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

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(ANL)



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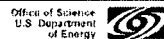
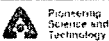
Acknowledgments

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 - Program Manager: Tien Duong
- **Center for Microanalysis of Materials partially supported by**
 - U.S. DOE under grant DEFG02-91ER45439

**THANK
YOU!**

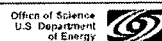
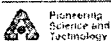
ATD Program

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

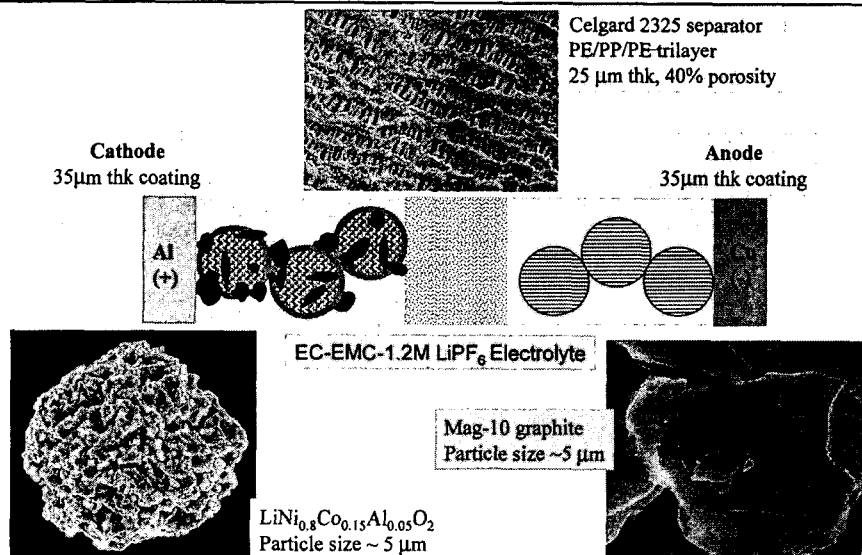


Objectives of the diagnostic studies

- 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



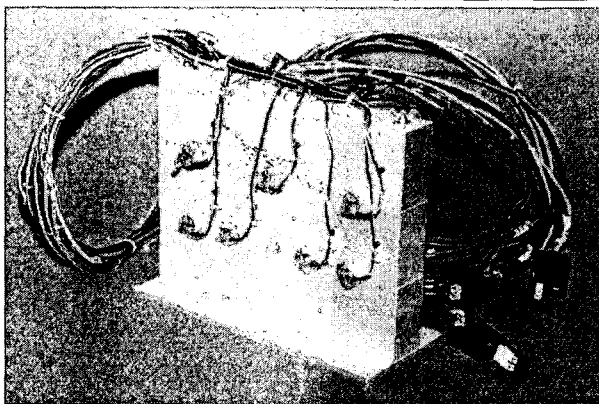
Cell Chemistry



Abraham et al., *Electrochimica Acta* 49 (2004), pp. 4763-4775

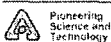


Accelerated aging conducted on 1Ah cylindrical cells

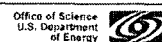


Calendar life aging: Cells stored in an elevated temperature oven
Cycle life aging: Cells cycled at elevated temperature

Cells properties (capacity and impedance) measured periodically

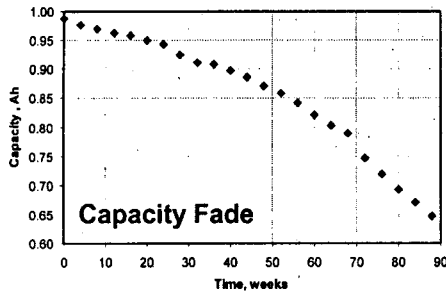


Bloom et al., *J. Power Sources*, 124 (2003) p 538

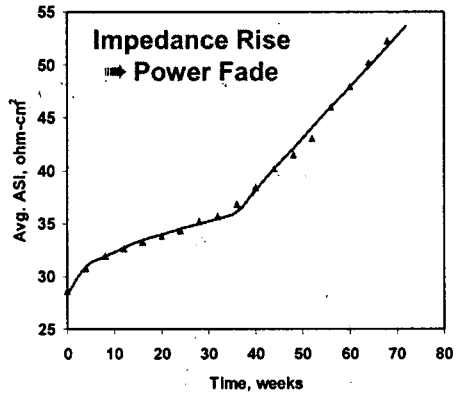


On aging, cells lose capacity and power

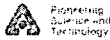
- Data from 1Ah cells



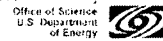
45°C data



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

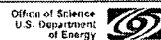
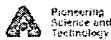
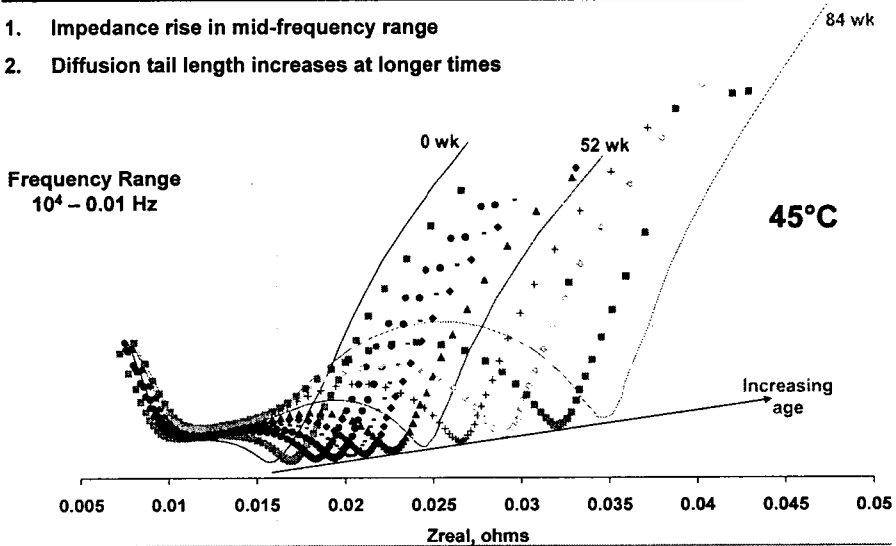


Bloom et al., J. Power Sources, 124 (2003) p 538

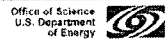
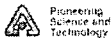
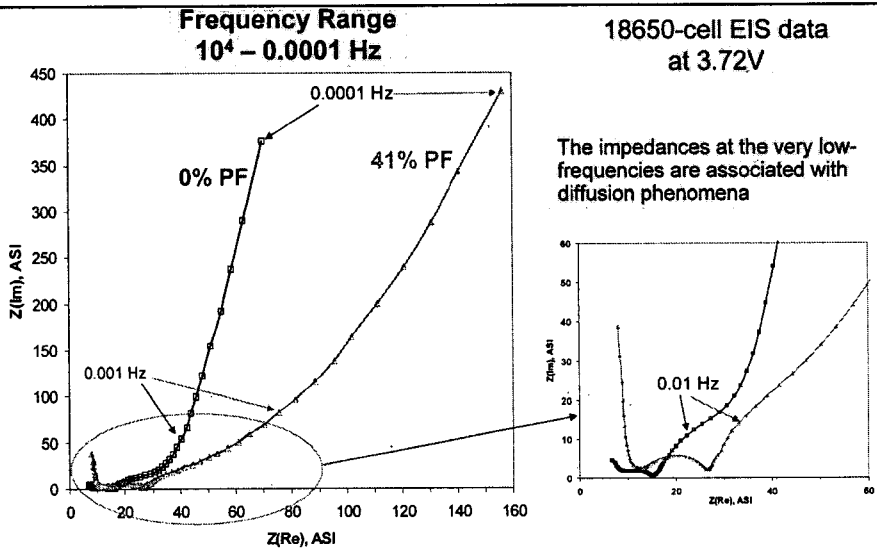


AC impedance data provides important clues on cell behavior during aging

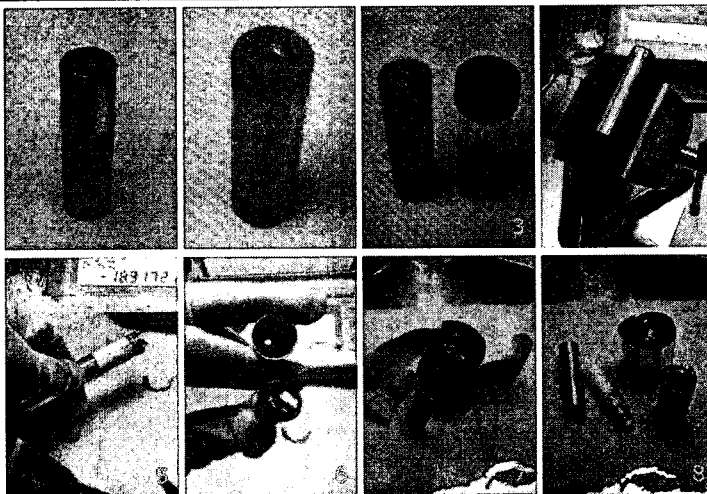
1. Impedance rise in mid-frequency range
2. Diffusion tail length increases at longer times



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



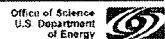
Aged cells are disassembled, and cell components examined to determine sources of impedance rise



Limitation: Cell opening may induce artifacts

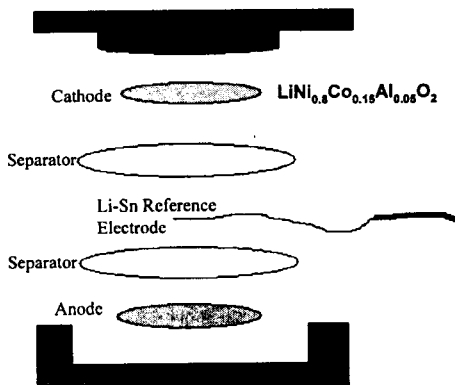


Courtesy: Dr. Yoo-Eup Hyung



Reference electrode cell measurements

- Quantifies impedance contributions of each electrode

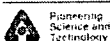


Reference Electrode Cell

Reference Electrode Cell

- 15.5 cm² harvested electrodes
- Li-Sn reference wire
- EC:EMC(3:7) + 1.2M LiPF₆ electrolyte

Measurements in Ar glove box



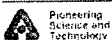
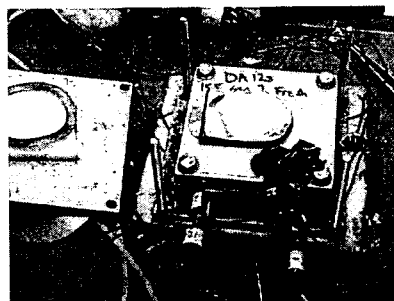
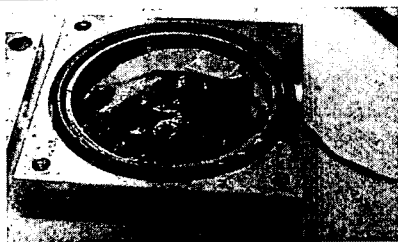
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Abraham et al., *Electrochimica Acta* 49 (2004), pp. 4763-4775

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Reference electrode cell assembly

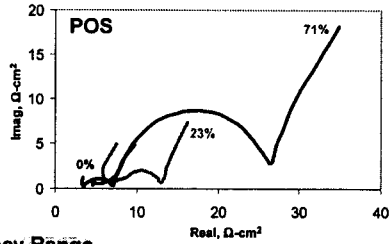
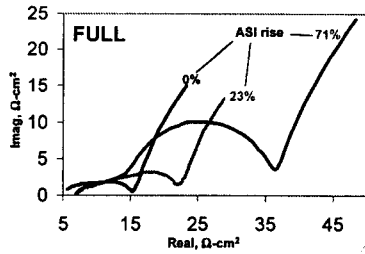


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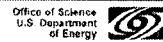
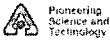
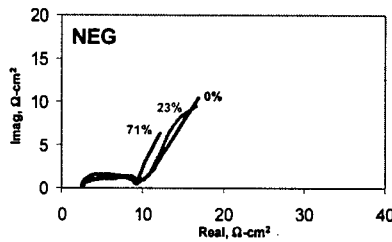


Typical EIS Data on Electrodes Harvested from 1 Ah Cells after 45°C aging (Reference Electrode Cell)



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.

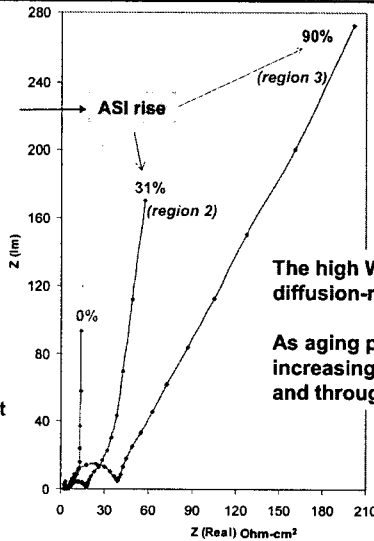


Positive electrodes harvested from aged cells show significant Warburg impedance at v. low frequencies

Frequency Range
 $10^5 - 0.00025$ Hz

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

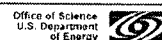
0% PF samples exhibit mainly capacitive behavior at very low frequencies



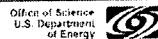
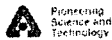
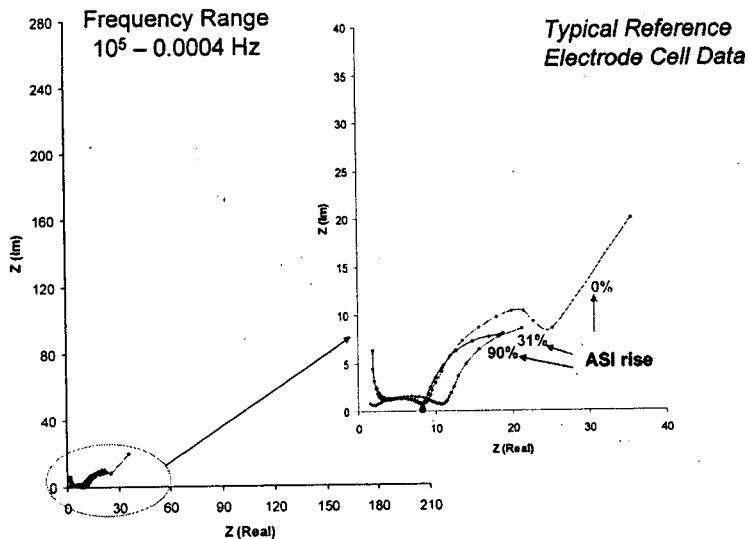
Typical Reference Electrode Cell Data

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



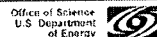
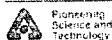
Negative electrodes harvested from aged cells show small differences in impedance at v. low frequencies



EIS data summary

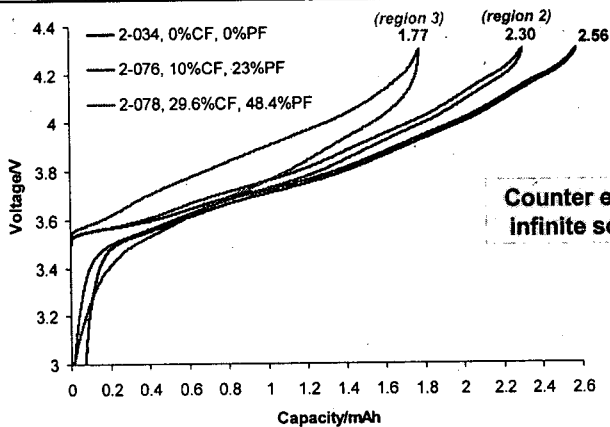
- **Aging of 18650-cells produces**
 - Relatively large-changes in the very low frequency portion of the EIS curve, compared to changes in the mid-frequency portion
 - Associated with diffusion-related phenomena

- **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

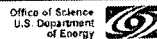
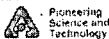


Cathodes Harvested from 18650 Cells

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

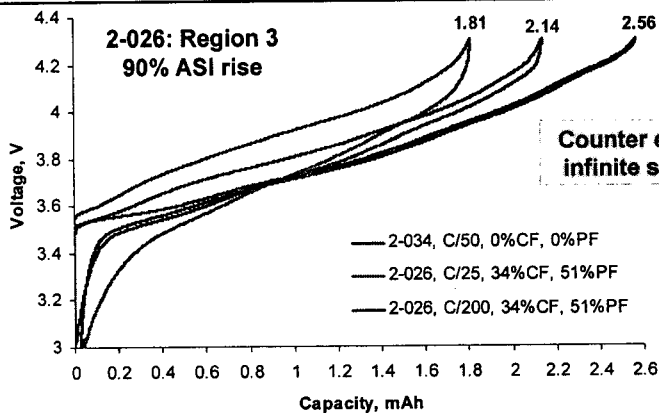


- Aging produces capacity loss in the positive electrode
- Significant hysteresis observed for higher power fade samples (from 'region 3')



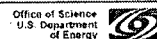
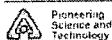
Cathodes Harvested from 18650 Cells

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



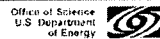
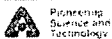
For Cell 2-026 --

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.



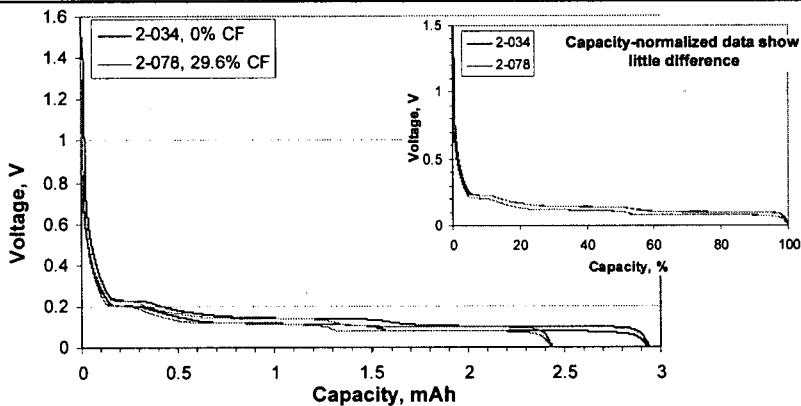
Positive Electrode capacity data summary

- **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

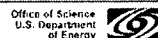
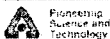


Summary for Anodes Harvested from 18650 Cells

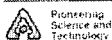
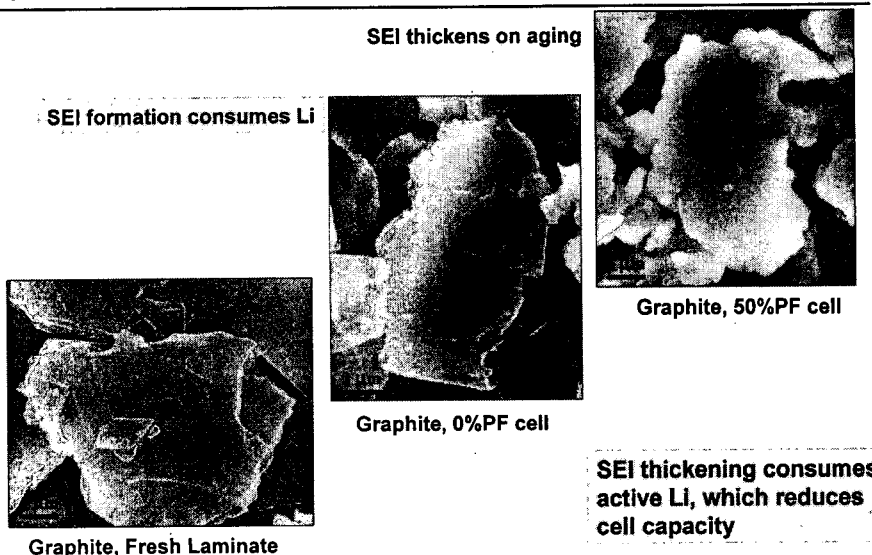
Capacity Data vs. Li – 1.6 sq. cm. coin cells, 0.064 mA (nominally C/25)



- 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.

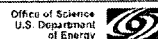


Capacity loss also related to graphite SEI changes - graphite degradation not evident



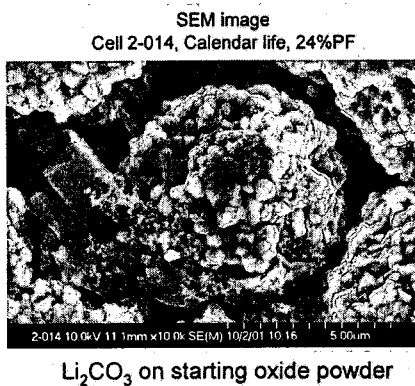
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Abraham et al., *Electrochimica Acta* 49 (2004), p 5097



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



Al current collector

Not affected by aging

PVdF binder

No obvious degradation

Carbons

Bulk carbon content unaffected

Graphite not damaged during aging

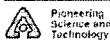
Oxide

Crystal structure changes in oxide
bulk and surface appear minimal

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

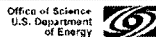
Electrode surface films observed
after formation cycling

- these films change on aging



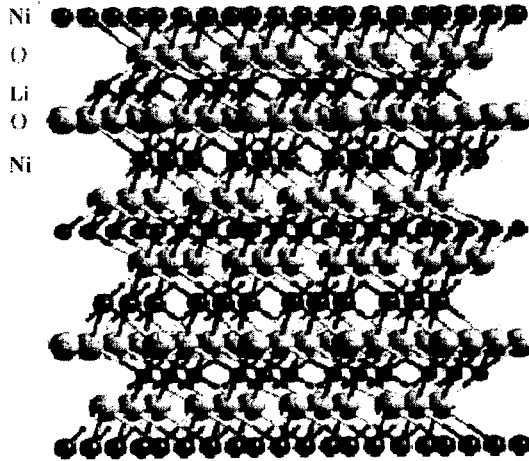
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Abraham et al., *Power Sources for Transportation Applications*, ECS Proceedings, 2003



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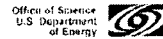
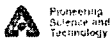
LiNiO₂ Crystal Structure



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

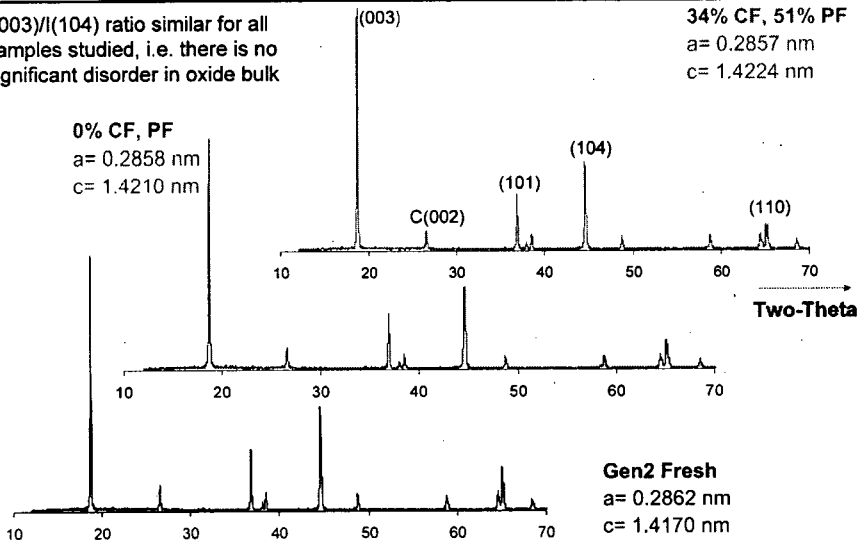


XRD data show that the oxide bulk is not damaged by any significant amount – some lattice parameter changes observed

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

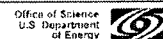
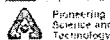
34% CF, 51% PF
a = 0.2857 nm
c = 1.4224 nm

0% CF, PF
a = 0.2858 nm
c = 1.4210 nm



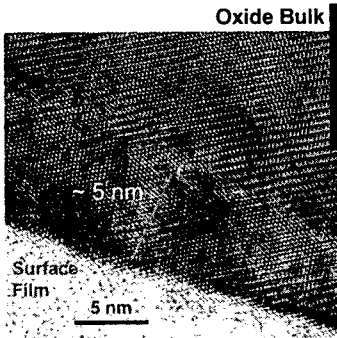
Gen2 Fresh
a = 0.2862 nm
c = 1.4170 nm

Cells discharged to 3.1V before disassembly



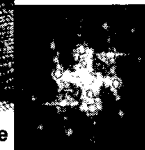
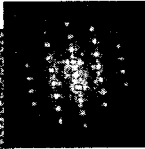
$Li_xNi_{1-x}O$ -type surface layer present on oxide particles

High-resolution
Electron Microscopy



Oxide Bulk

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

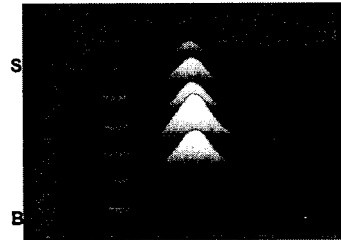


Oxide Surface

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

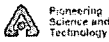
(003) reflections absent
in oxide surface

EELS data



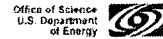
O K-edge data

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



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Science and
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Abraham et al., J. Electrochem. Soc., 150 (2003) pp. A1450-A1456.



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

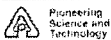
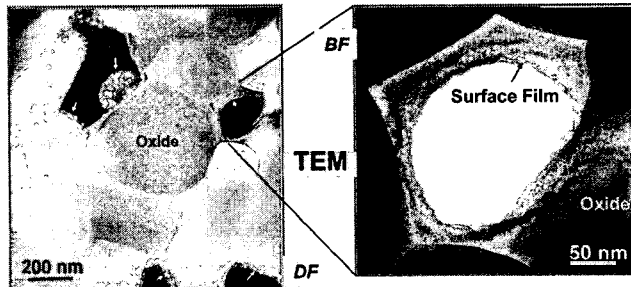


SEM image showing surface films

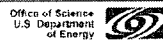
All images from unrinsed samples
Surface films include electrolyte residue

- 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



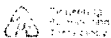
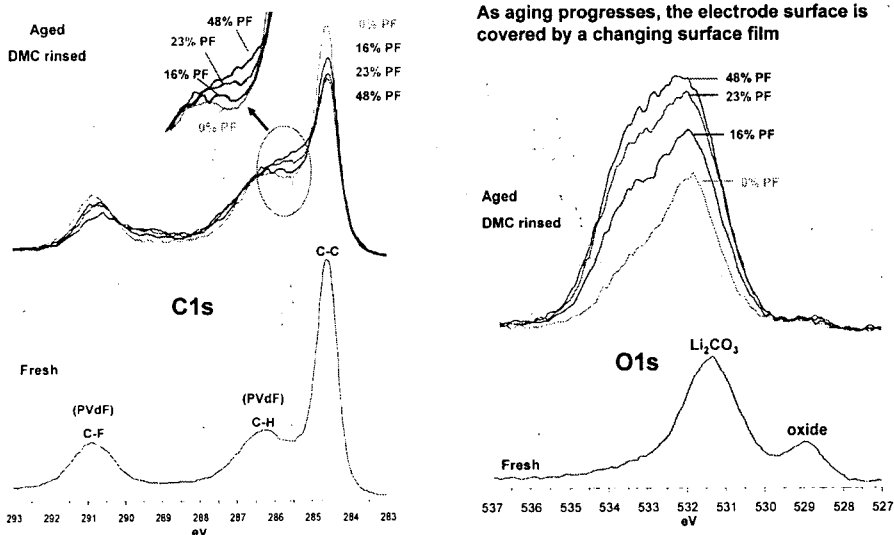
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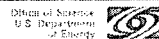
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C1s and O1s XPS spectra of (+) electrode samples show clear and reproducible changes on aging

Analysis area ~ 1 mm²
Analysis depth ~ 5 nm



Abraham et al., J. Electrochem. Soc., 149 (2002) p A1358

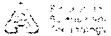
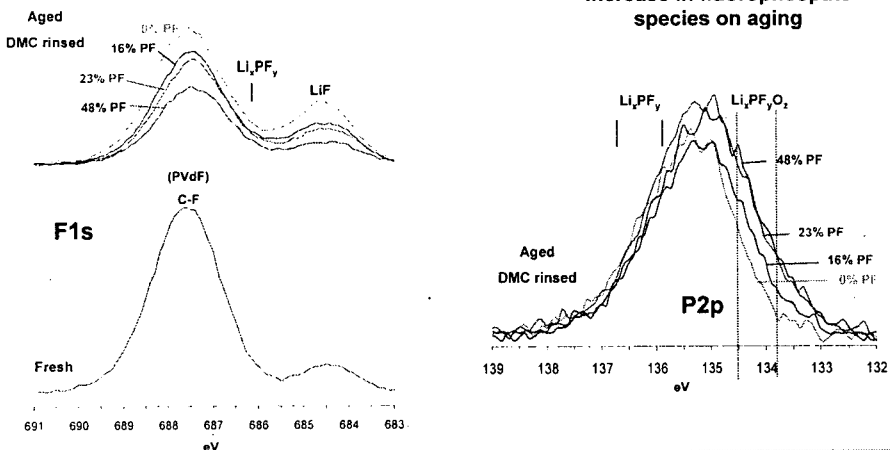


F1s and P2p XPS spectra show abundance of inorganic products on (+) electrode sample surface

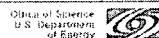
Analysis area ~ 1 mm²
Analysis depth ~ 5 nm

Binder peak intensity lower for aged samples indicating coverage

Increase in fluorophosphate species on aging

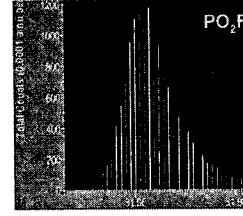
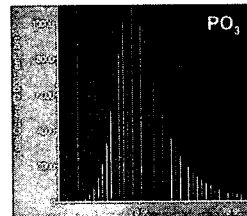
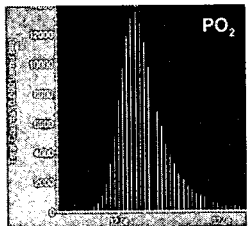
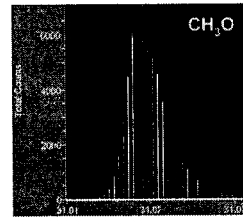
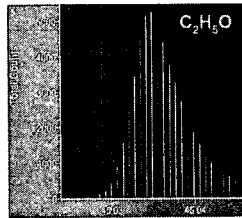
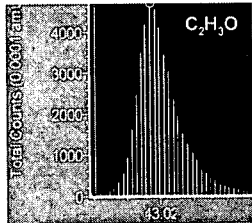


Abraham et al., J. Electrochem. Soc., 149 (2002) p A1358

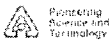


High-Resolution TOF-SIMS Data Show Abundance of R-O and P-O Fragments

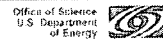
Analysis area = 0.1 mm²
Analysis depth = 1 nm



35% PF cathode, 2h DMC soak



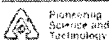
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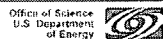
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Oxide analysis data summary

- **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

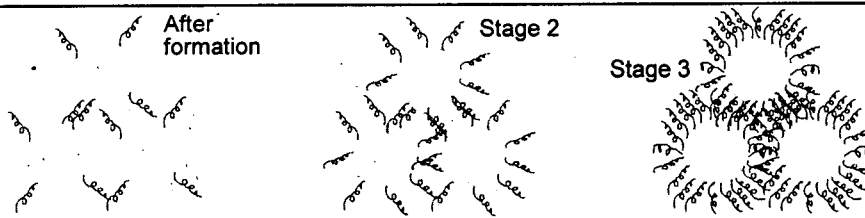


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Schematic showing progressive surface film build-up on oxide particles that can hinder Li-ion diffusion



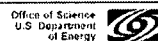
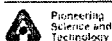
Stages 1, 2 and 3 are probably progressive manifestations of the same phenomenon

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

