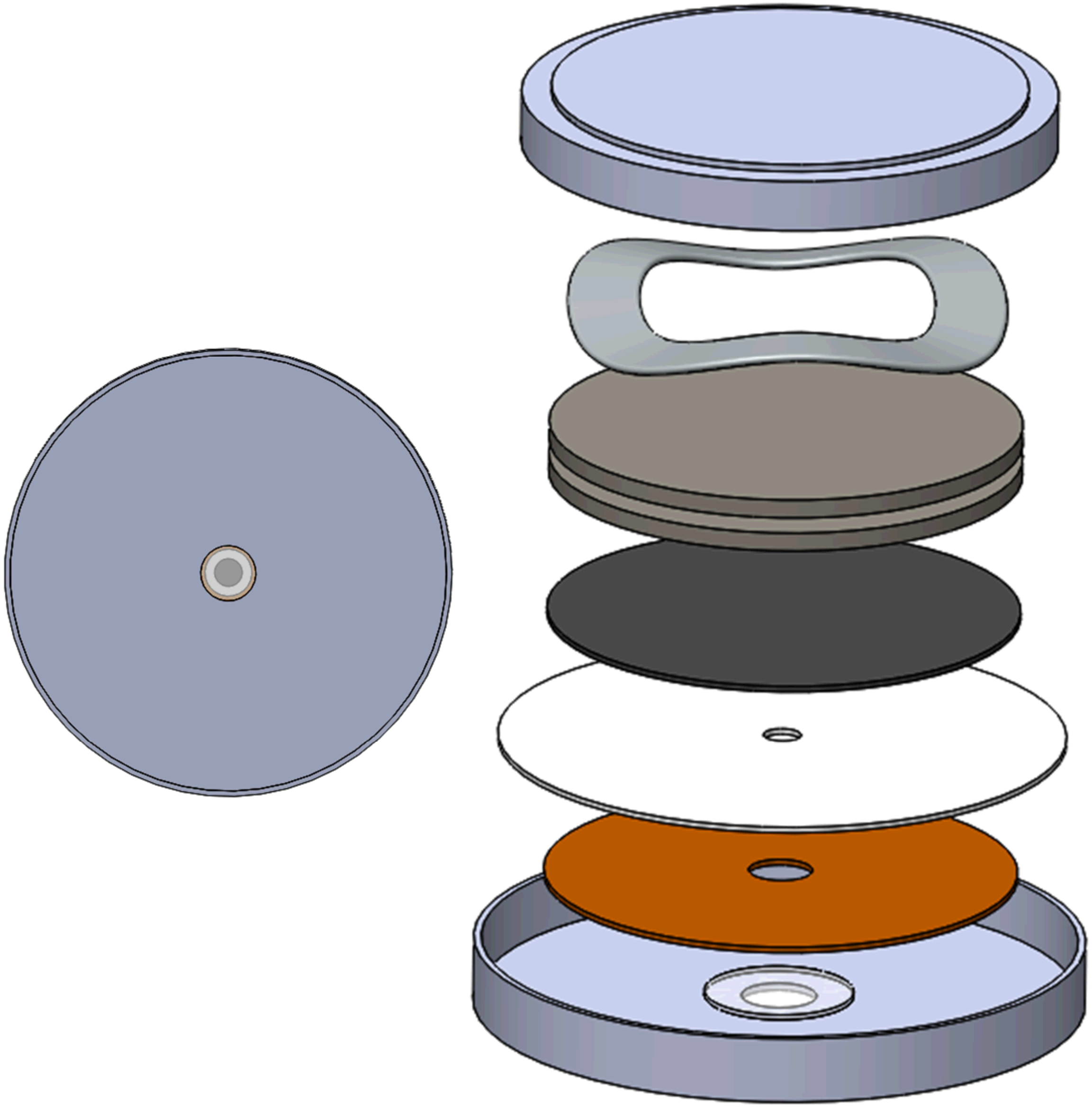
Electrolyte Peaks



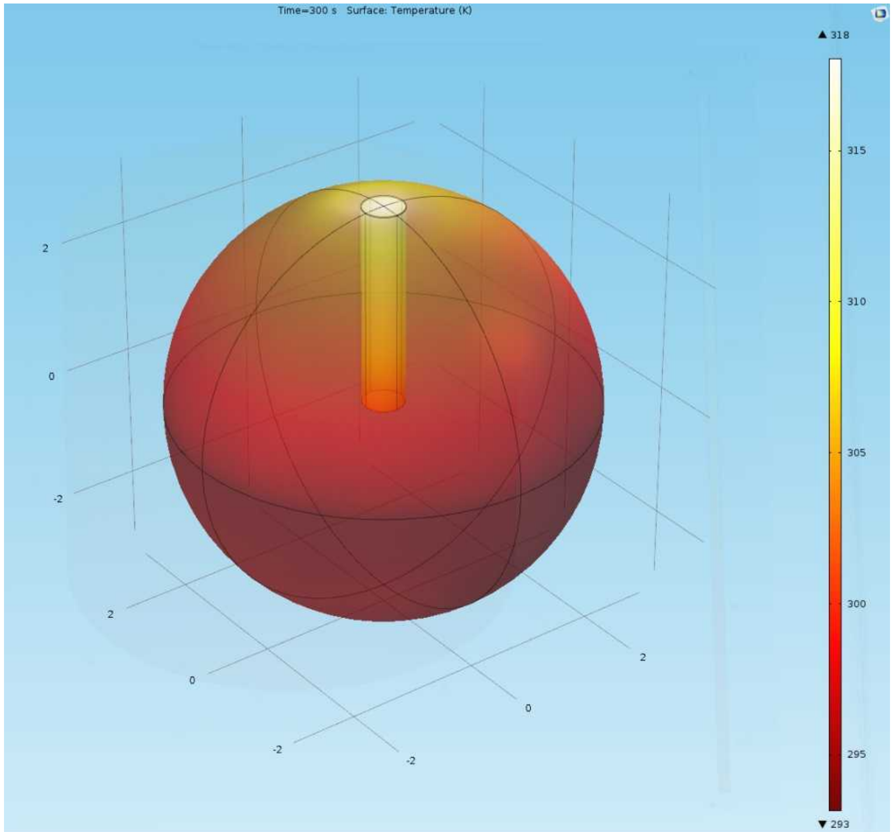


75% SOC




Stainless Steel Cup
Stainless Steel Wave-spring
Stainless Steel Spacer Disk
Stainless Steel Spacer Disk
$LiCoO_2$ Cathode on Aluminum
Separator
Graphite Anode on Copper
5mm Round Coverslip
Stainless Steel Cup

Raman – Laser heating of $LiCoO_2$ Particles



Depth of laser : 3 um (uniform heat generated)
Laser spot = 600 nm
Laser Power = 0.25 mW
Total Time =300 s

Particle size: 6um diameter
Bottom half surface kept at 293.14 K (“conductive”)
Insulated on top half (“air”)

Max temperature = 318 K = 44.85^{o}C
Max increase in temperature = 25^{o}C

Study 1, Time Dependent

$$(\rho C_p)_{\text{eff}} \frac{\partial T}{\partial t} + \rho C_p \mathbf{u} \cdot \nabla T = \nabla \cdot (k_{\text{eff}} \nabla T) + Q + Q_{\text{vd}} + Q_p$$

$$(\rho C_p)_{\text{eff}} = \theta_{\text{p}} \rho_{\text{p}} C_{p,\text{p}} + (1 - \theta_{\text{p}}) \rho C_p$$

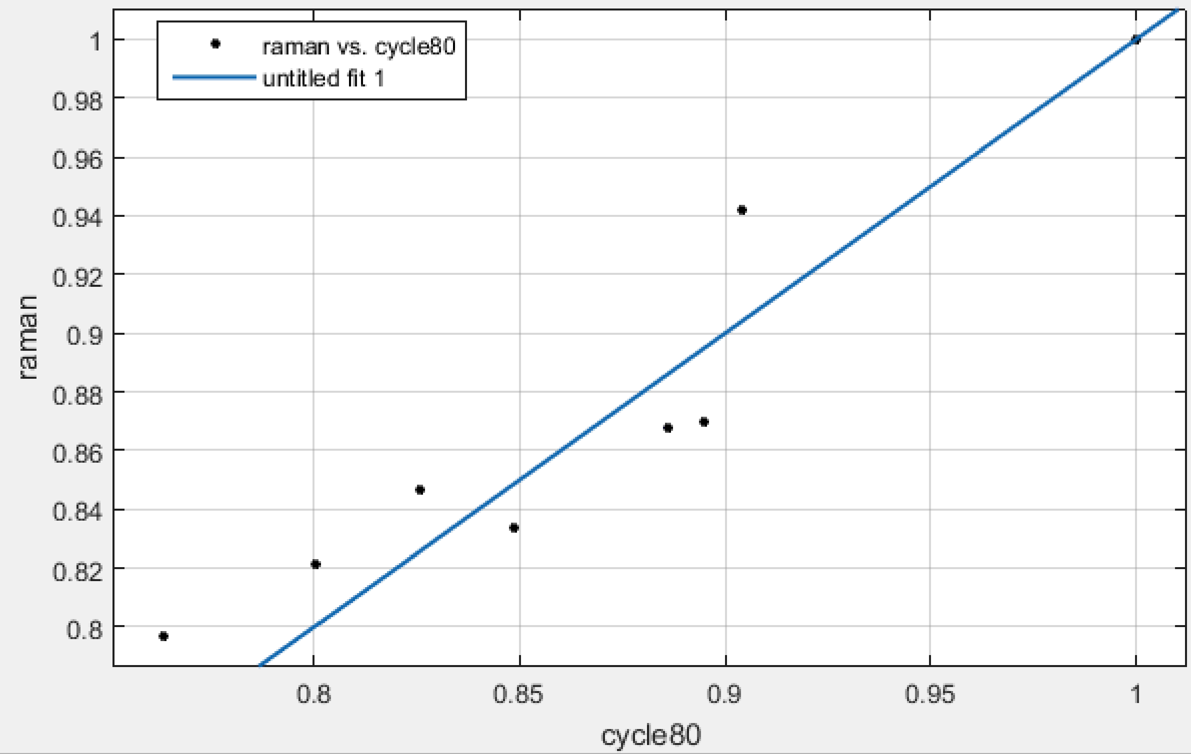
$$k_{\text{eff}} = \theta_{\text{p}} k_{\text{p}} + (1 - \theta_{\text{p}}) k$$

Density of LCO = 5.05 g/cc
Heat capacity: 71.62 J/molK
Thermal Conductivity: 2.165 W/mK

Results

General model:
f(x) = x+c
Coefficients (with 95% confidence bounds):
c = 0 (fixed at bound)

Goodness of fit:
SSE: 0.004646
R-square: 0.8523
Adjusted R-square: 0.8708
RMSE: 0.0241



The fit explains 85.23% of the total variation in the data about the average

Raman Spectroscopy

- Molecules have vibrational modes dependent on: orientation, atomic mass, bond order
- Change in polarizability (size, shape, or orientation of the electron cloud that surrounds the molecules)
  - Occurs in symmetric stretching but not asymmetric stretching
- Visible right – molecules absorb and re-emit (some is absorbed by the molecular vibrations – re-emit at new frequency)
- Inelastic scattering

Tools

- Electrochemical Techniques
  - Current Interrupt
    - Gain insight to the cell resistance – electronic, ionic, and diffusional response
  - Discharge Current testing
    - Vary the discharge current to look at rate capability of the cell
    - How does it evolve over cycling? As a function of different c-rate aging?
- Spectroscopic Techniques
  - Raman
    - Probe individual $LiCoO_2$ particles both in-situ and ex-situ
    - Look at structural changes → Lithiation state (State of Charge)
- Microscopy Techniques
  - SEM
    - Look at mechanical damage to particles after various rate cycling