Battery Characterization Across Time- and Length-Scales

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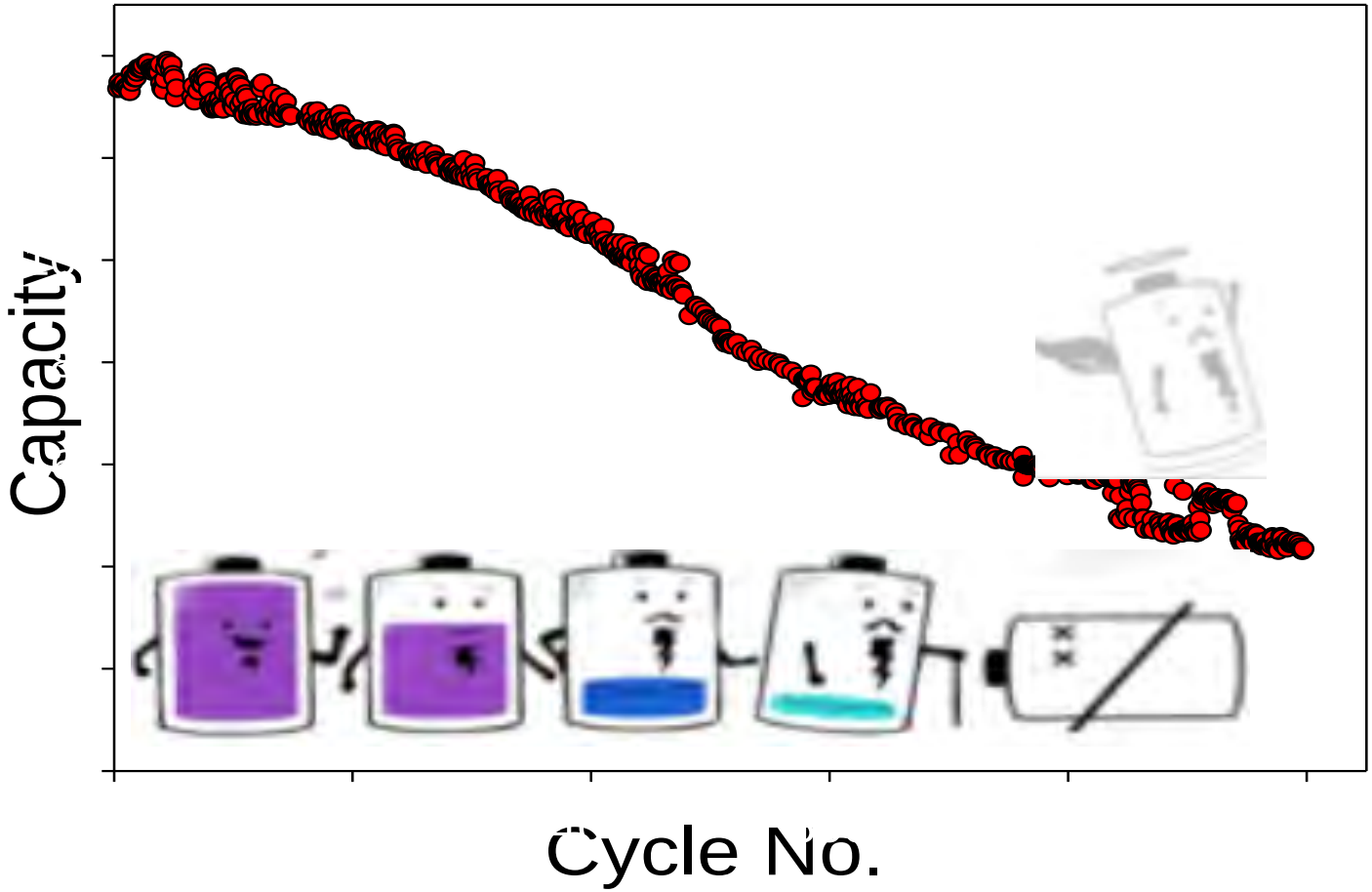
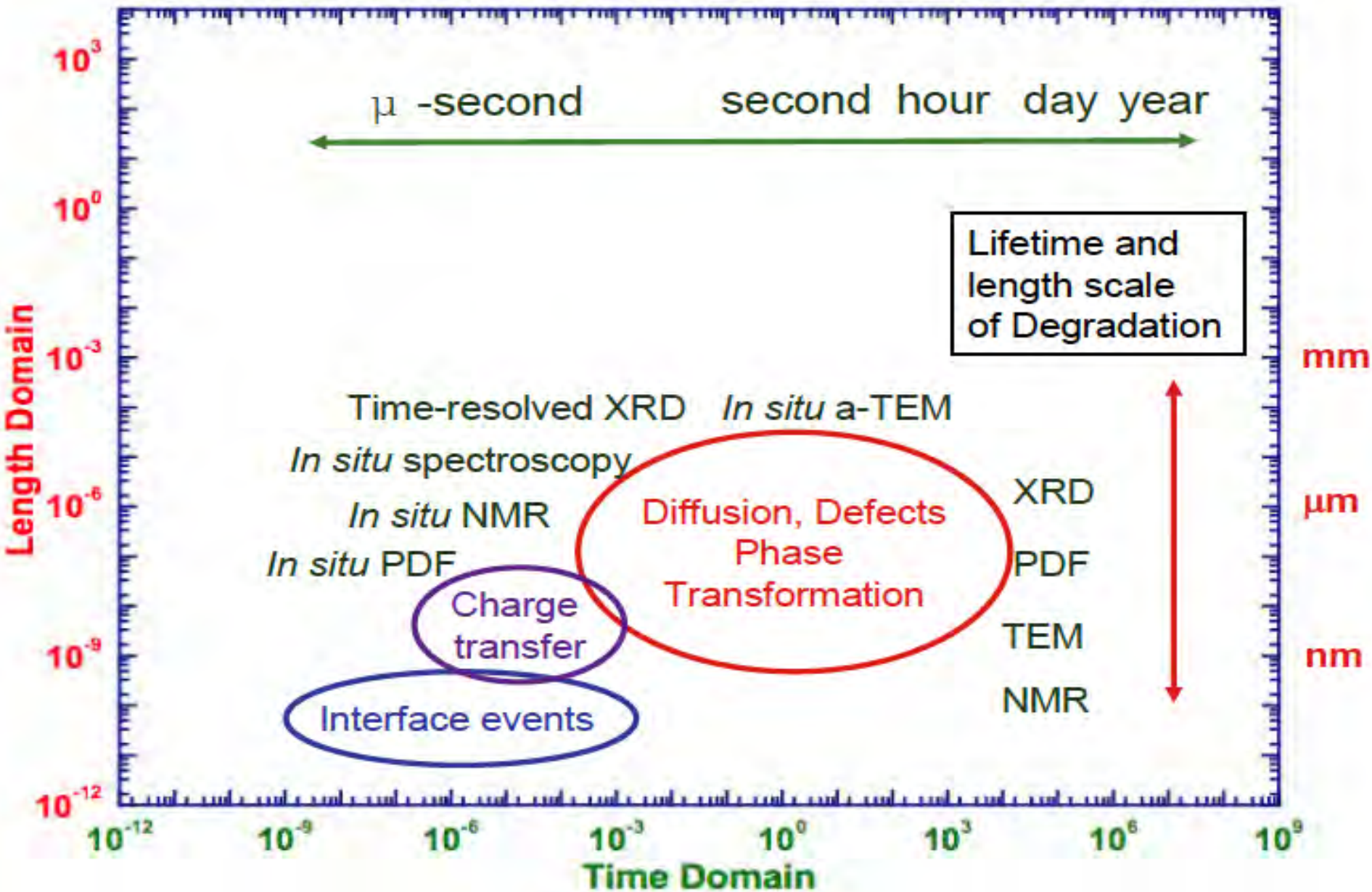
(Li-ion) Battery Cells – Mechanism(s) of Failure



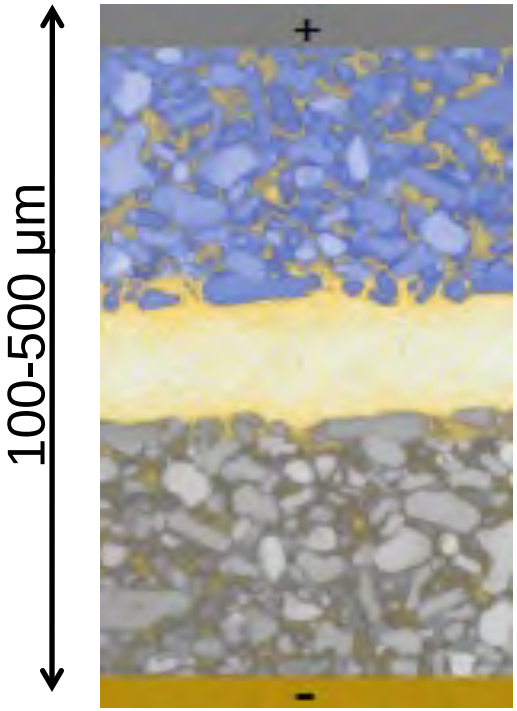
What is the origin and mechanism of these "irreversible" processes that determine cycle- and calendar-life of Li-ion cells?

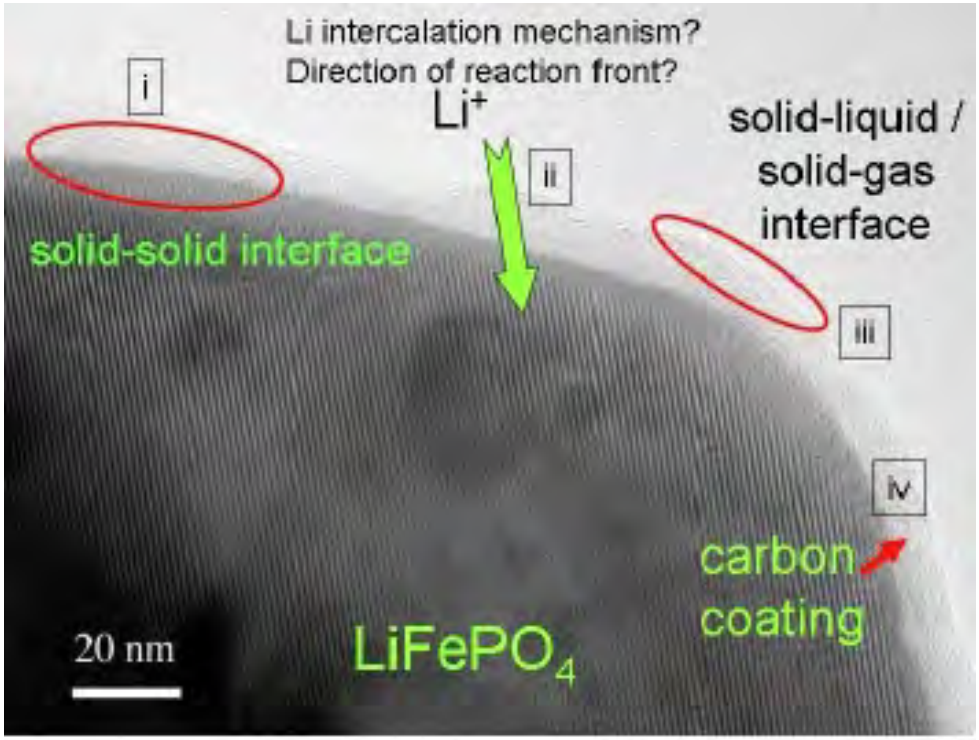
Brief History of Electric Energy Storage Systems Diagnostics



Morphology and Topology of Li-cell

H. Gabrish, UNO

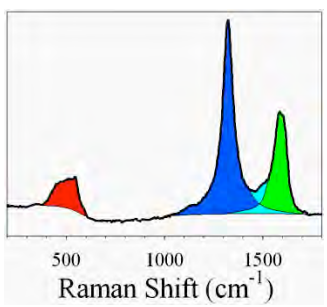




- A battery system involves interactions among various states of matter.
- A simple electrode design must be meticulously optimized for every active material chemistry, particle size, morphology and topology.

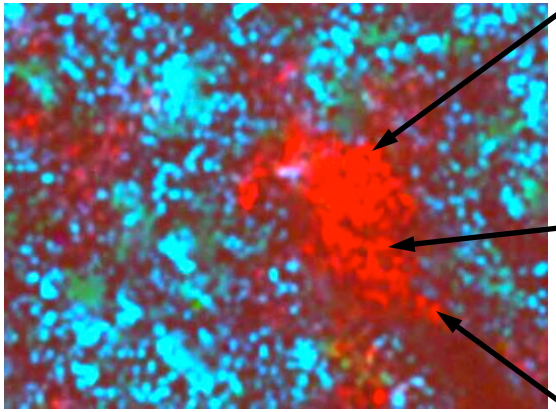
The laminated cell design is strikingly similar to the original design of Volta pile, now more than 200 years old!

Ex situ Micro-Raman Imaging of Tested Composite Cathodes



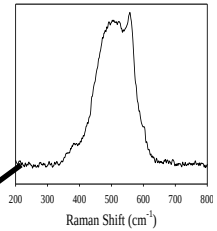
- $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
- graphite
- acetylene black

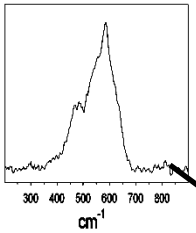
15 µm



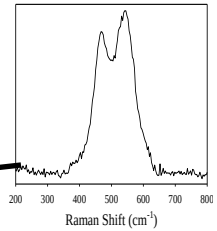
45% of C/2 capacity loss

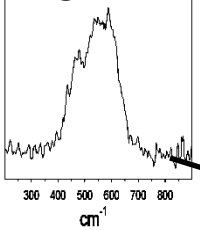
Discharged



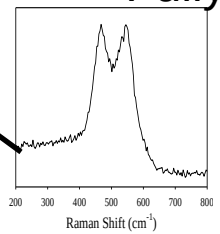


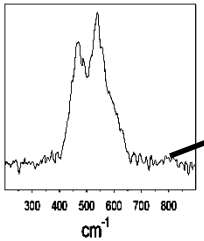
Partially charged



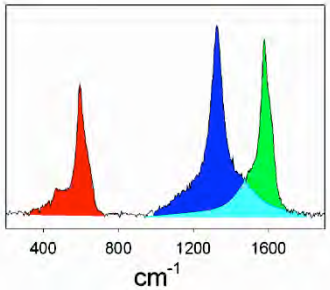


Fully charged

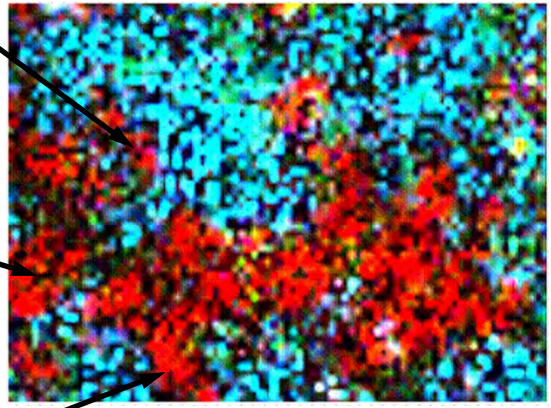




- $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$
- graphite
- acetylene black



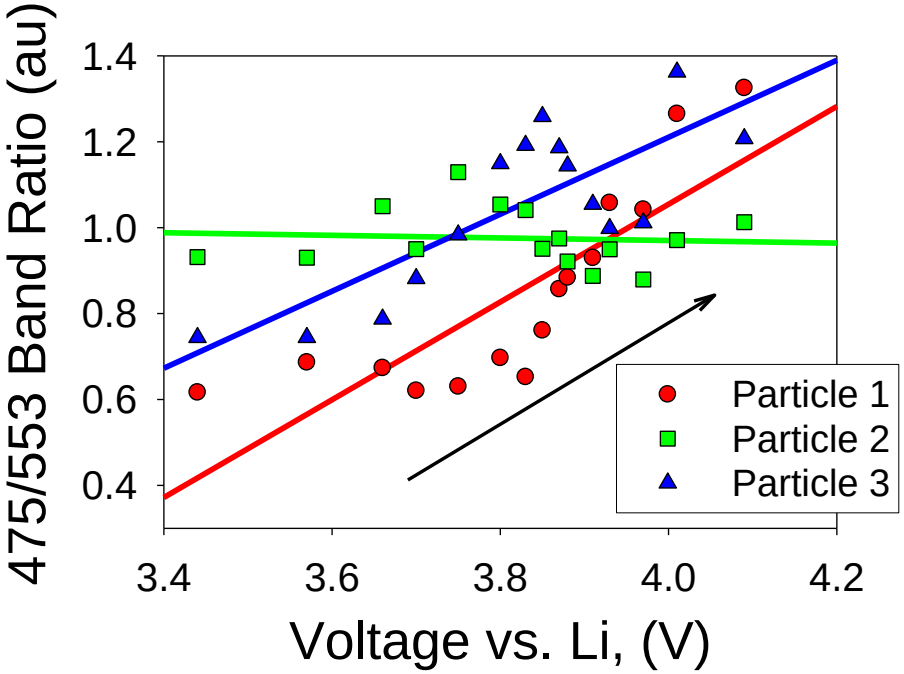
15 µm

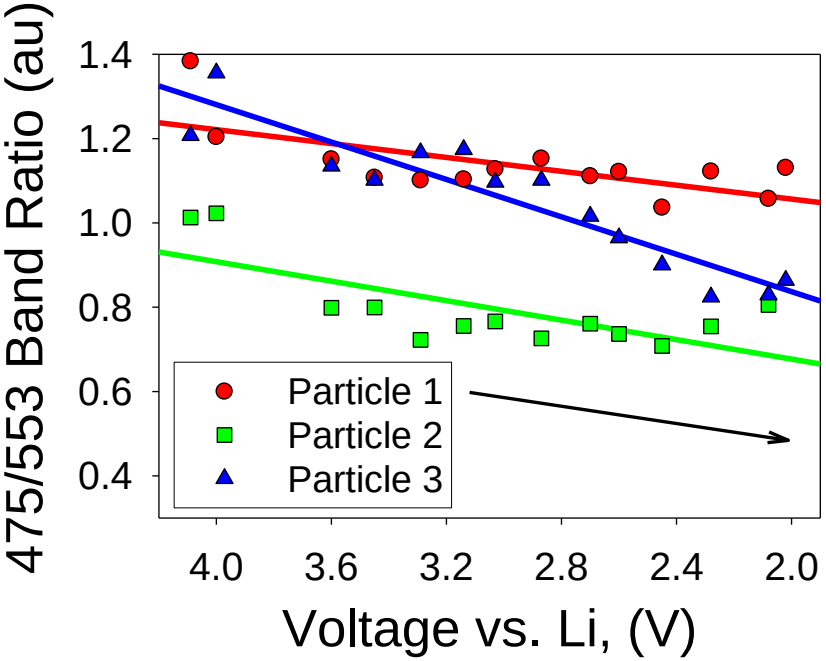


40% of C/2 capacity loss

- Non-uniform final SOC of $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ particles despite deep discharge at the and of cycling.
- Carbon black retreat/redistribution at the surface of composite electrodes.
- Kinetic barriers: electronic and/or ionic arise during electrode degradation.

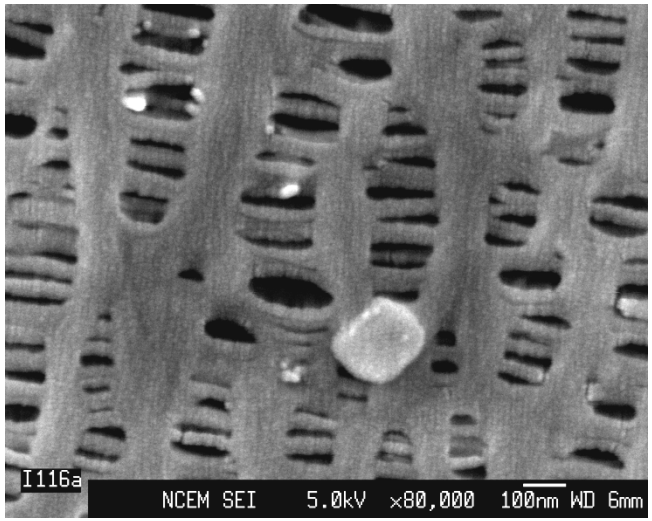
Charge-Discharge Curves of $Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ Individual Particles



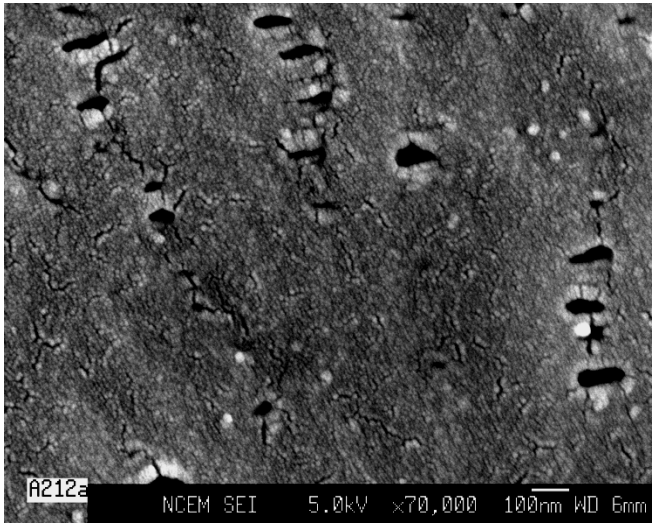


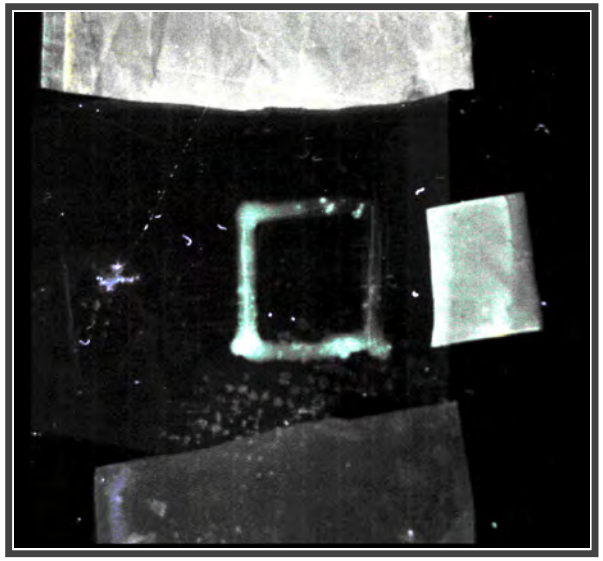
- Non-uniform current distribution in the aged composite cathodes.
- Kinetic barriers: electronic and/or ionic arise during electrode degradation.
- Local electronic and ionic barriers constantly evolve within composite electrodes

Degradation of Li-ion Cells

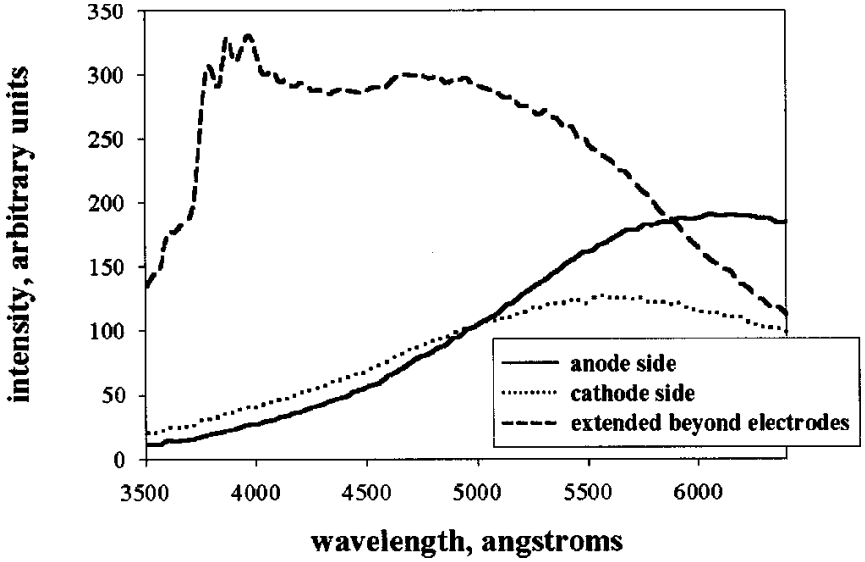


SEM images of separators from fresh and cycled cells





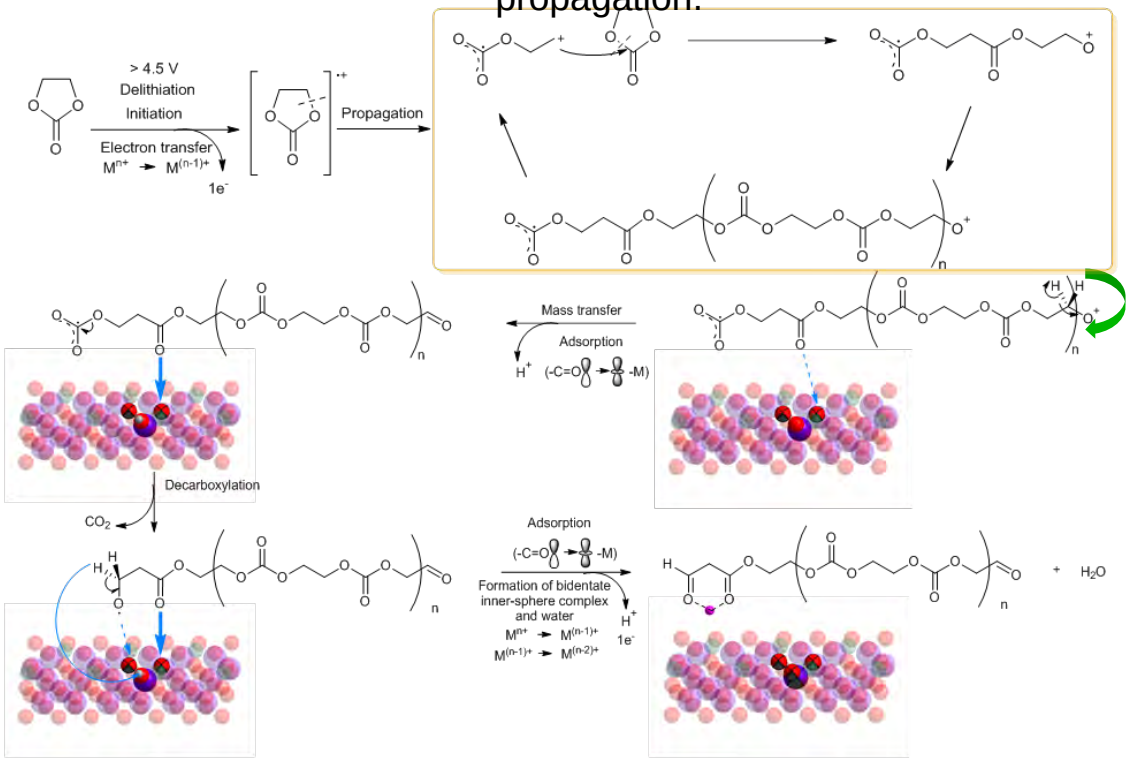
Fluorescence spectra of aged separator



Kostecki et al, J. Electrochemical Society, 151, A522 2004

The Mechanism of Formation of Mn and Ni β-diketone Complexes at $LiNi_{0.5}Mn_{1.5}O_4$ Cathode

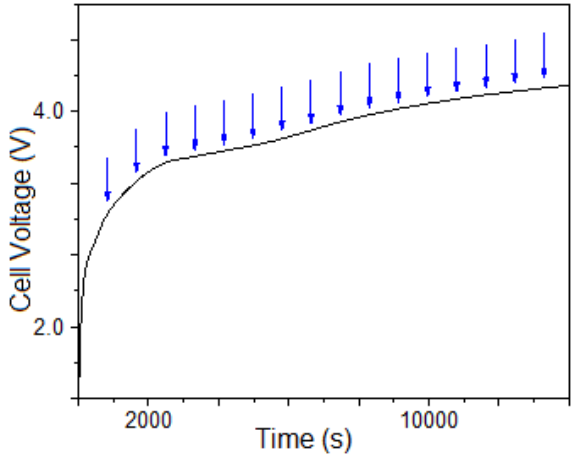
- EC oxidation occurs preferentially at Ni^{4+} sites in the presence of oxygen vacancies at the LMNO surface.
  - EC oxidation occurs via two PCET reactions, β-diketone ligand adsorption and polymer side-chain propagation.

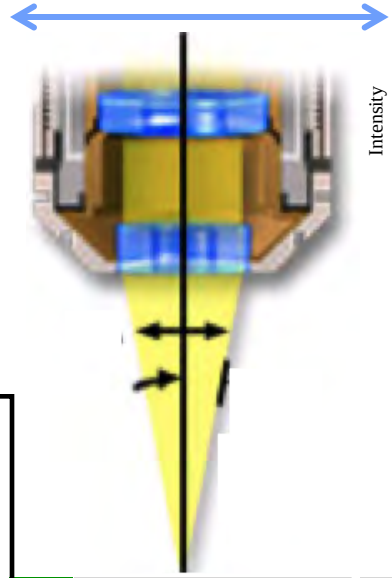


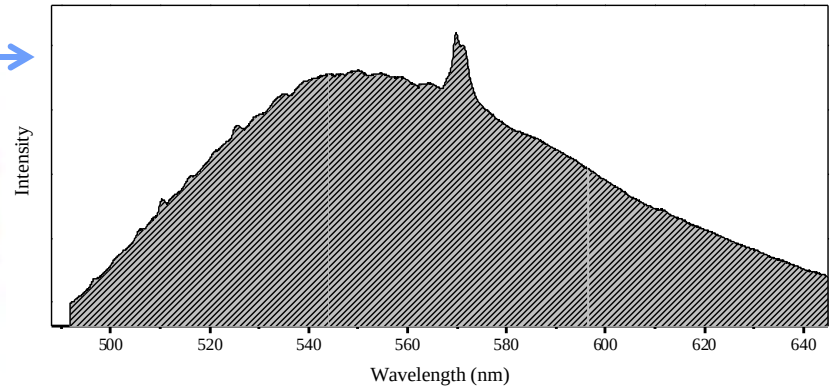
- EC oxidation leads to the formation of insoluble Mn^{III}/Mn^{II}(β-diketone) and Ni^{II}(β-diketone) fluorescent complexes with long polymer side-chain.
- Decarboxylation reaction of EC is also valid for the mechanism of formation of Mn/Ni oxalates and Mn/Ni carbonates, which are found among electrolyte decomposition products.

A. Jarry, S. Gottis, Y.-S. Yu, J. Roque-Rosell, C. Kim, J. Cabana, J. Kerr, R. Kostecki, Journal of the American Chemical Society, 137 (2015) 3533

In Situ Fluorescence Studies of Chemical Cross-Talk in Model Li-ion Cells







Positive Electrode:

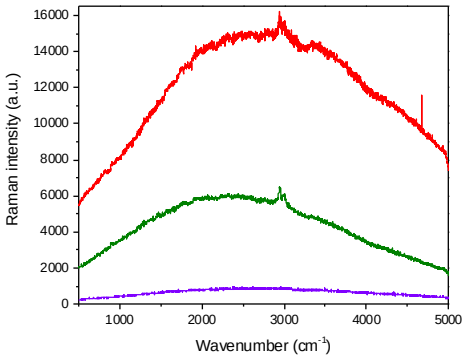
86 %wt Toda-HE-5050 NMC
8%wt Solvay 5130 PVDF binder
4%wt Timcal SFG-6 graphite
2 %wt Timcal Super P
6.9 mg/cm^2 active-material loading density
37.1% electrode porosity
35-µm-thick coating
15-µm-thick Al current collector

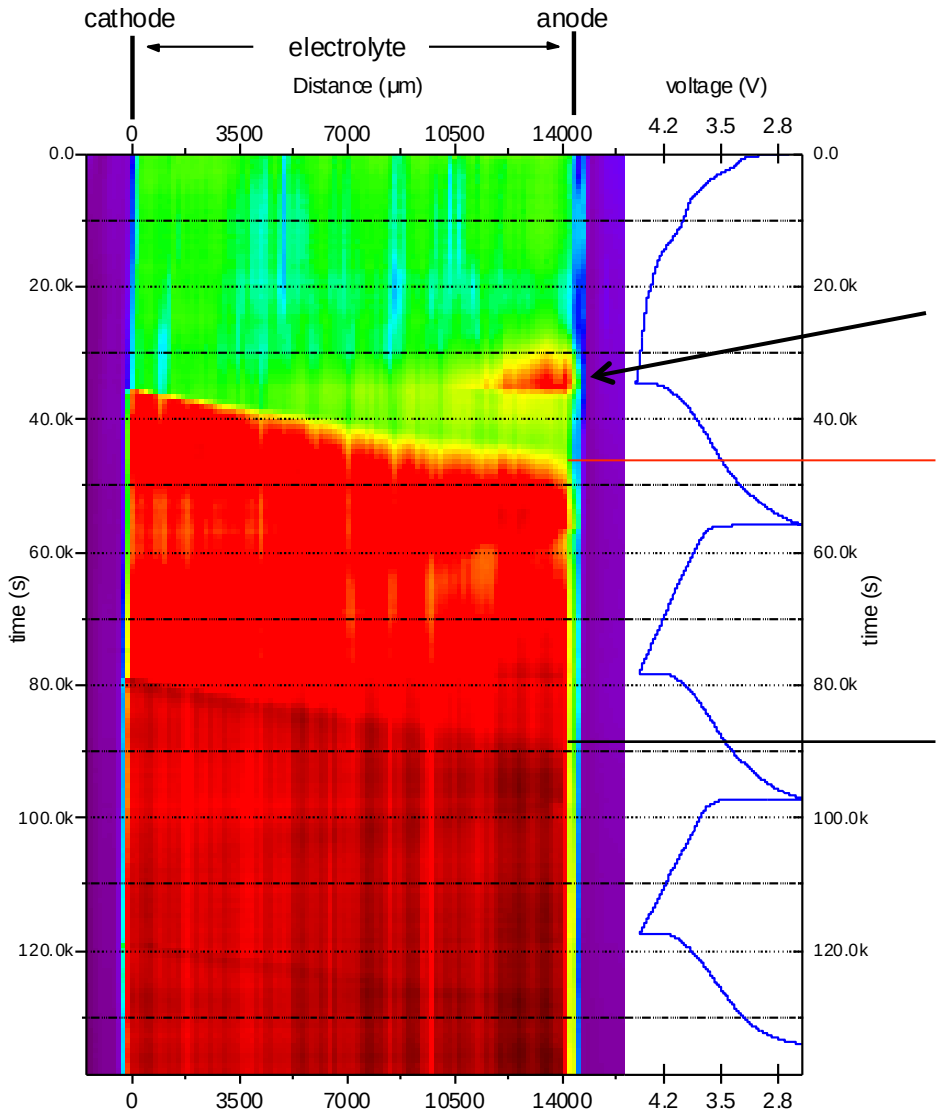
Negative Electrode:

89.8 %wt ConocoPhillips: CGP-A12 graphite
6%wt KF-9300 Kureha PVDF binder
4 %wt Timcal Super P
0.17 %wt Oxalic Acid
5.7 mg/cm^2 active-material loading density
26% electrode porosity
40-µm-thick coating
10-µm-thick Cu current collector

Interfacial reactions products contribute to the electrolyte fluorescence background which changes upon cell polarization

In Situ Fluorescence Studies of Chemical Cross-Talk in Model Li-ion Cells



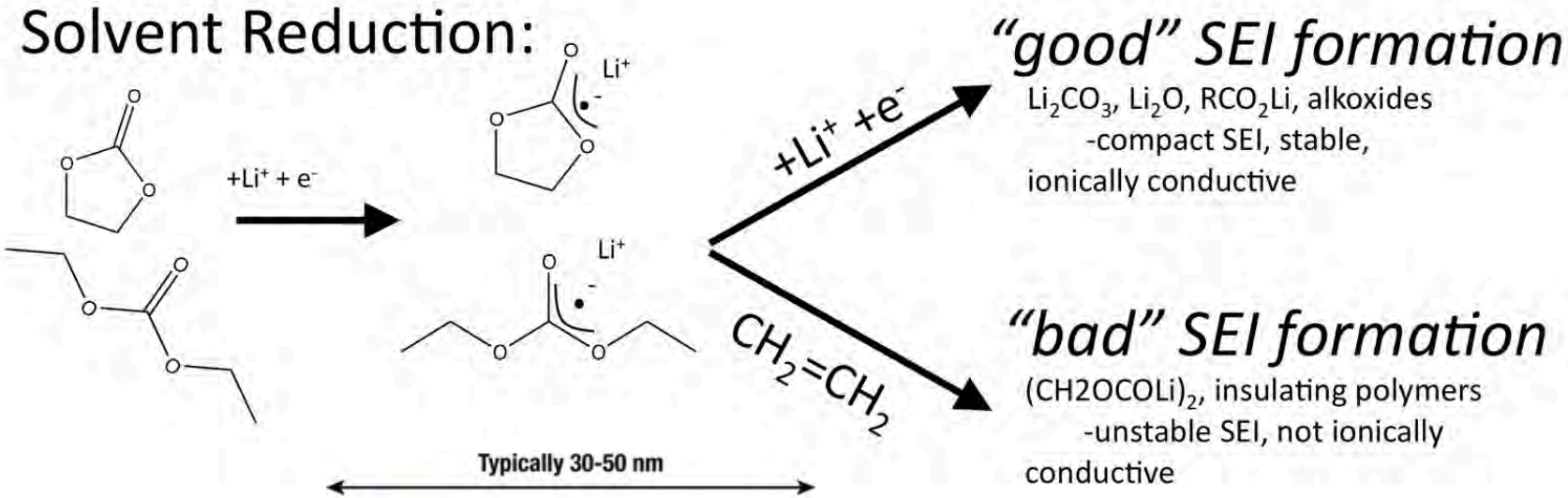


SEI formation on the graphite

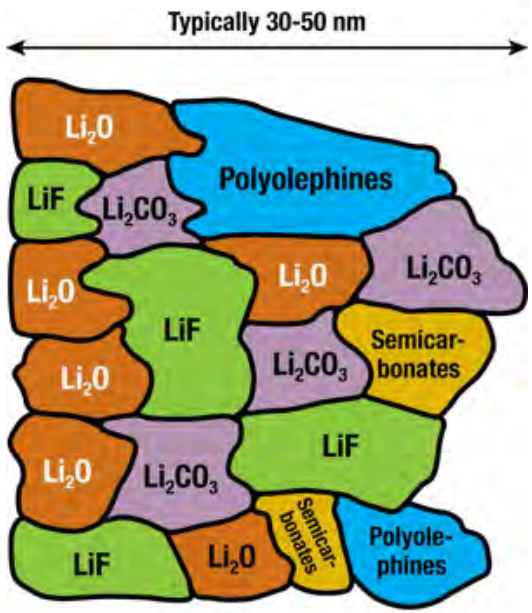
Products formed on the cathode migrate to the anode

Similar process repeats itself in 2nd cycle

Formation of Solid Electrolyte Interphases at Negative Electrodes



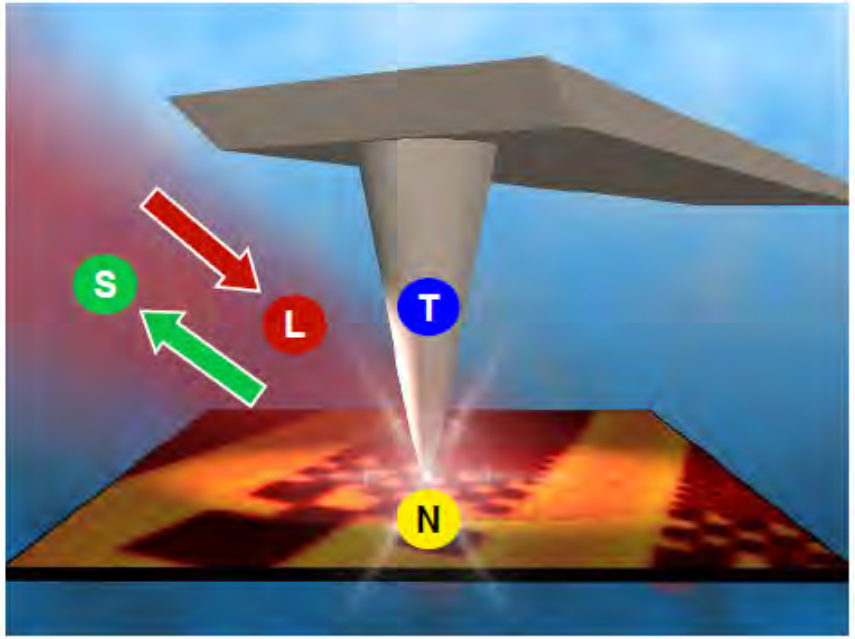
http://webb.cm.utexas.edu/research/research_SEI.html



SEI Interface:
Lithium Intercalation into Graphite

Near-Field Microscopy

Simultaneous measurement of mechanical topography and optical near-fields



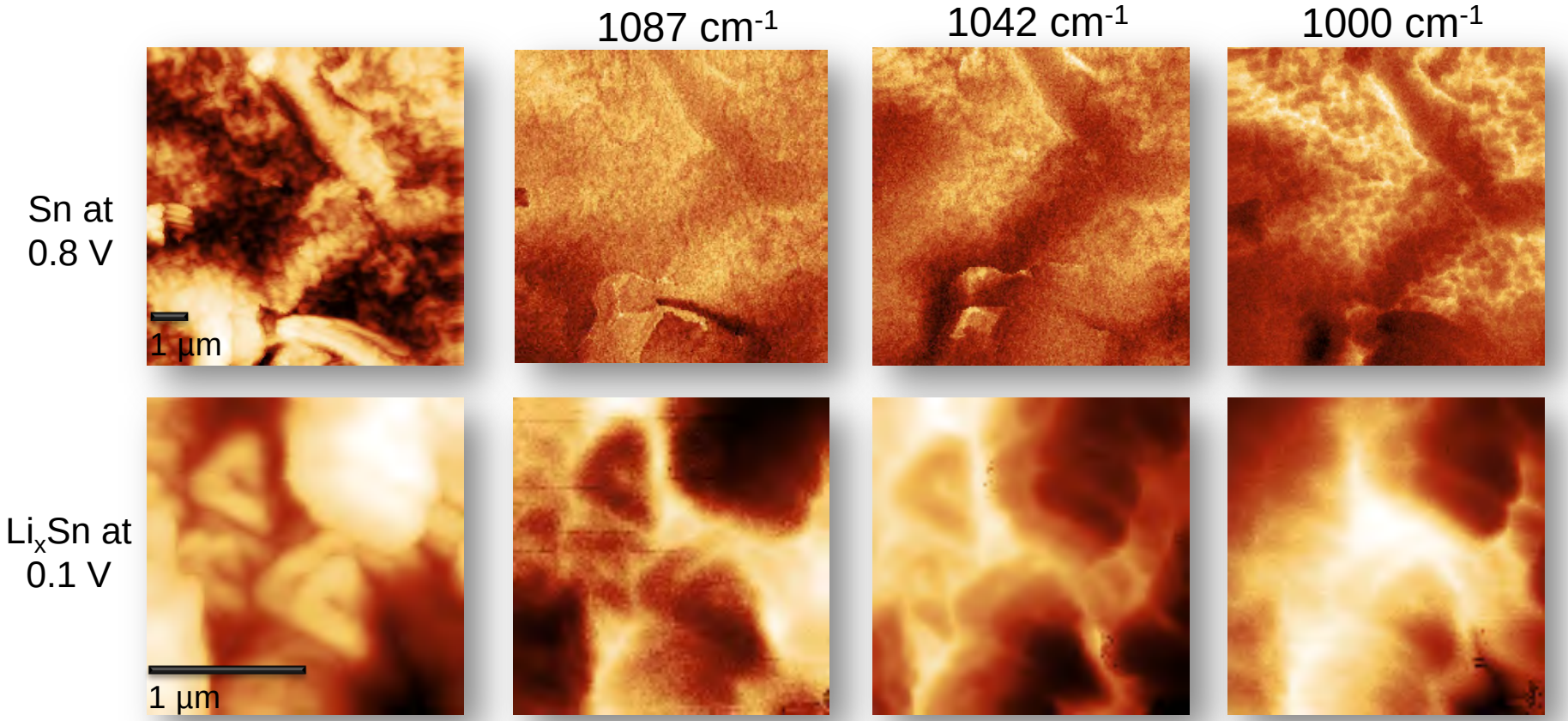
- A focused laser-beam L illuminates a commercial AFM tip T
- The tip generates a nano-focus N about the size of the tip-radius of 10 nm (Lightning Rod Effect)
- The near-field interaction between the tip and the sample modifies the **elastically**-scattered light S
- By scanning the sample surface with the tip, an optical image with 10nm spatial resolution is created

Characterize and monitor dynamics of bulk and interfacial elementary reactions

- Very high surface sensitivity and discrimination against species in solution
- Nanometer scale (<100nm) *in situ* imaging with high spectral and temporal resolving power

Near-Field IR Imaging of SEI

Topography **Near-Field IR Images at Single Wavelengths**



- Topography and IR chemical composition images were recorded in a single measurement
  - Structural and chemical information in a single step at 20 nm resolution
- Changes in N-F signal intensity and contrast as the function of the incident IR wavelength represents variations of SEI layer chemical composition

e^- →

← Li^+

SEI

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