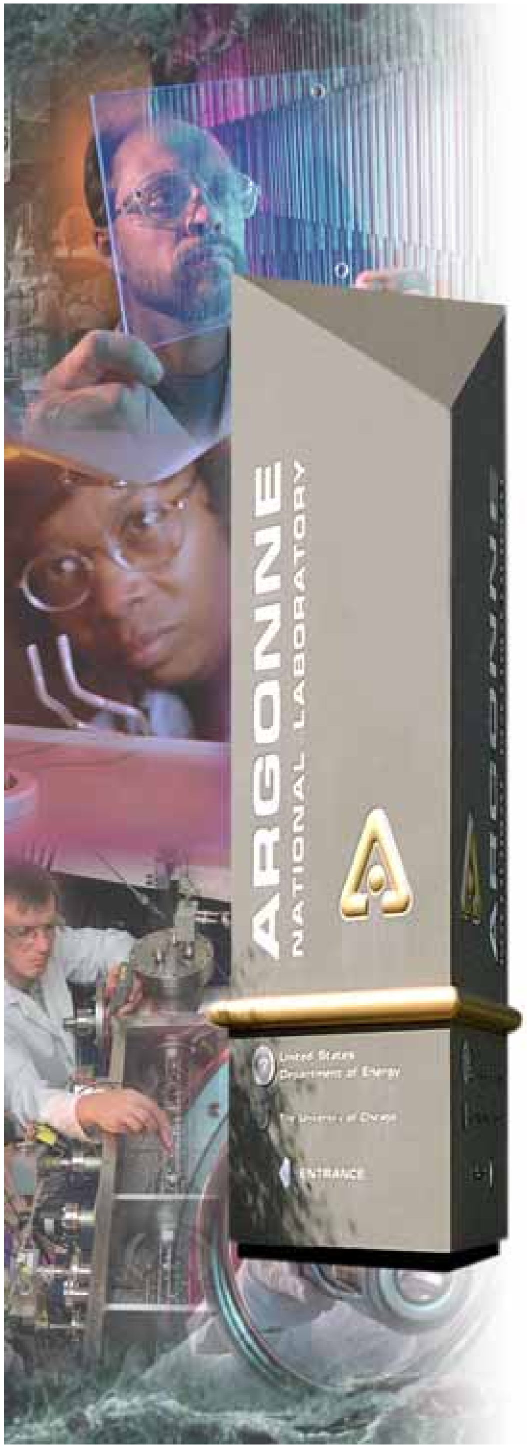


Determining Factors that Affect the Aging Behavior of High-Power Lithium-Ion Cells

Daniel Abraham

Y. Hyung, A. Jansen, I. Bloom, D. Dees, G. Henriksen

Argonne National Laboratory

Office of Science
U.S. Department of Energy

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago

ATD Program

- **Objective**
  - Assist developers of high-power Li-Ion batteries to overcome cost, life, abuse tolerance, and low-temperature performance barriers

- **Multi-laboratory effort**

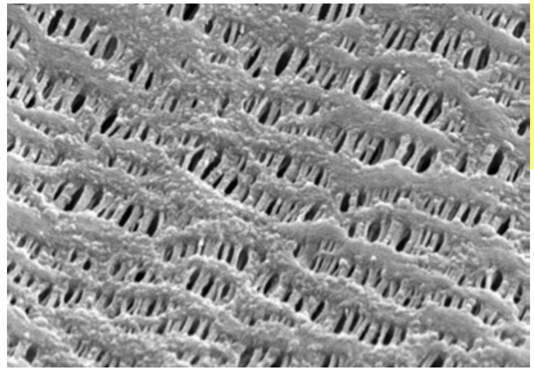
Objectives of the diagnostic studies

- Develop diagnostic tools to study cell degradation mechanisms

- Determine causes that limit the calendar life of Gen 2 lithium-ion cells

- Suggest and/or implement solutions to improve life of high-power lithium-ion cells

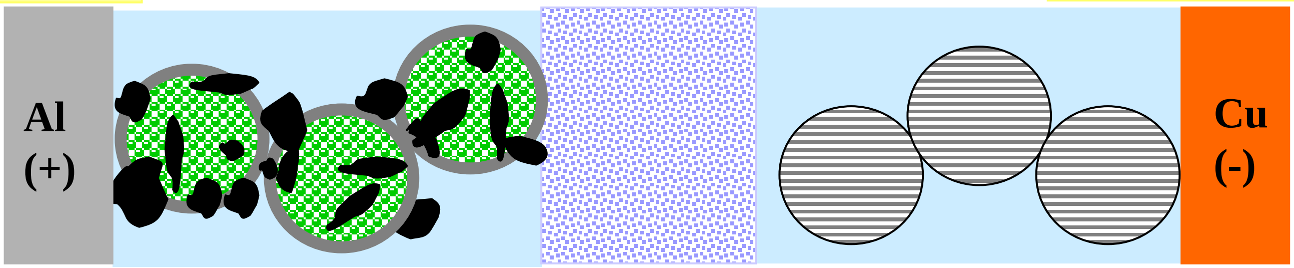
Cell Chemistry

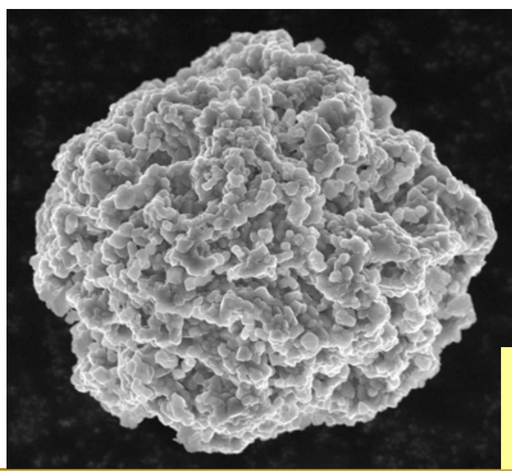


Celgard 2325 separator
PE/PP/PE trilayer
25 µm thk, 40% porosity

Cathode
35µm thk coating

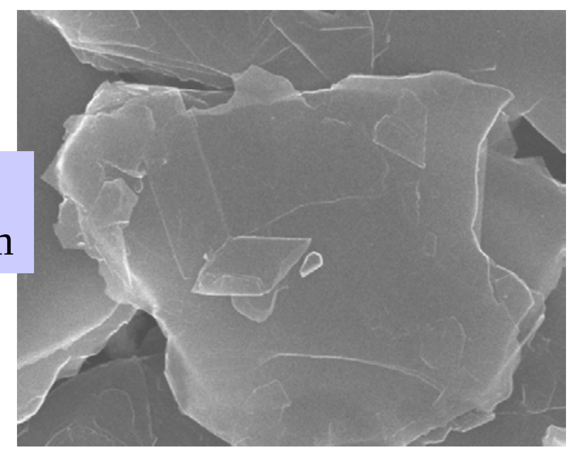
Anode
35µm thk coating





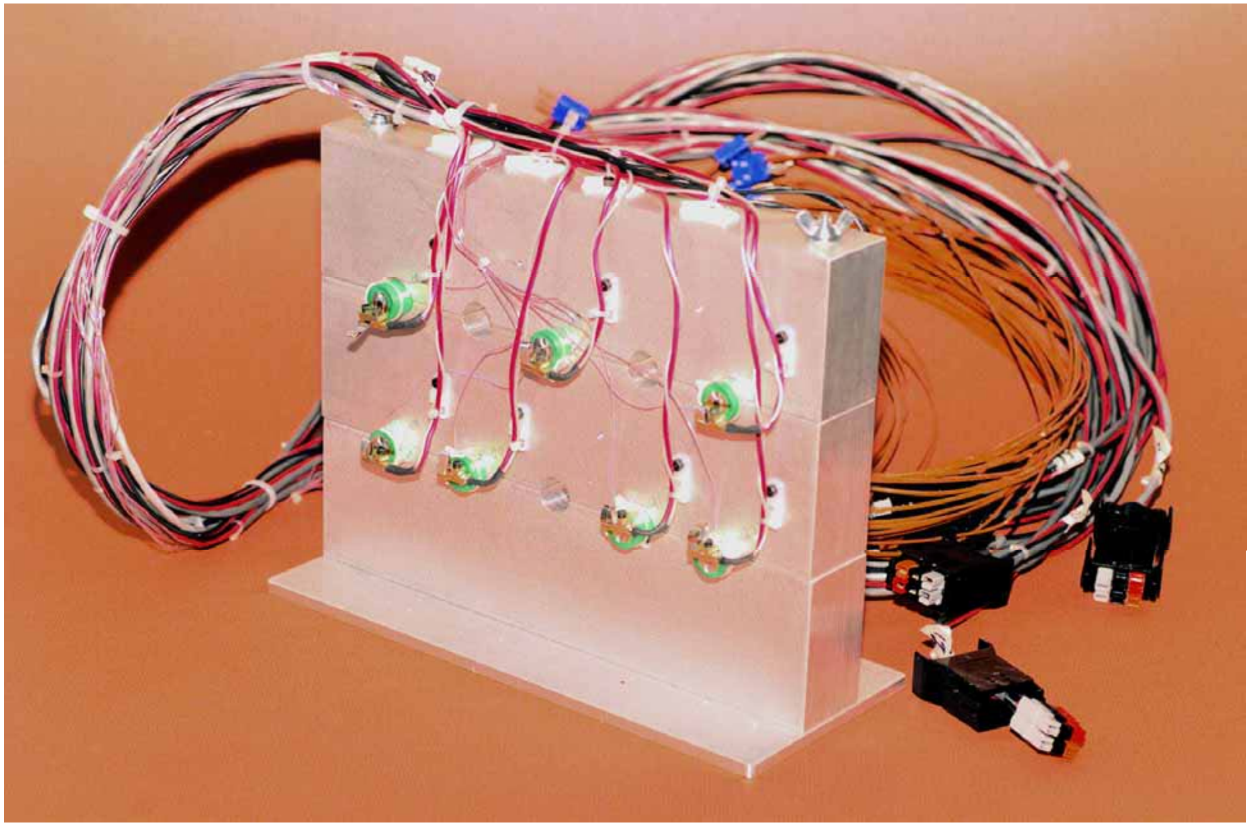
EC-EMC-1.2M $LiPF_6$ Electrolyte

Mag-10 graphite
Particle size ~5 µm



$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Particle size ~ 5 µm

Accelerated aging conducted on 1Ah cylindrical cells



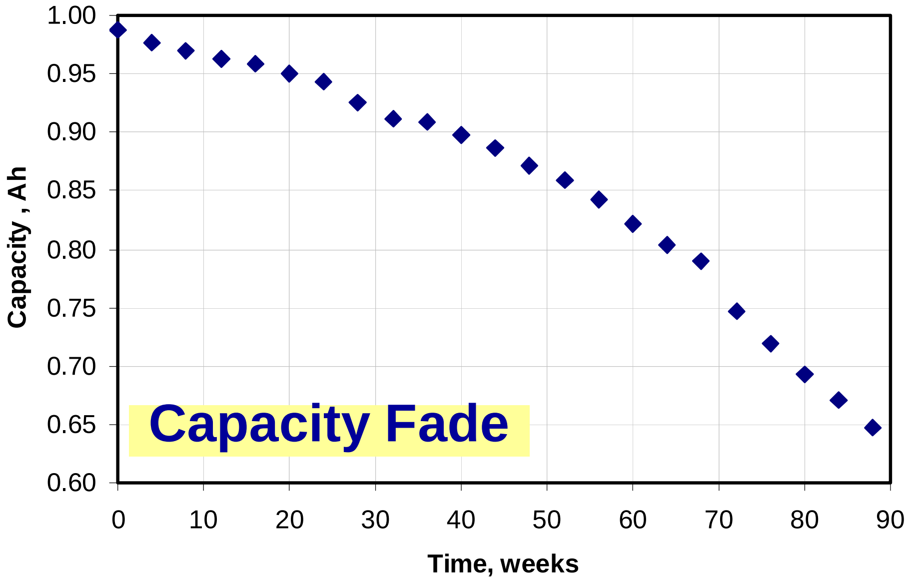
Calendar life aging: Cells stored in an elevated temperature oven
Cycle life aging: Cells cycled at elevated temperature

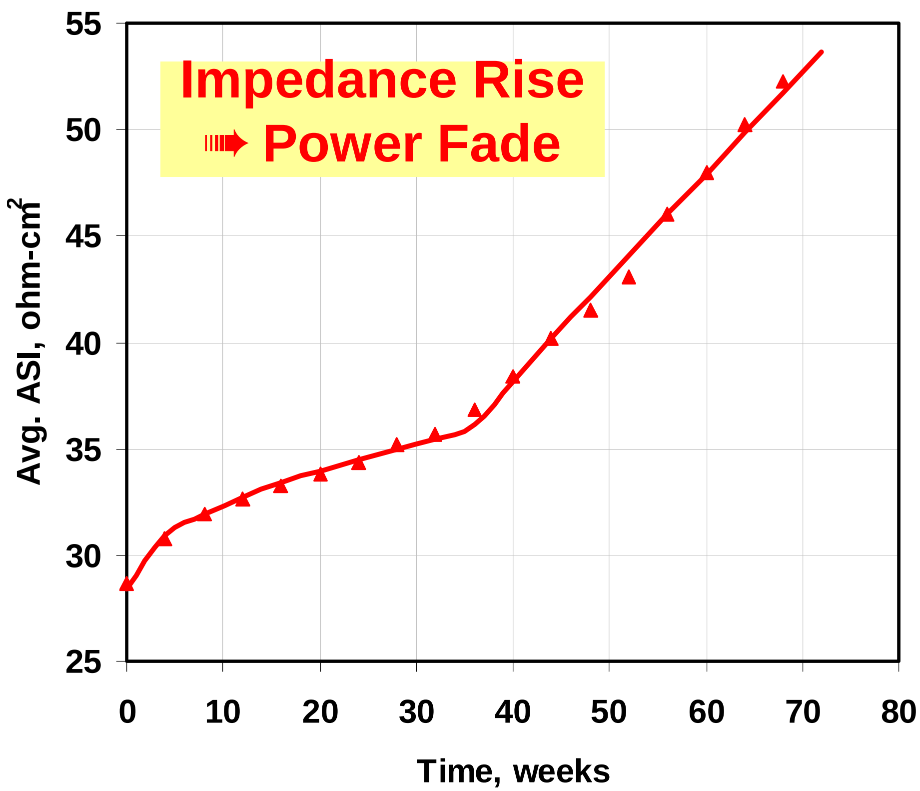
Cells properties (capacity and impedance) measured periodically

On aging, cells lose capacity and power

- Data from 1Ah cells

45°C data

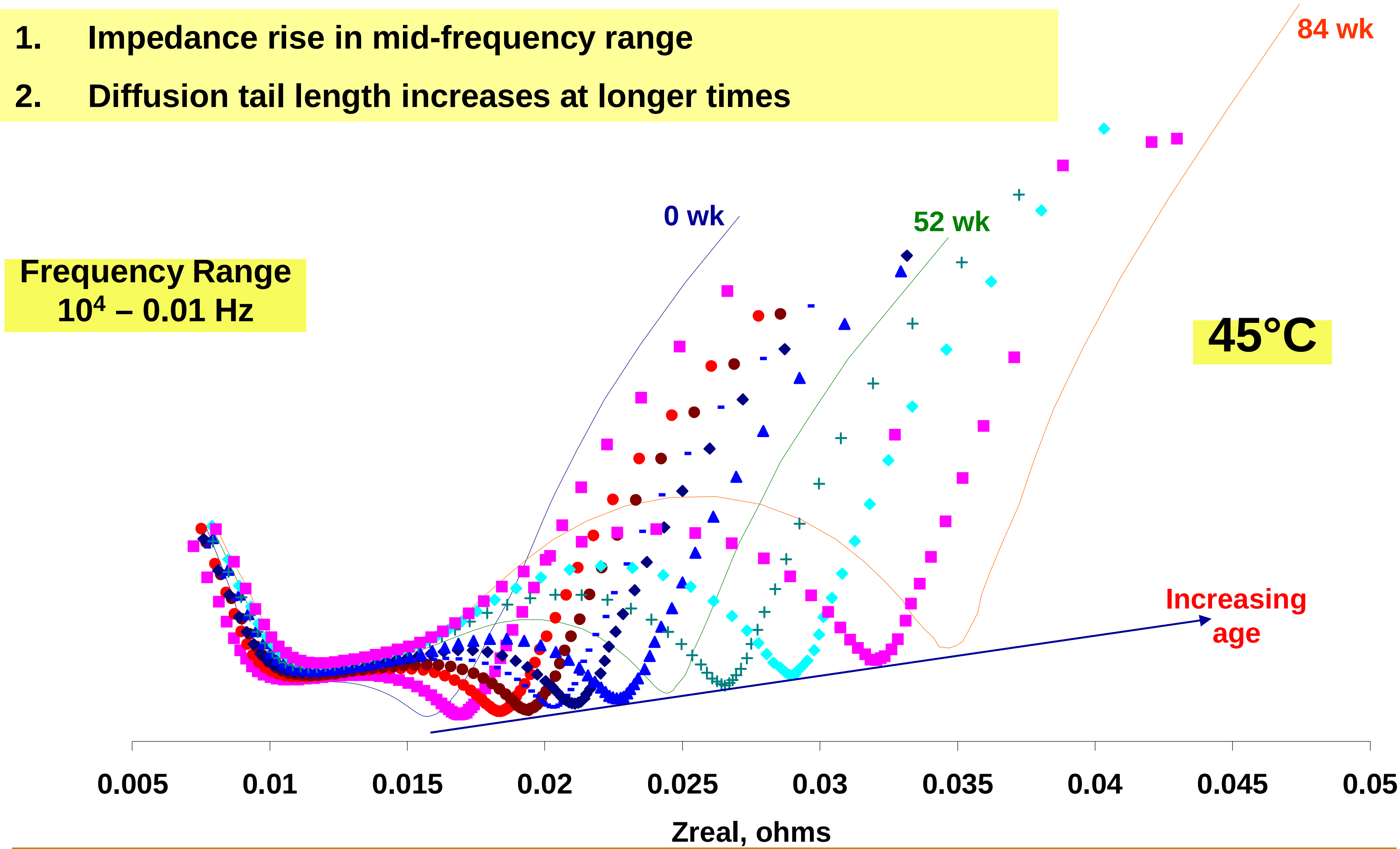




Cell property degradation shows time, temperature, state-of-charge, cycling and chemistry dependence

AC impedance data provides important clues on cell behavior during aging

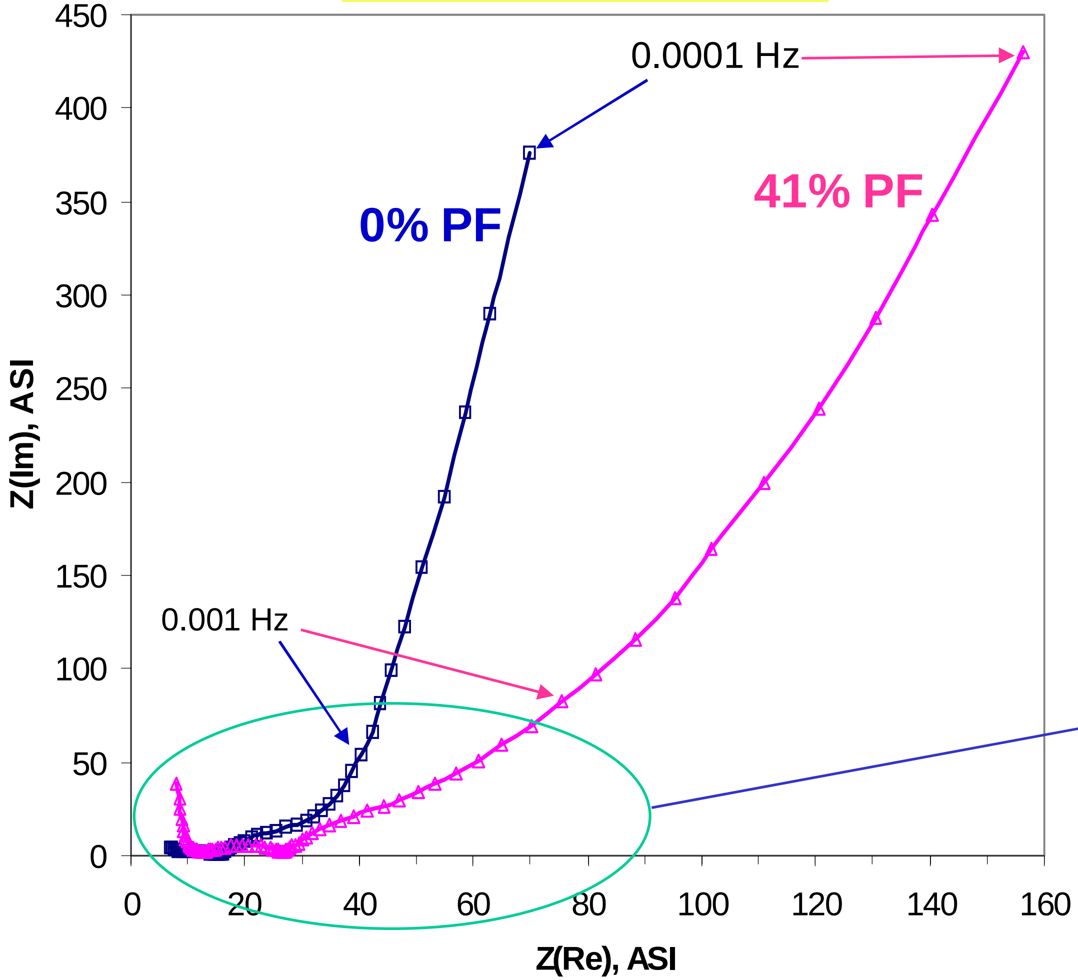
1. **Impedance rise in mid-frequency range**
2. **Diffusion tail length increases at longer times**



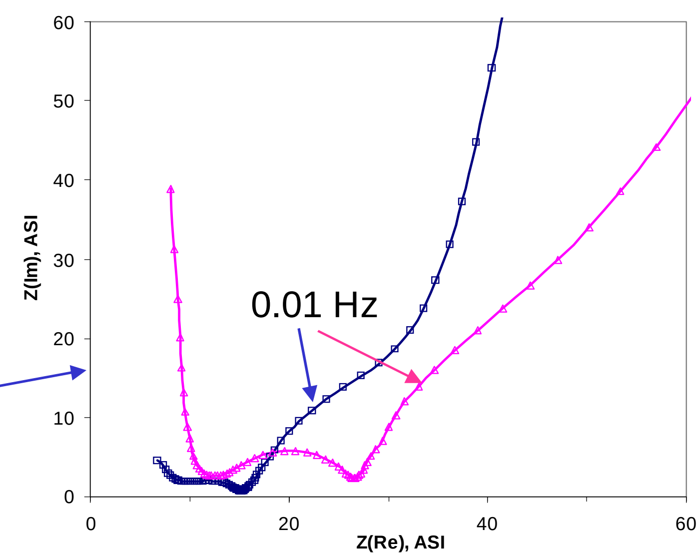
Very low-frequency portions of 18650-cell EIS data reveal significant differences after aging

Frequency Range
10^4 – 0.0001 Hz

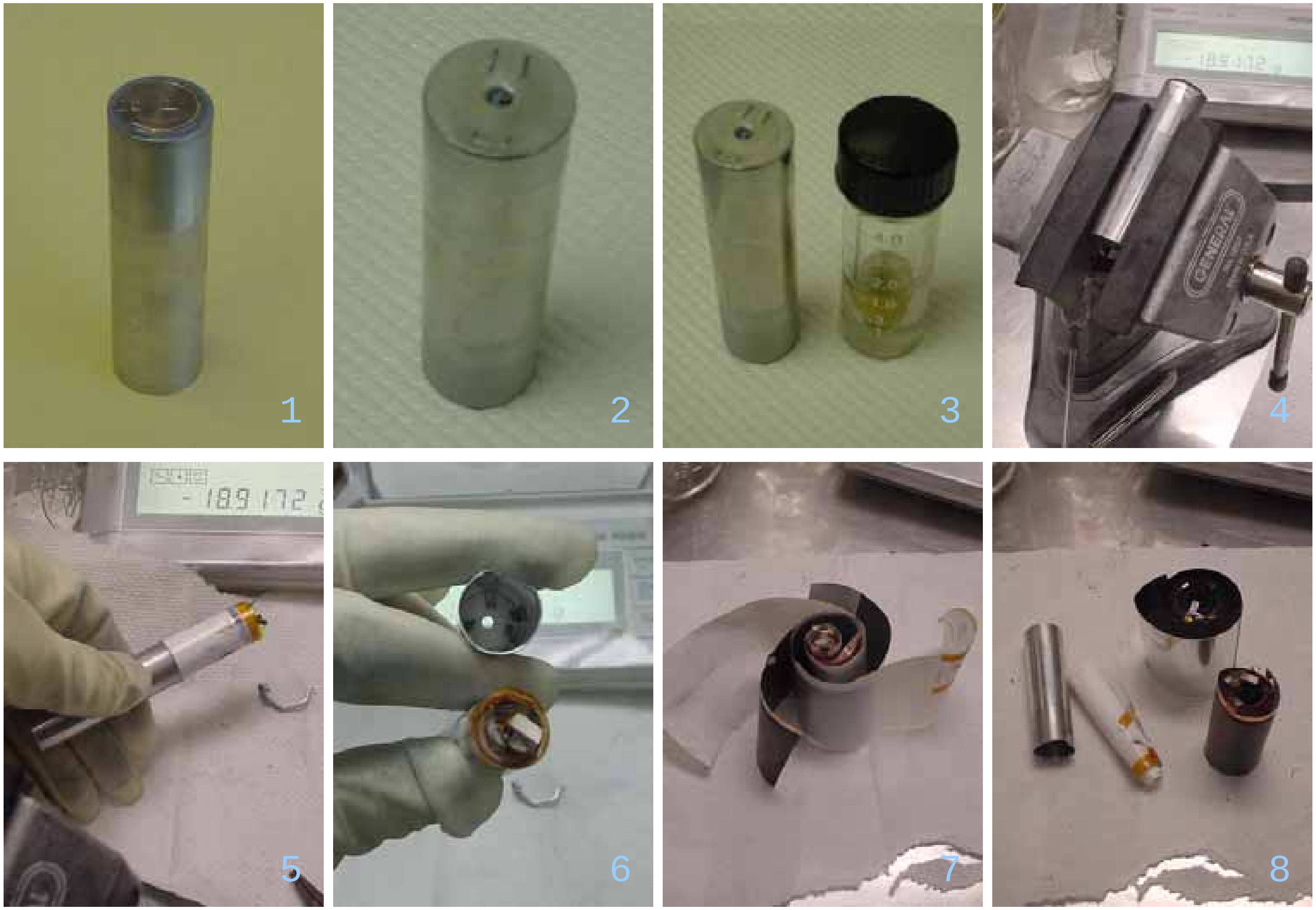
18650-cell EIS data
at 3.72V



The impedances at the very low-frequencies are associated with diffusion phenomena



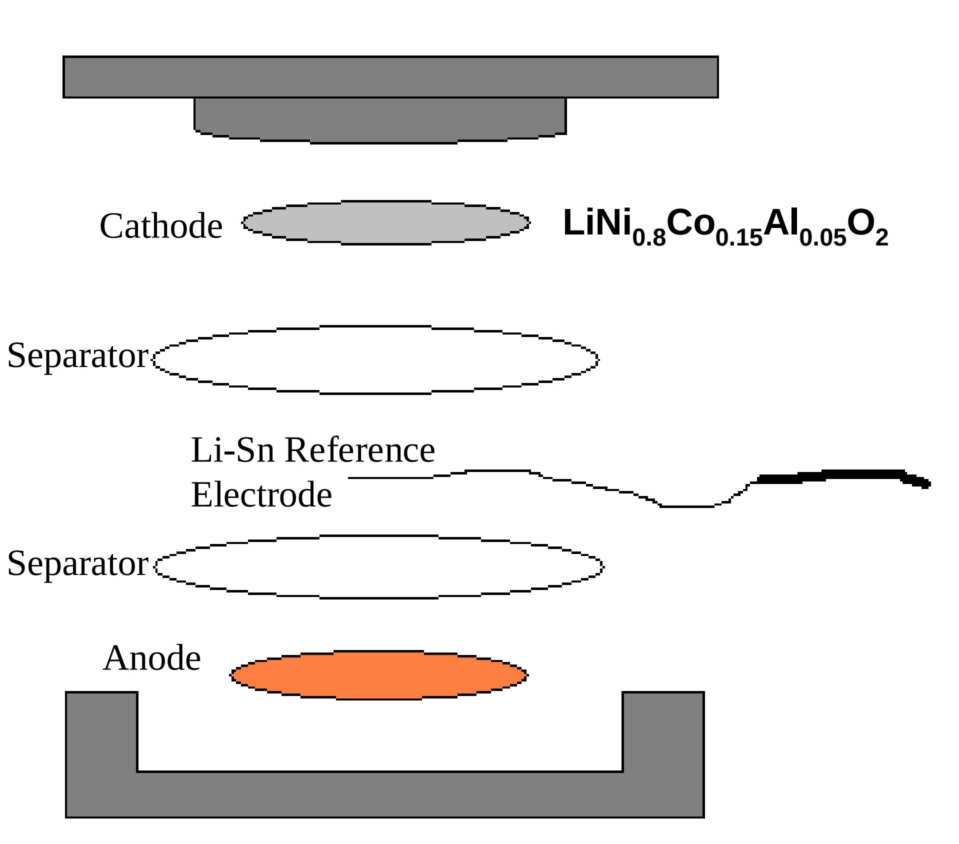
Aged cells are disassembled, and cell components examined to determine sources of impedance rise



Limitation: Cell opening may induce artifacts

Reference electrode cell measurements

- Quantifies impedance contributions of each electrode



Reference Electrode Cell

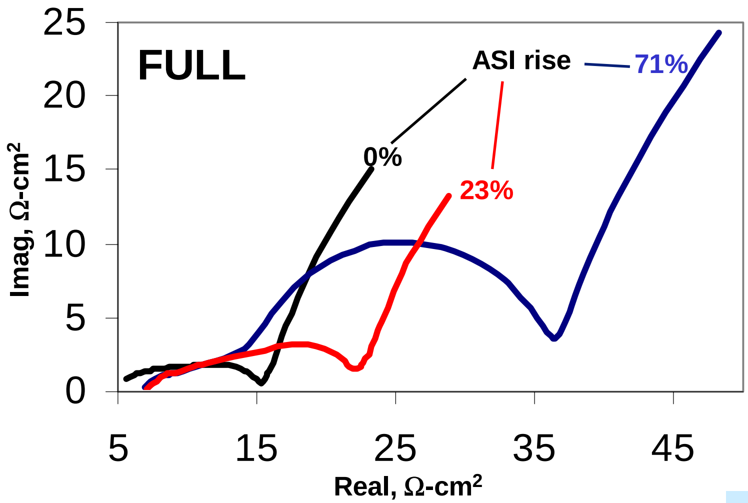
Reference Electrode Cell

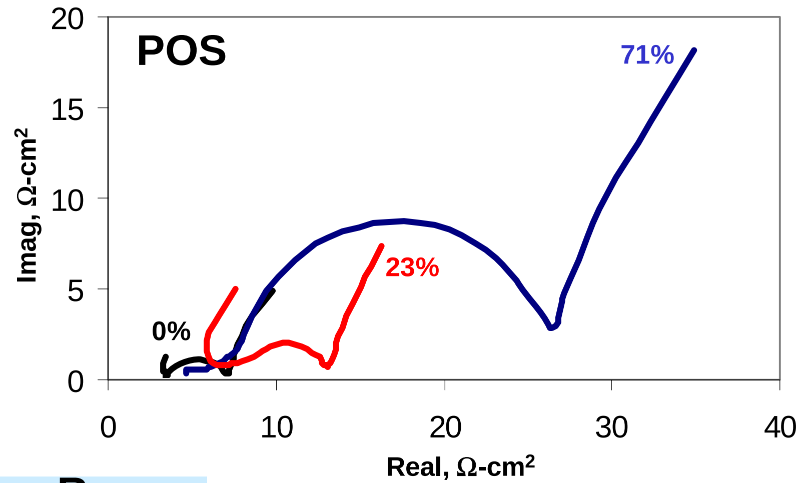
- 15.5 cm^2 harvested electrodes
- Li-Sn reference wire
- EC:EMC(3:7) +1.2M $LiPF_6$ electrolyte

Measurements in Ar glove box

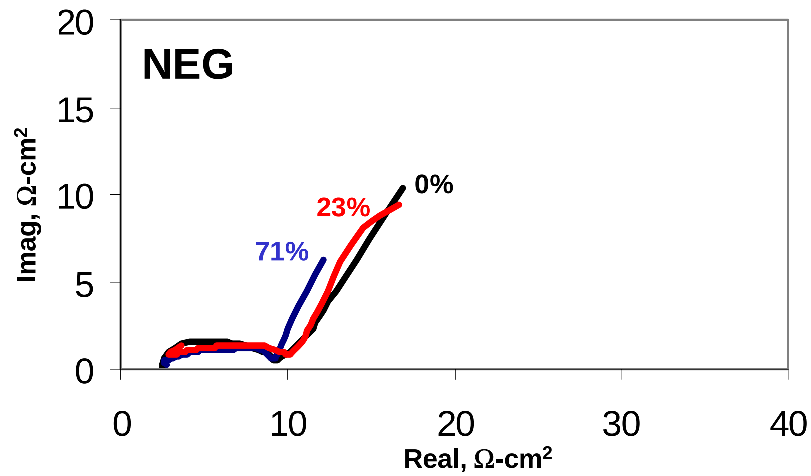
Reference electrode cell assembly

Typical EIS Data on Electrodes Harvested from 1 Ah Cells after 45°C aging *(Reference Electrode Cell)*





Frequency Range
10^5 – 0.01 Hz



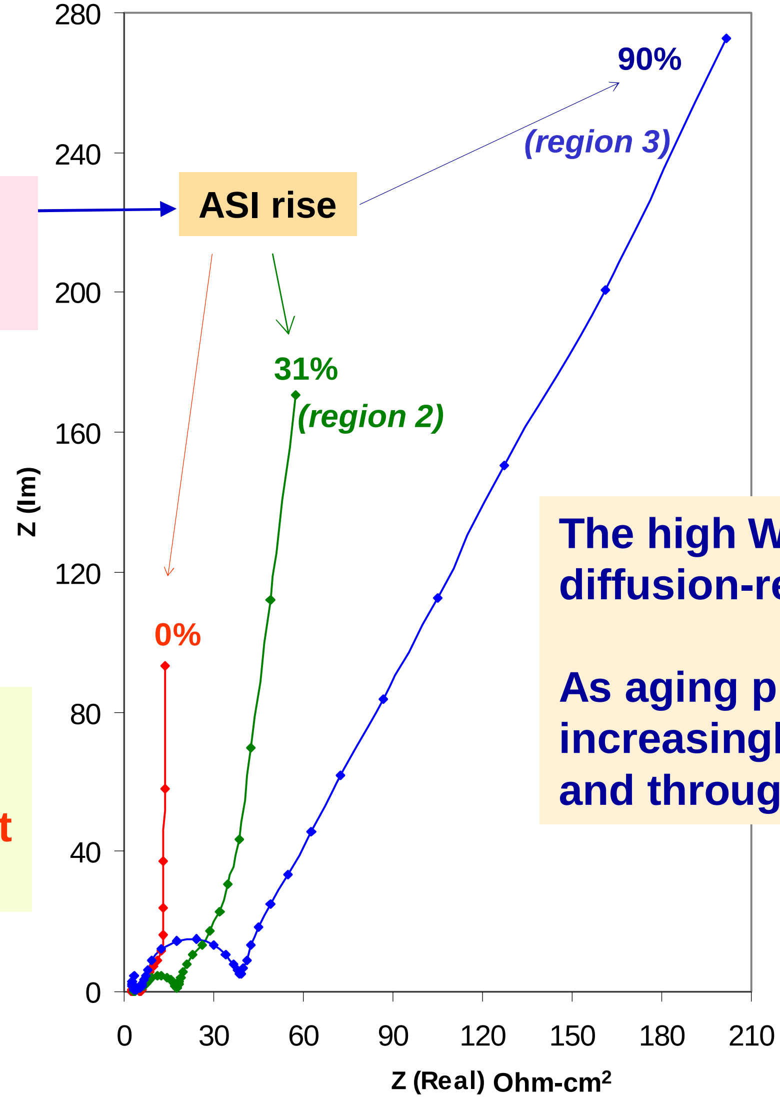
Positive electrode impedance increase is dominant. Furthermore, this increase is related to changes at the positive electrode-electrolyte interface.

Positive electrodes harvested from aged cells show significant Warburg impedance at v. low frequencies

Frequency Range
10^5 – 0.00025 Hz

Refers to the 18650-cell from which the electrodes were extracted

Typical Reference Electrode Cell Data

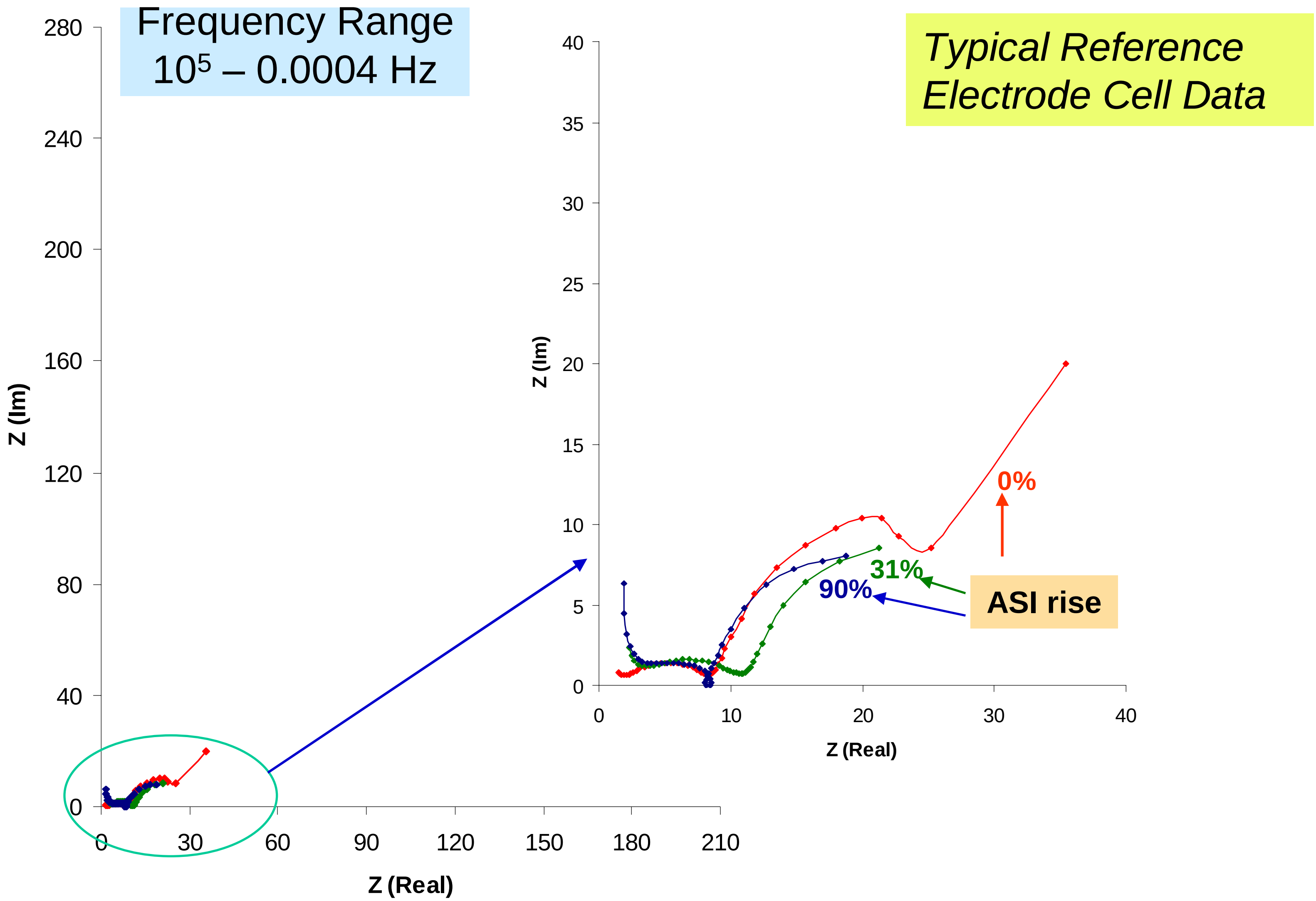


0% PF samples exhibit mainly capacitive behavior at very low frequencies

The high Warburg impedance indicates diffusion-related limitations on aging.

As aging progress, it becomes increasingly harder to transport Li into and through the oxide particles

Negative electrodes harvested from aged cells show small differences in impedance at v. low frequencies

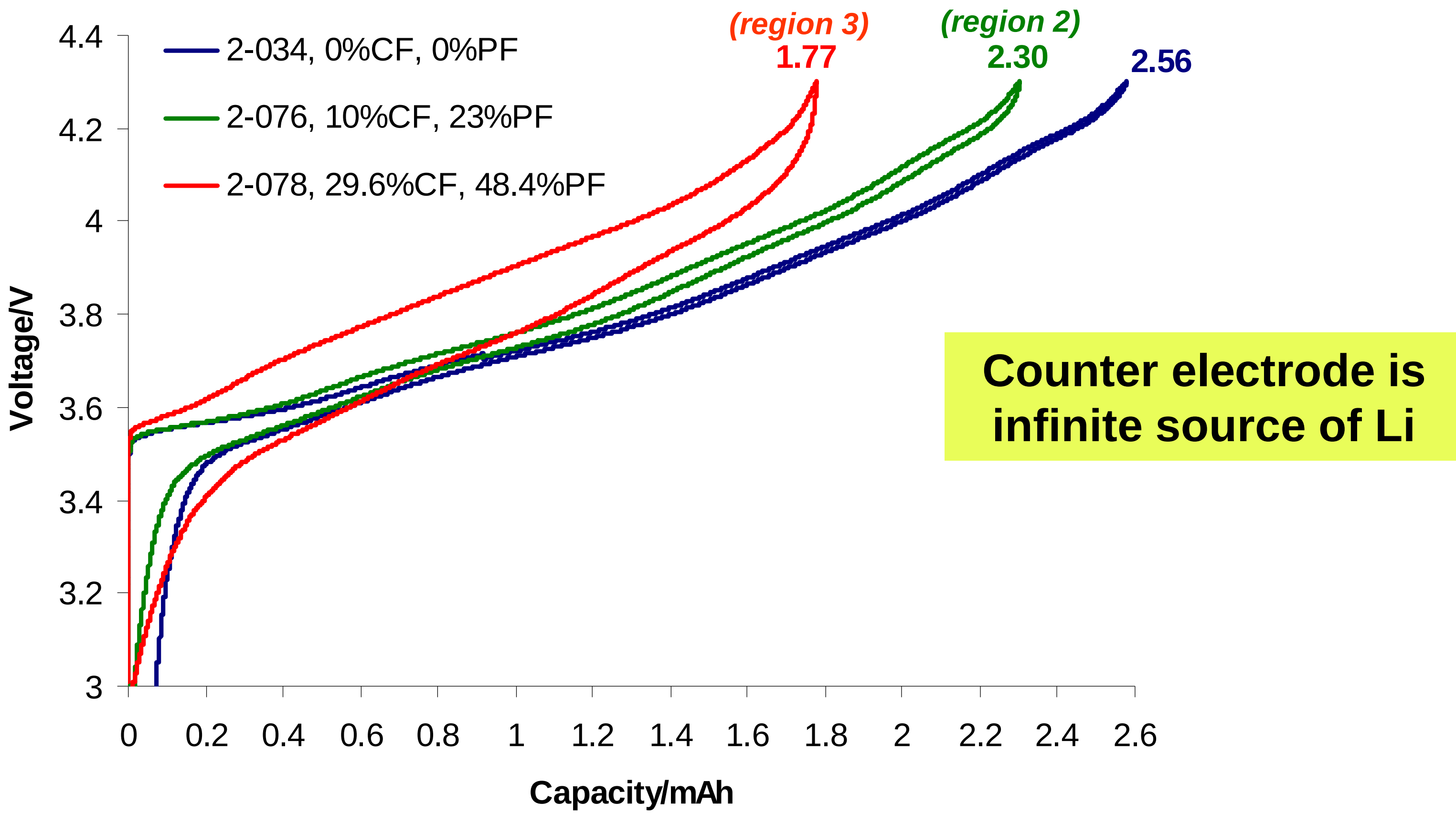


EIS data summary

- **Aging of 18650-cells produces**
  - ➢ Relatively large-changes in the very low frequency portion of the EIS curve, compared to changes in the mid-frequency portion
    - - *Associated with diffusion-related phenomena*
- **Reference data with electrodes harvested from 18650-cells show that**
  - ➢ Impedance increases in the low-frequency portion of the EIS curve are associated with the positive electrode
  - ➢ Oxide particles slow down on aging *(especially apparent in "region 3')*
    - - *The impedance rise, power fade, and also a significant portion of the capacity fade, results from the inability of the oxide to deliver lithium at high-rates*

Cathodes Harvested from 18650 Cells

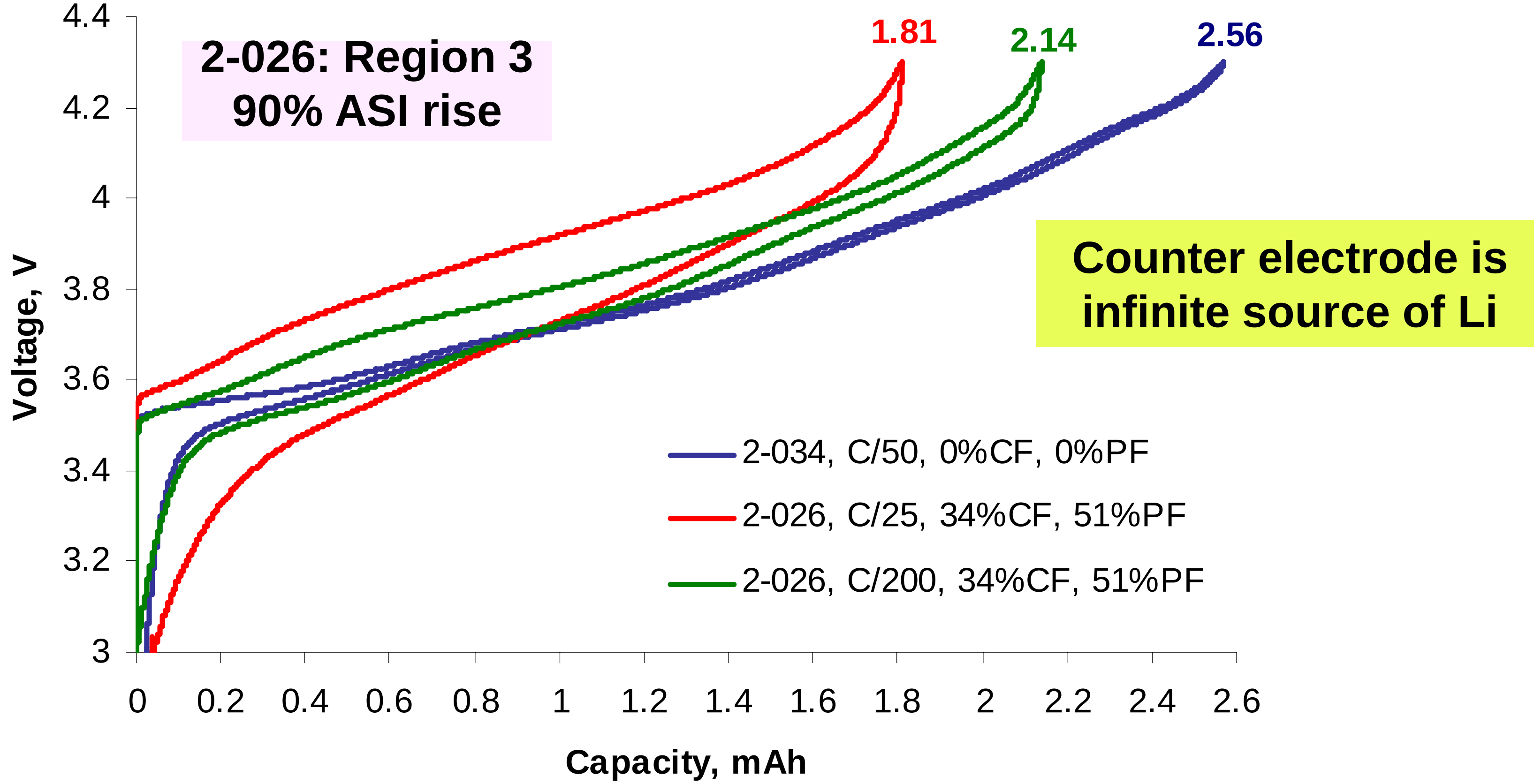
Capacity Data vs. Li – *1.6 sq. cm. coin cells, 0.064 mA (nominally C/25)*



- Aging produces capacity loss in the positive electrode
- Significant hysteresis observed for higher power fade samples (from 'region 3)

Cathodes Harvested from 18650 Cells

Capacity Data vs. Li – *1.6 sq. cm. coin cells*



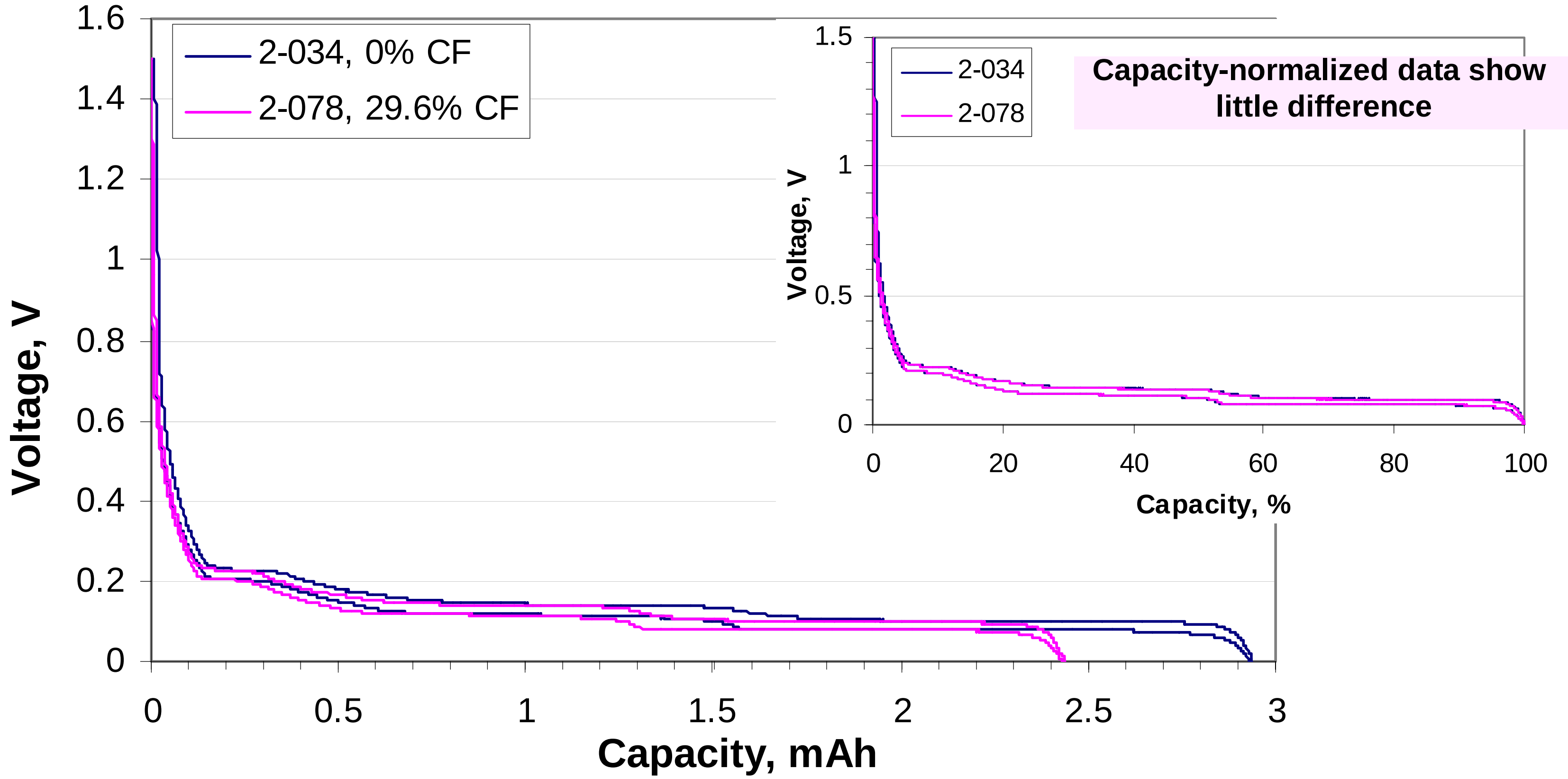
For Cell 2-026 --
Hysteresis persists even at C/200 rate. But, note ~0.33 mAh capacity gain from cycling at slower rates! Still, capacity is ~0.4 mAh smaller than that for 2-034.

Positive Electrode capacity data summary

- **Samples from aged cells have lower capacity than samples from cells that are not aged**
  - ➢ For same rate cycling, this capacity decline increases with cell age
  - ➢ When cycled at slower rates
    - - *Samples from 'region 2' cells show little capacity gain*
    - - *Samples from 'region 3' show significant capacity gain*
- **Oxide particles 'slow down' with cell age**
  - ➢ A significant portion of 18650-cell capacity loss may be associated with the inability of oxide particles to deliver or accept Li at the C/1 and C/25 rates. This is especially true for 'region 3' cells.
  - ➢ Some capacity loss is associated with particle isolation, which may result from (i) electronically insulating oxide surface films, (ii) oxide particle damage, (iii) secondary particle fragmentation

Summary for Anodes Harvested from 18650 Cells

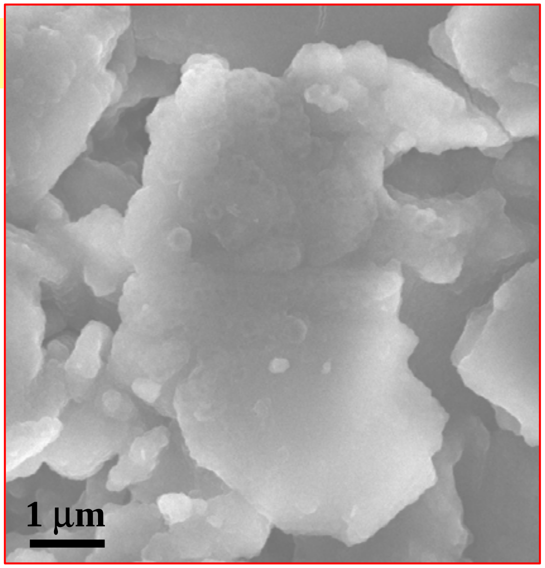
Capacity Data vs. Li – *1.6 sq. cm. coin cells, 0.064 mA (nominally C/25)*



- Negative electrode samples show some capacity loss on aging
  - Does not result from graphite damage. Most likely results from graphite particle isolation by electronically-insulating surface films.

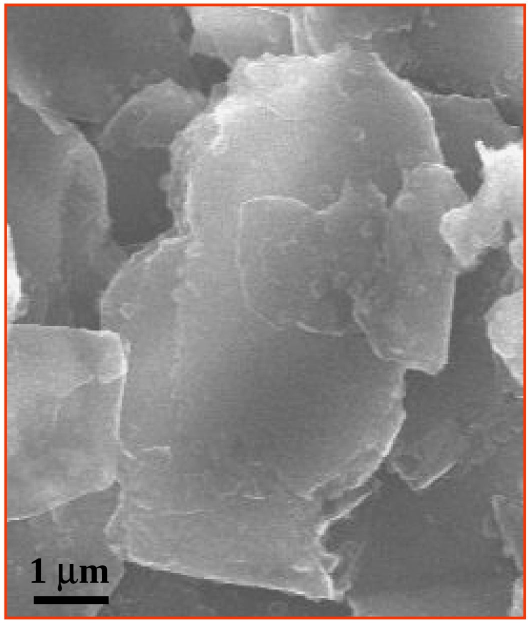
Capacity loss also related to graphite SEI changes
- graphite degradation not evident

SEI thickens on aging

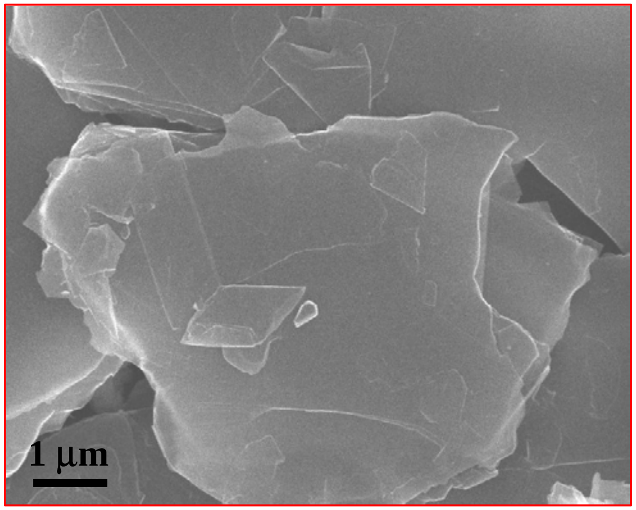


Graphite, 50%PF cell

SEI formation consumes Li



Graphite, 0%PF cell

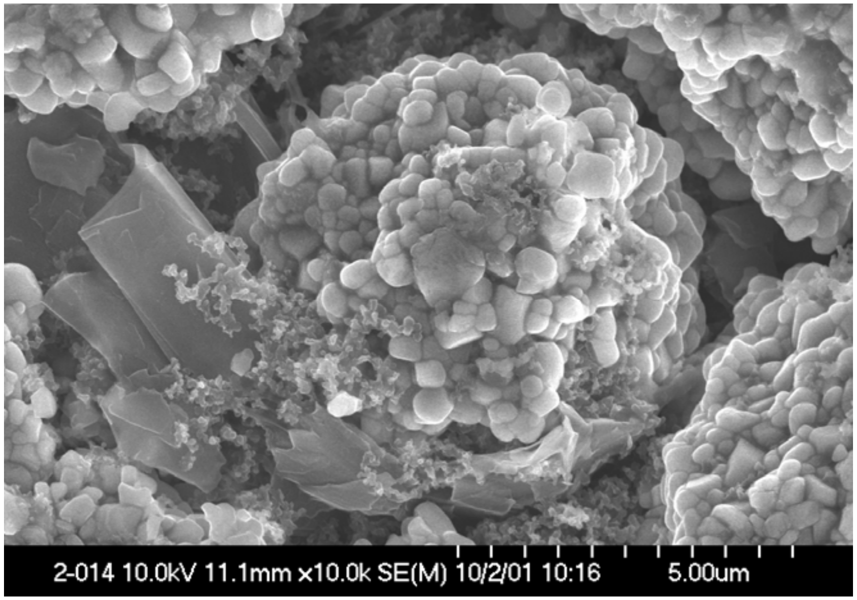


Graphite, Fresh Laminate

SEI thickening consumes active Li, which reduces cell capacity

Positive Electrode impedance rise can be correlated to electrode surface film changes

SEM image
Cell 2-014, Calendar life, 24%PF



Li_2CO_3 on starting oxide powder

Al current collector

Not affected by aging

PVdF binder

No obvious degradation

Carbons

Bulk carbon content unaffected

Graphite not damaged during aging

Oxide

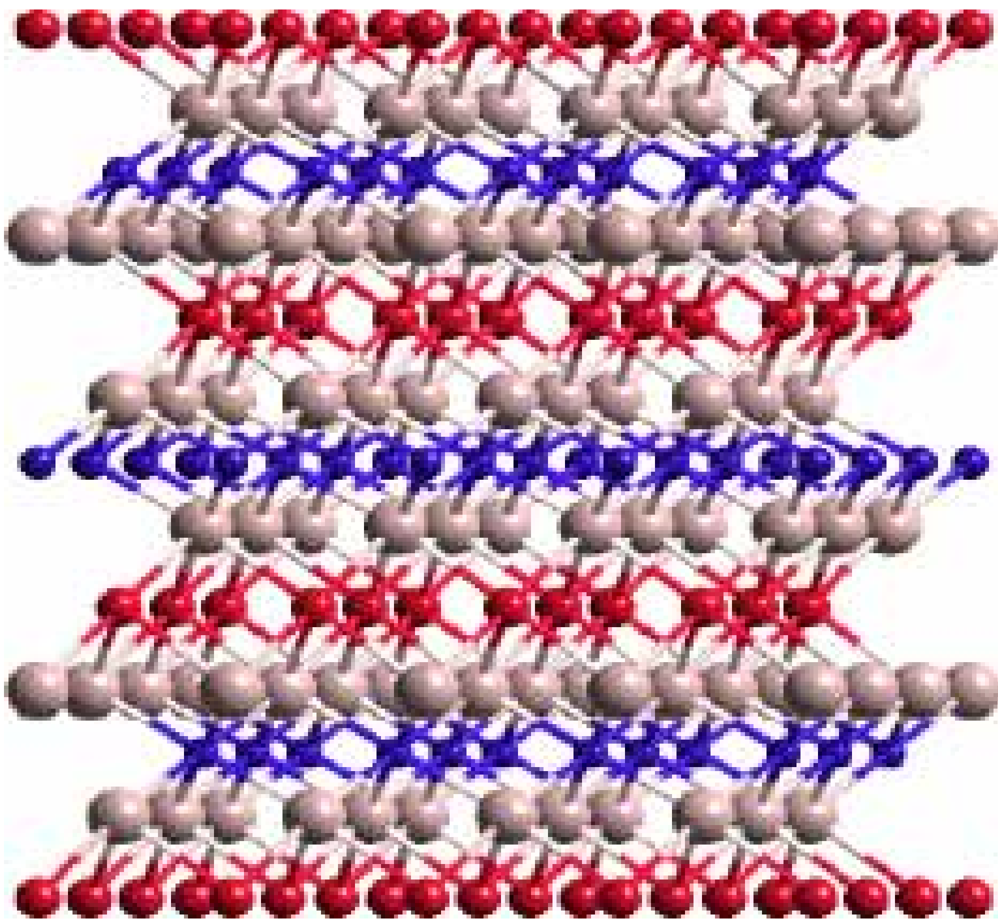
Crystal structure changes in oxide bulk and surface appear minimal

- some oxide damage observed in high power fade (~50%) samples

Electrode surface films observed after formation cycling

- these films change on aging

$LiNiO_2$ Crystal Structure



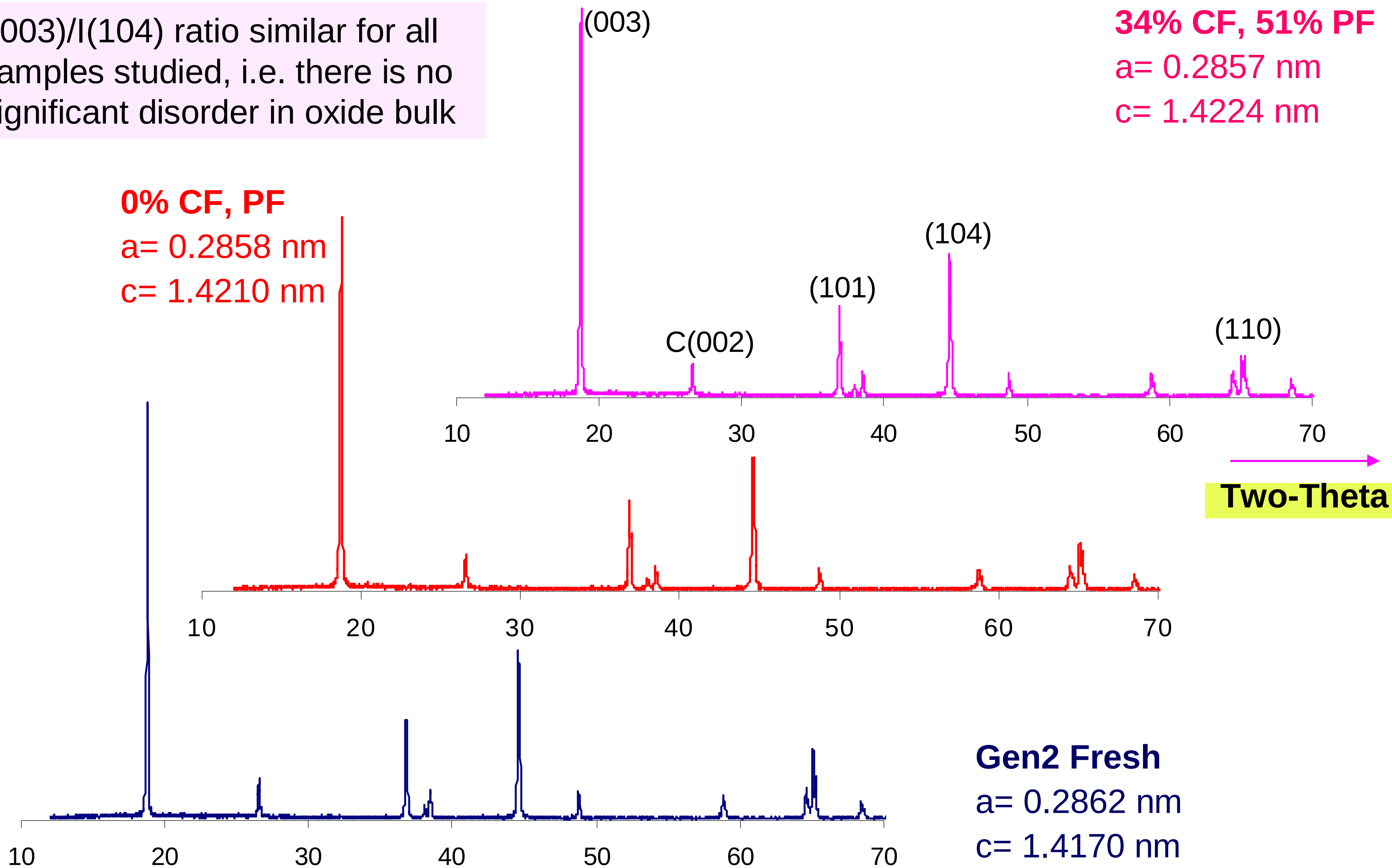
Li atoms enter and exit through edge planes

Impedance rise will result from edge plane changes
(a) structural changes
(b) surface films

Excessive delithiation can irreversibly damage the oxide particles

XRD data show that the oxide bulk is not damaged by any significant amount – *some lattice parameter changes observed*

I(003)/I(104) ratio similar for all samples studied, i.e. there is no significant disorder in oxide bulk



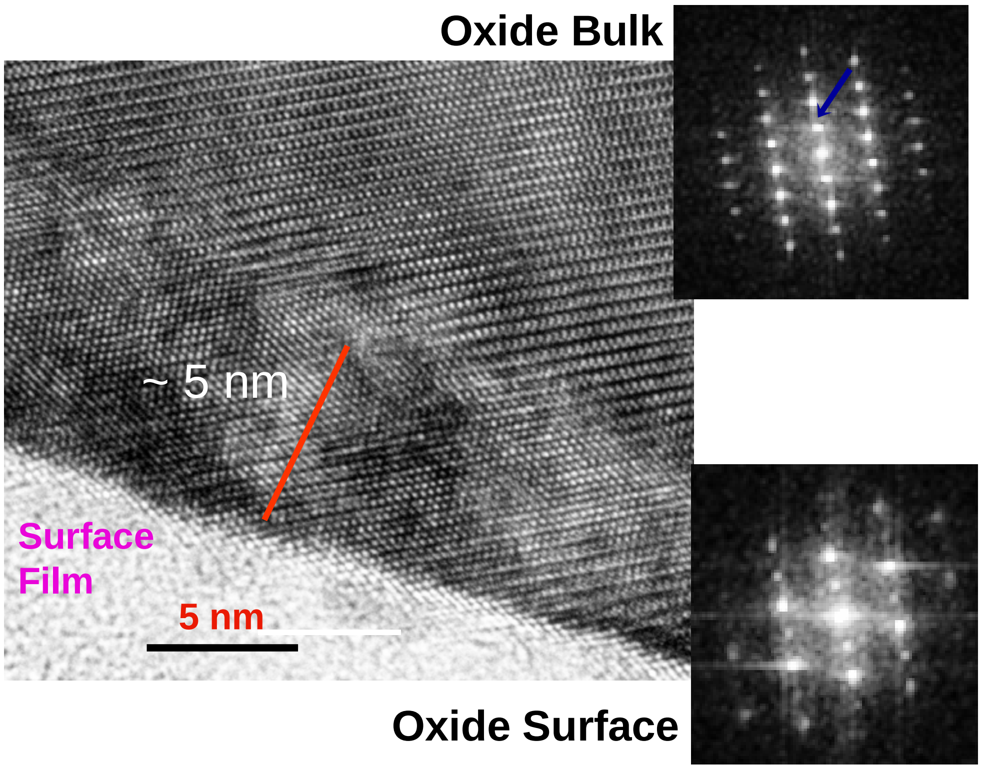
Cells discharged to 3.1V before disassembly

$Li_xNi_{1-x}O$ –type surface layer present on oxide particles

High-resolution Electron Microscopy

Ni-O-Li-O-Ni
(ordered rock salt)

Oxide Bulk

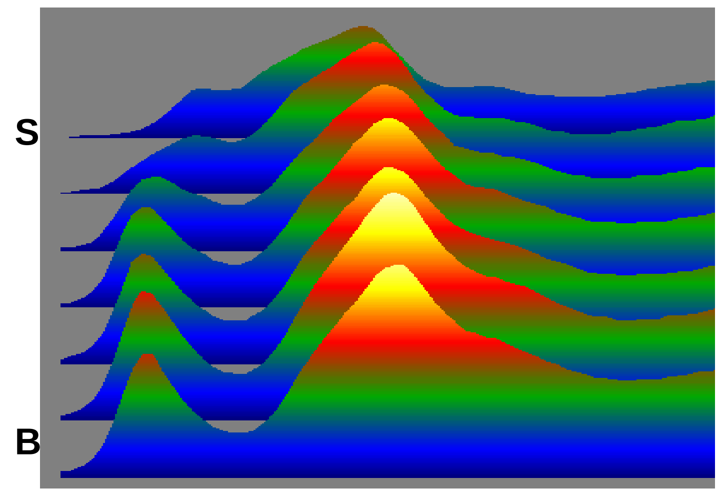


Oxide Surface

Ni-O-Ni-O-Ni
(rock salt)

(003) reflections absent in oxide surface

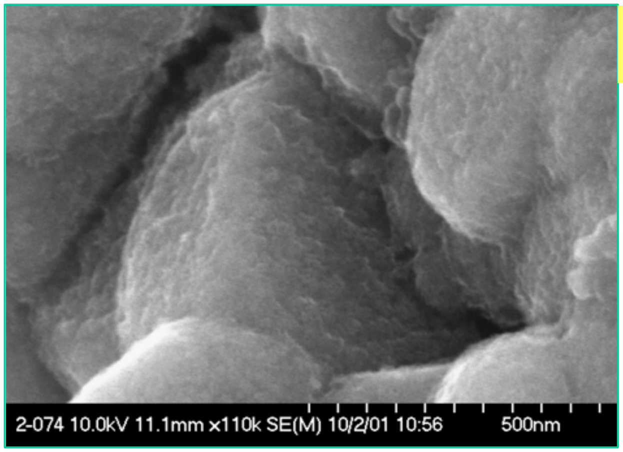
EELS data



O K-edge data

Distinct differences between surface and bulk are consistent with Ni^{+2} in surface layer and Ni^{+3} in bulk

Electron Microscopy Images Show Films on the Surface & in Pores between Primary Particles

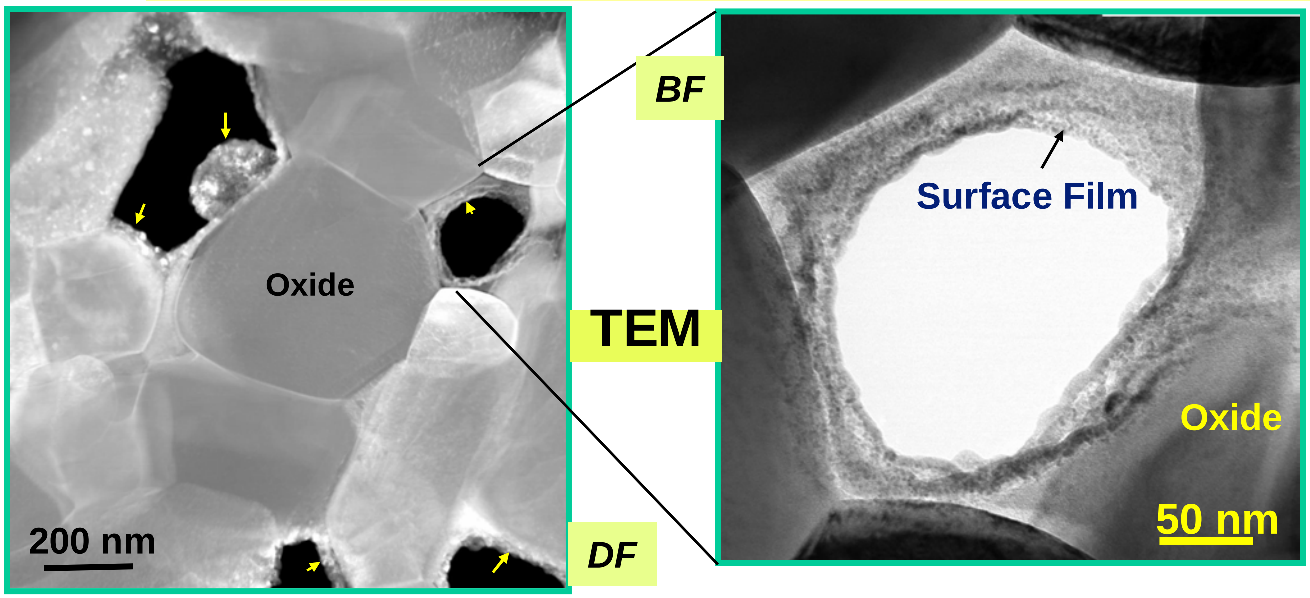


SEM image showing surface films

All images from unrinsed samples
Surface films include electrolyte residue

- **Not all oxide particles have direct access to electrolyte**
- **Oxide surface films could hinder Li-ion motion**

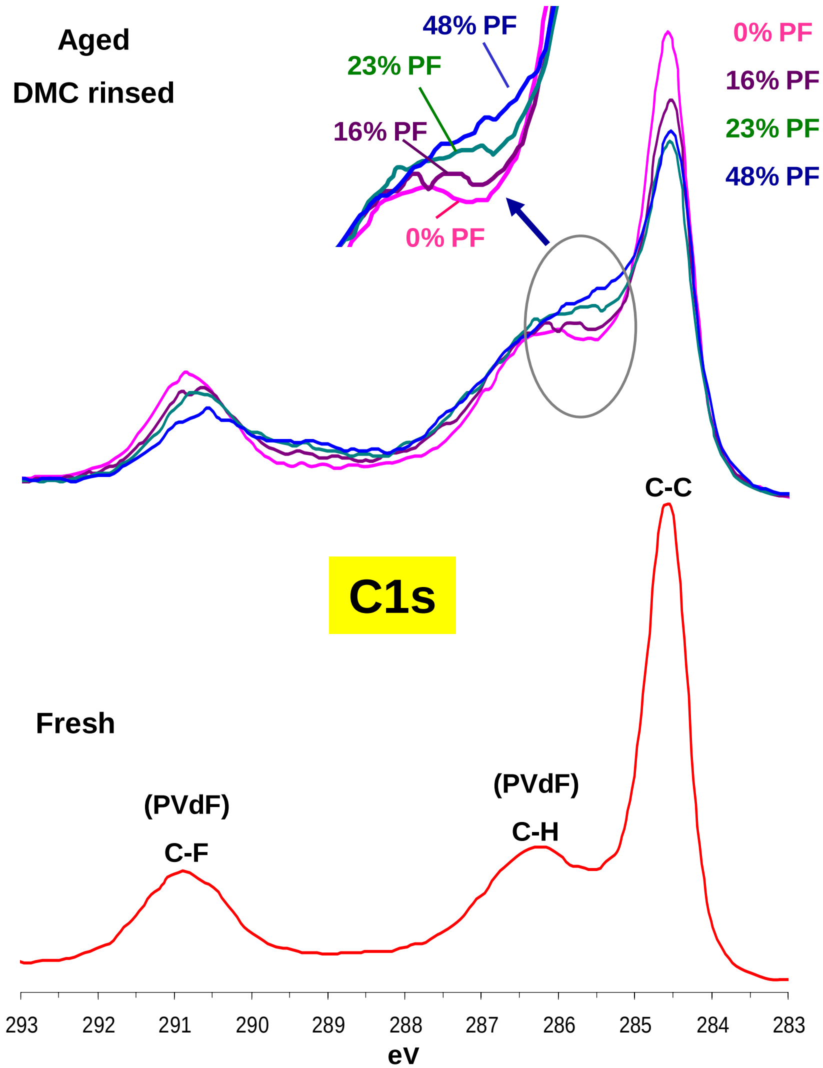
Blocking Li-diffusion pathways of particles with direct electrolyte access will also affect particles that do not have such access

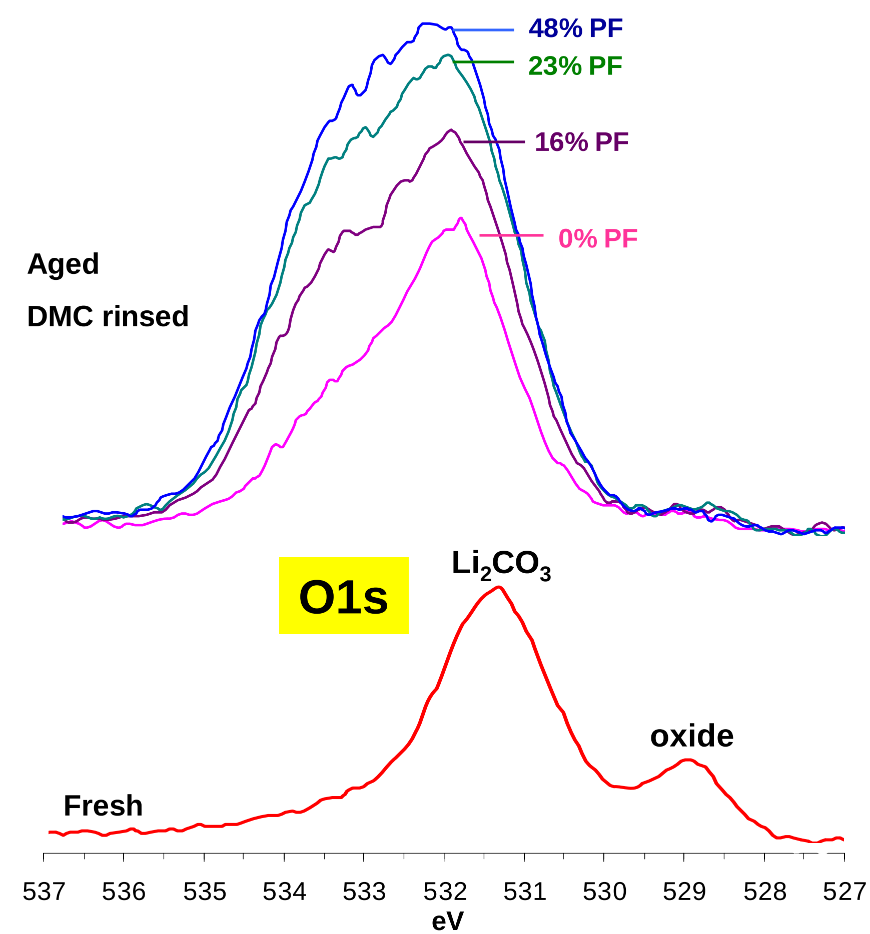


C1s and O1s XPS spectra of (+) electrode samples show clear and reproducible changes on aging

Analysis area ~ 1 mm^2
Analysis depth ~ 5 nm

As aging progresses, the electrode surface is covered by a changing surface film

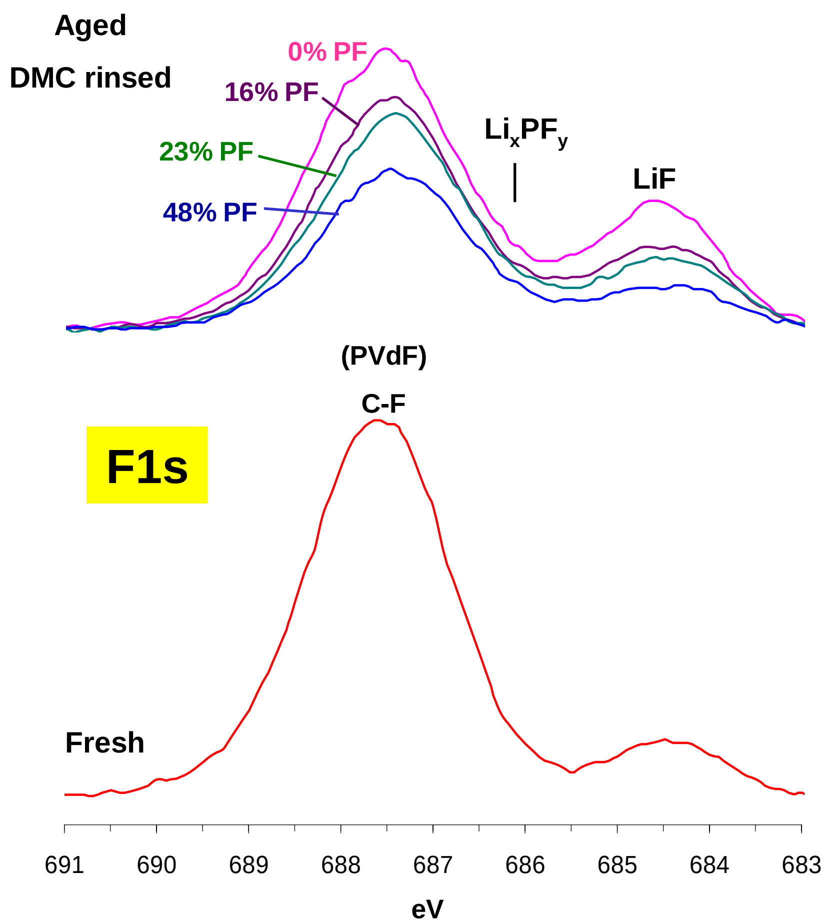




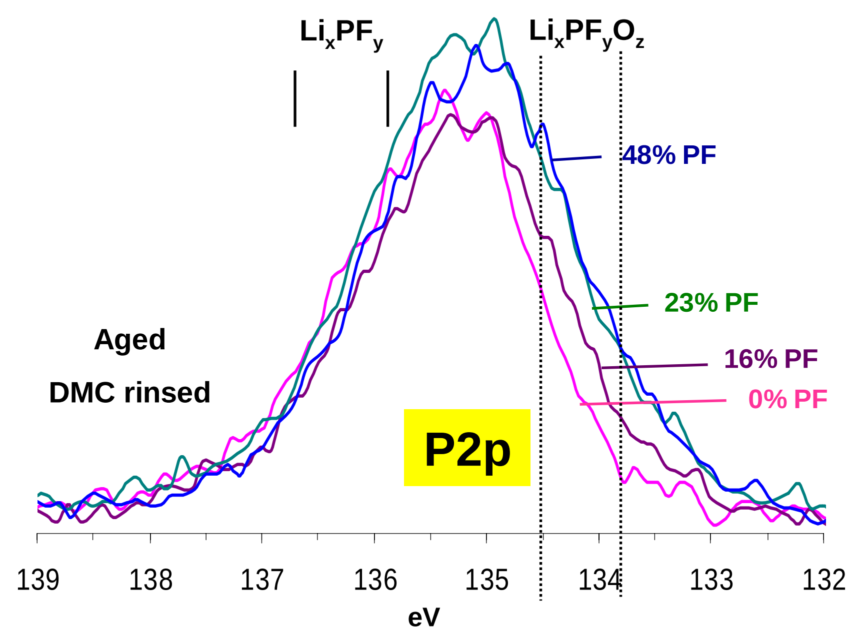
F1s and P2p XPS spectra show abundance of inorganic products on (+) electrode sample surface

Analysis area ~ 1 mm^2
Analysis depth ~ 5 nm

Binder peak intensity lower for aged samples indicating coverage

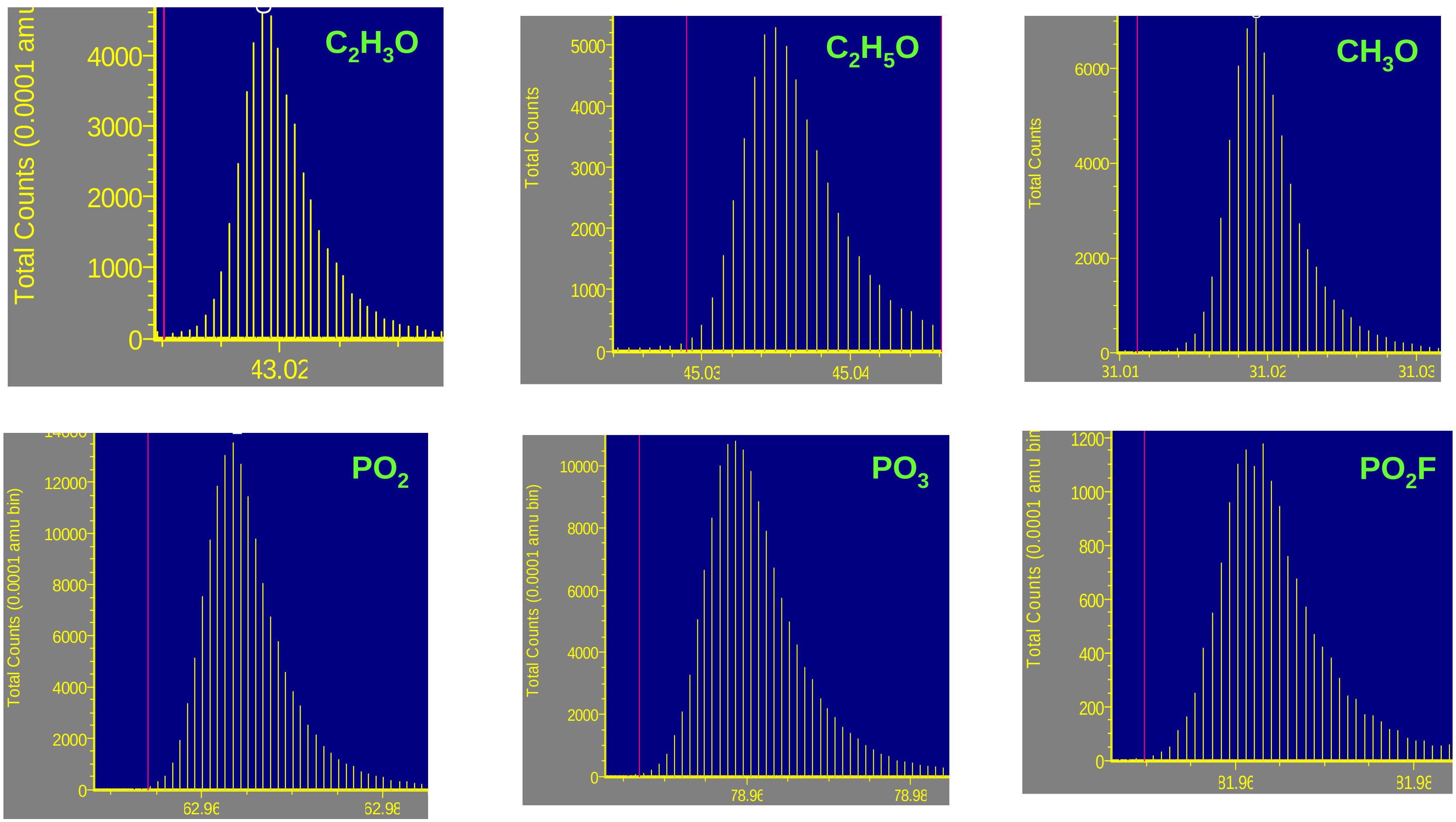


Increase in fluorophospate species on aging



High-Resolution TOF-SIMS Data Show Abundance of R-O and P-O Fragments

Analysis area ~ 0.1 mm^2
Analysis depth ~ 1 nm

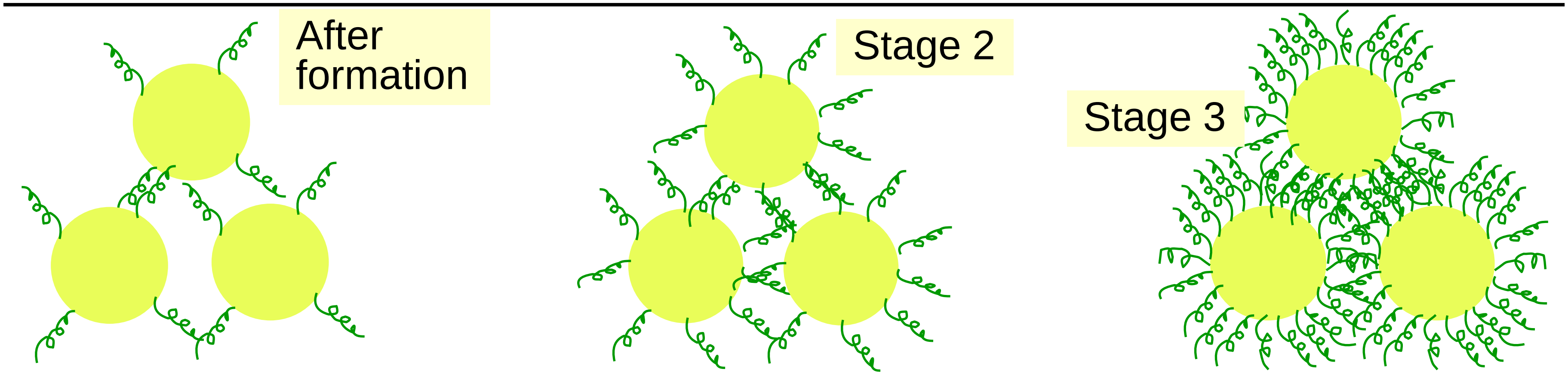


35% PF cathode, 2h DMC soak

Oxide analysis data summary

- **Crystal structure changes in oxide bulk and surface appear minimal**
  - But surface films are present on the particles
- **The positive electrode contains a distribution of particles, some of which are more likely to contribute Li-ions, especially at high rates**
  - More highly delithiated oxide particles are more likely to react with the electrolyte and form surface films
  - Localized surface films can preferentially isolate individual particles
  - Isolation/damage of the previously high-power oxide particles results in longer diffusion lengths

Schematic showing progressive surface film build-up on oxide particles that can hinder Li-ion diffusion



Stages 1, 2 and 3 are probably progressive manifestations of the same phenomenon

Formation cycling produces charged (ionic) species that are tethered to oxide particles

Stage 1 rise results from increased oxide surface coverage produced by raising the temperature to 55°C – this stage is absent for cells aged at 25°C

During stage 2, oxide surface coverage gradually increases, increasing impedance

The transition from stage 2 to stage 3 results from increasing interaction (cross linking) between the charged species from various particles, increasing electrolyte viscosity in electrode pores and therefore the impedance

Conclusions and Future Work

- **Cell capacity fade results from**
  - Increasing thickness of negative electrode SEI layer
  - Isolation of oxide particles in the positive electrode
- **Cell power fade is dominated by impedance increase at the positive electrode**
  - Localized isolation of oxide particles by surface films
  - Structural changes in certain oxide particles

- **Identify reaction mechanisms that control capacity and power loss**
  - TOF-SIMS experiments are in progress

Acknowledgments

- **Research supported by**
  - U.S. DOE, Freedom CAR & Vehicle Technologies, Advanced Technology Development (ATD) Program
  - Program Manager: Tien Duong
- **Center for Microanalysis of Materials partially supported by**
  - U.S. DOE under grant DEFG02-91ER45439