Studies on the Local State of Charge (SOC) and Underlying Structures in Lithium Battery Electrodes

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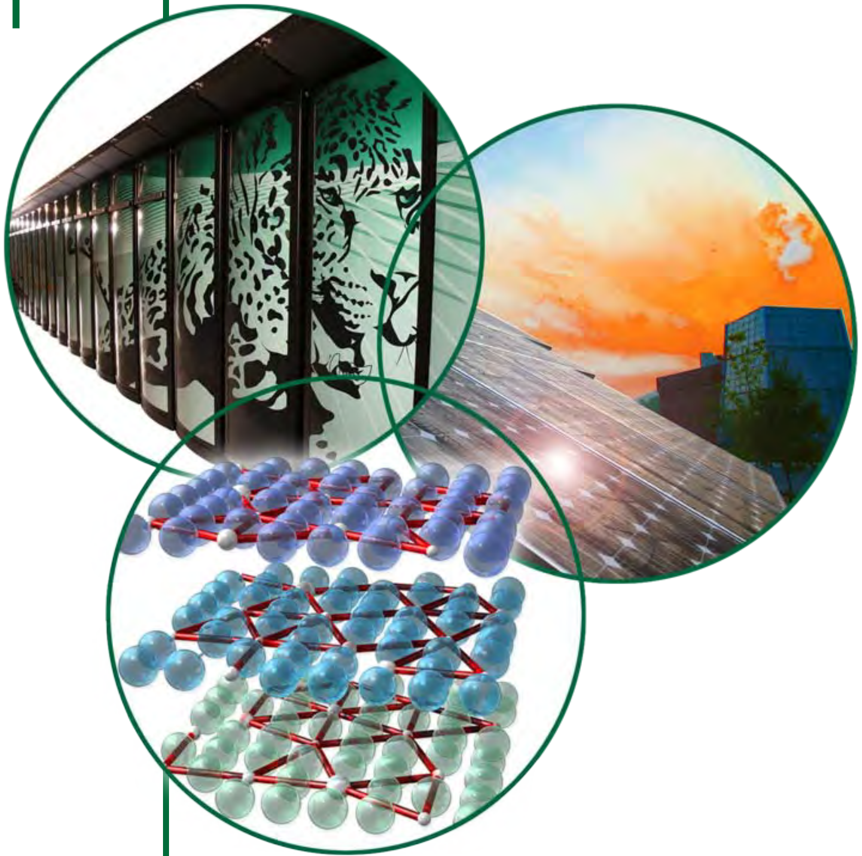
Oak Ridge National Laboratory



DOE Annual Merit Review
Energy Storage
May 12th 2011
Arlington VA

Project ID: ES106

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

Project Start Date : 10/1/2010 (FY2011)

Percentage Complete : 65%

Barriers

Cycle life and Capacity fade

Rate Performance

SEI Stability

Surface Degradation and Structural changes

Budget

FY 2010 : 230K

(June Fin Plan : Capital request)

FY 2011 : 400K

Collaborators/Partners

Dr. S. K. Martha
Post Doctoral Researcher

Non funding partners

Ford Motor Co.

Dawn Bernardi
Raji Chandrasekaran
Andy Drews
Ann O'Neill
Jeffrey Remillard

Toda Inc

Mr. Toyoji Sugisawa

Project Objectives

- **Correlate local electrode and interfacial properties at sub-micron level to the macroscopic electrochemical performance .**

- **Investigate local inhomogenity, composition, structural changes during lithiation-delithiation of high energy lithium electrodes.**

- **Dynamical/*in situ* studies for spatio-temporal mapping of commercial electrodes subjected to stress/abuse.**

Programmatic Milestones

Task 1: Electrode Fabrication and Electrochemical Testing

Subtask 1.1 : Electrochemical performance of Excess Lithia Compositions from Toda Inc.
Progress/Status : Work in progress (70% complete)

Task 2: Ex-situ SoC analysis of commercial and Laboratory Fabricated High Energy Cathodes
Subtask 2.1 Local SoC Analysis of Commercial fresh and degraded $LiCoNiAlO_2$ *(Gen-2) Electrodes*
Progress/Status : Completed (in collaboration with Ford Motor Co.)

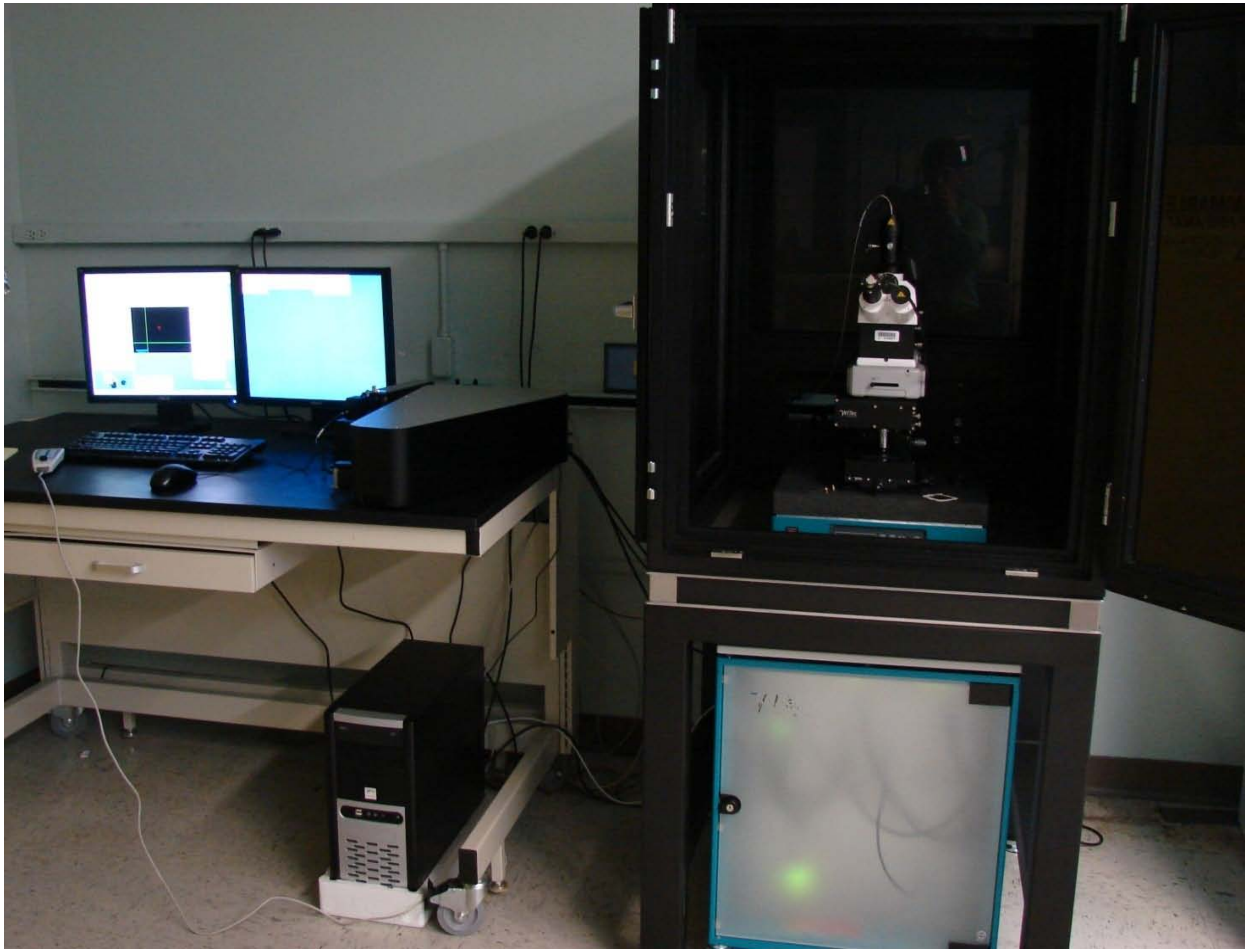
Subtask 2.2 Local SoC studies of high energy Lithium Rich compositions
Progress/Status: Work in progress

Task-3 In-situ SoC and Structural Studies at Cell Level

Subtask 3.1 Development of in-house fabricated optical Raman Cell in "edge" configuration

Progress/Status: Work in progress

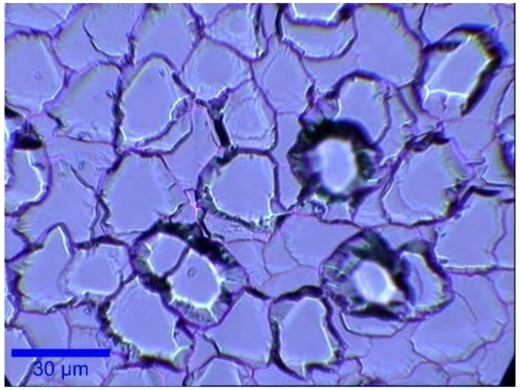
Confocal Micro Raman–AFM Setup



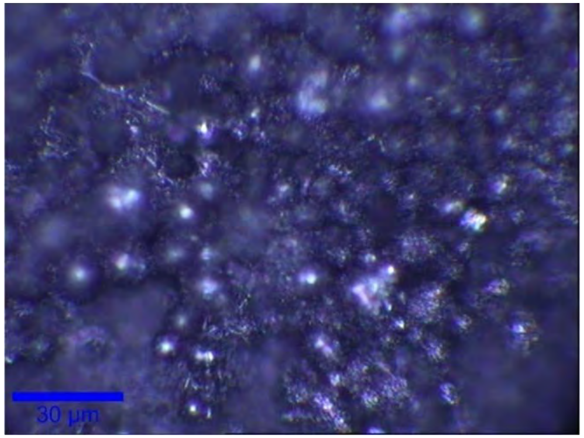
Confocal x-y spatial resolution ~ 350 nm
Confocal along depth (z) ~ 700 nm
Excitation Laser 532 nm

Silicon

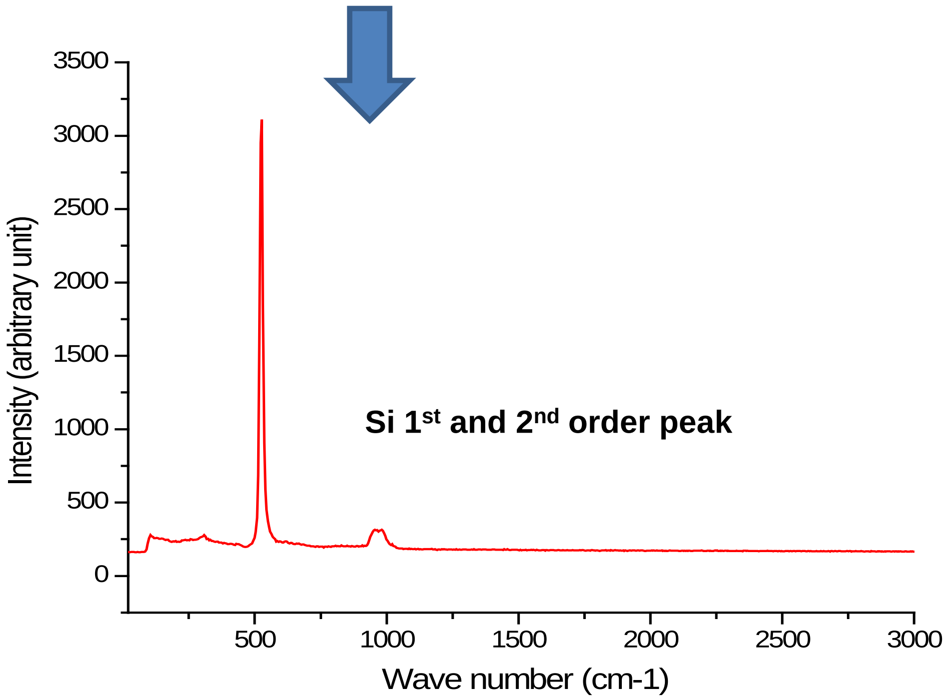
Excess Lithia Composition

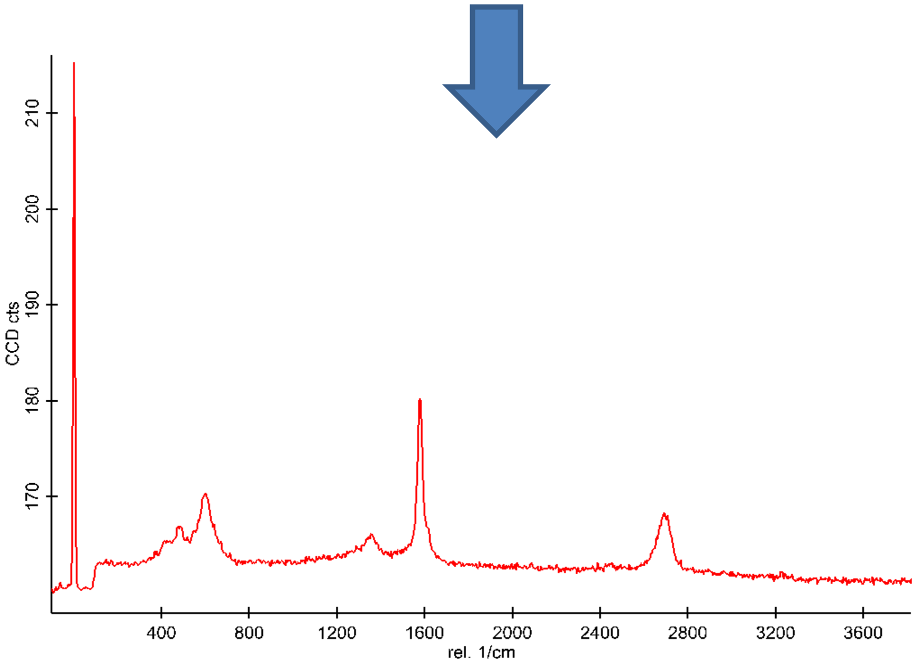


Video Image
50X



532 nm Excitation
Grating 600 lines/mm
50X

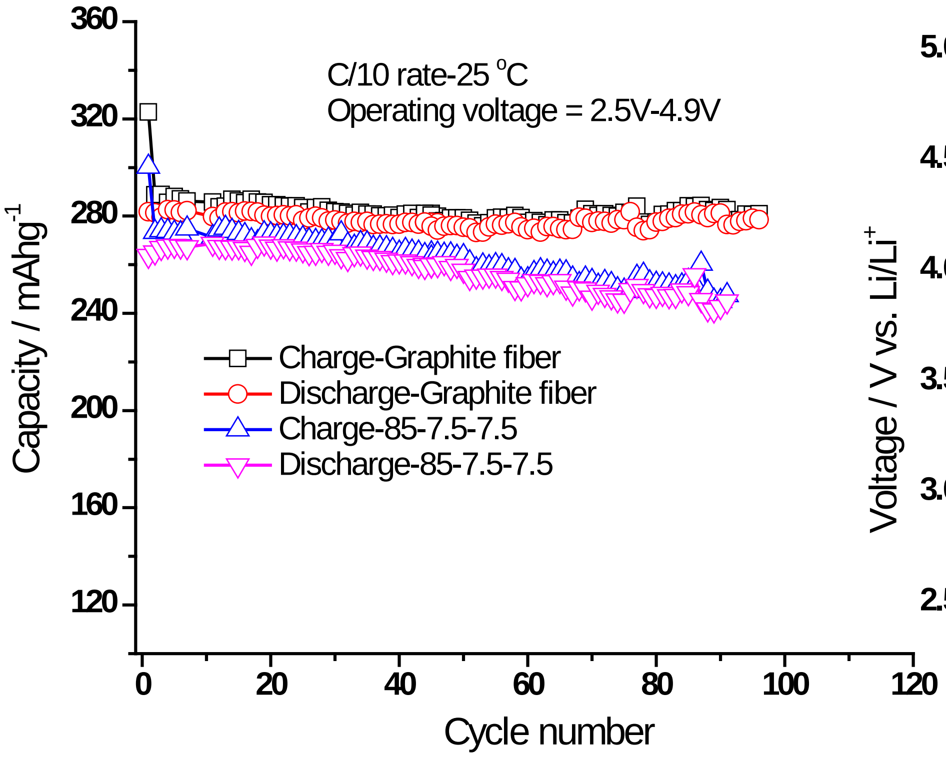


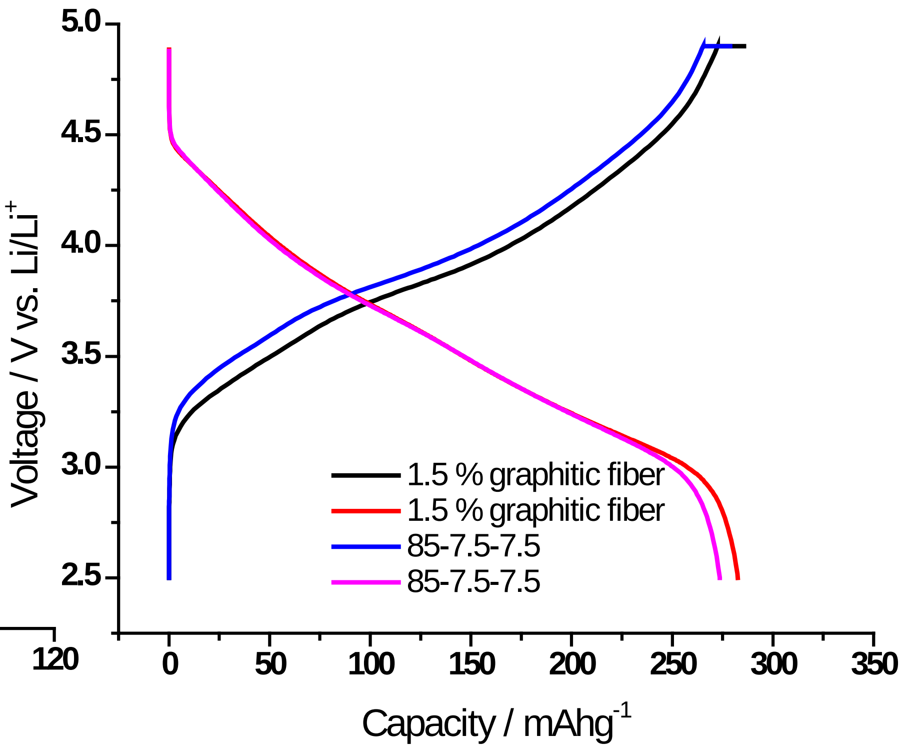


Task-1 Electrochemical Performance of $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$

Two types of composition

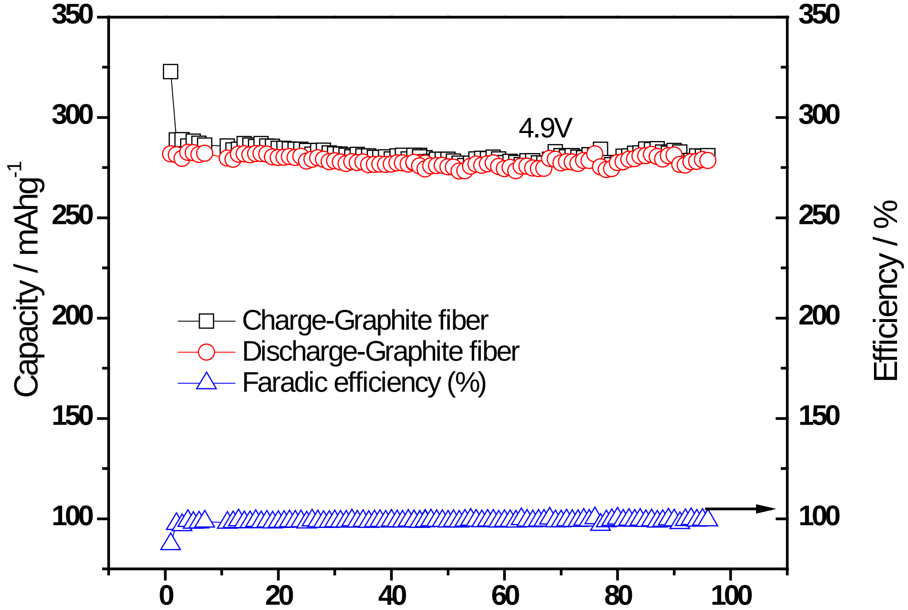
1. **Conventional slurry 85 % active mass- 7.5% each of PVDF and C-black**
2. **Instead of 7.5% C-black- 1.5 % Carbon fiber and 6 % Carbon black**

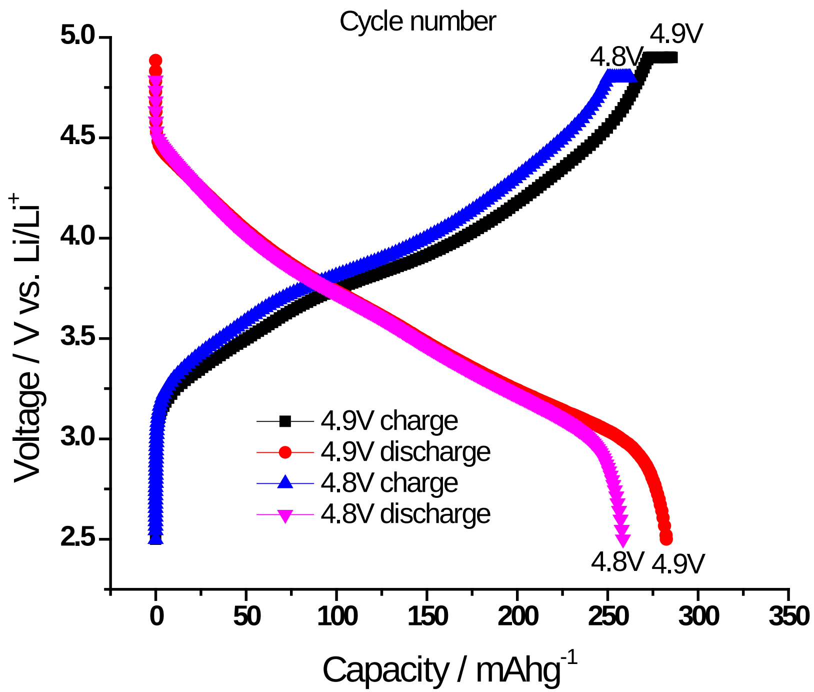




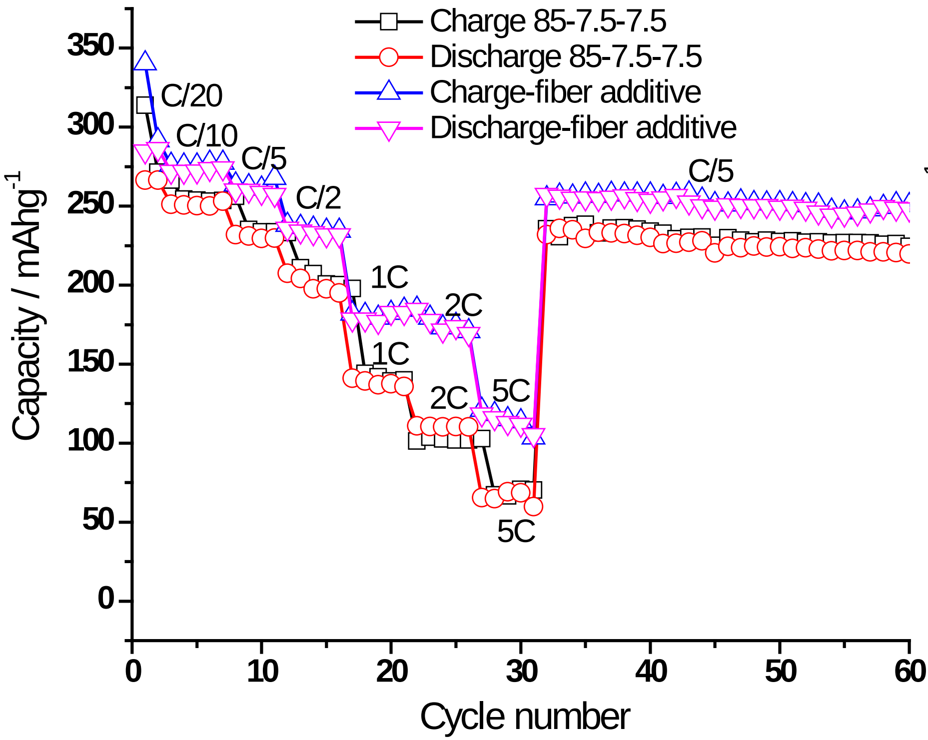
Materials Supplier Toda Inc.

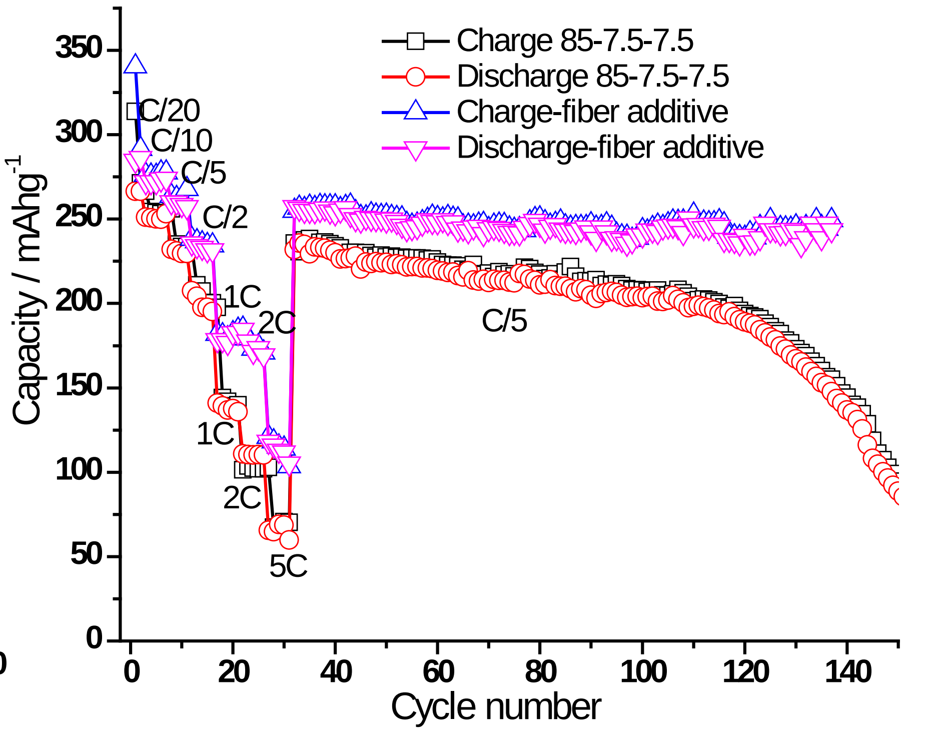
Cycling Efficiency





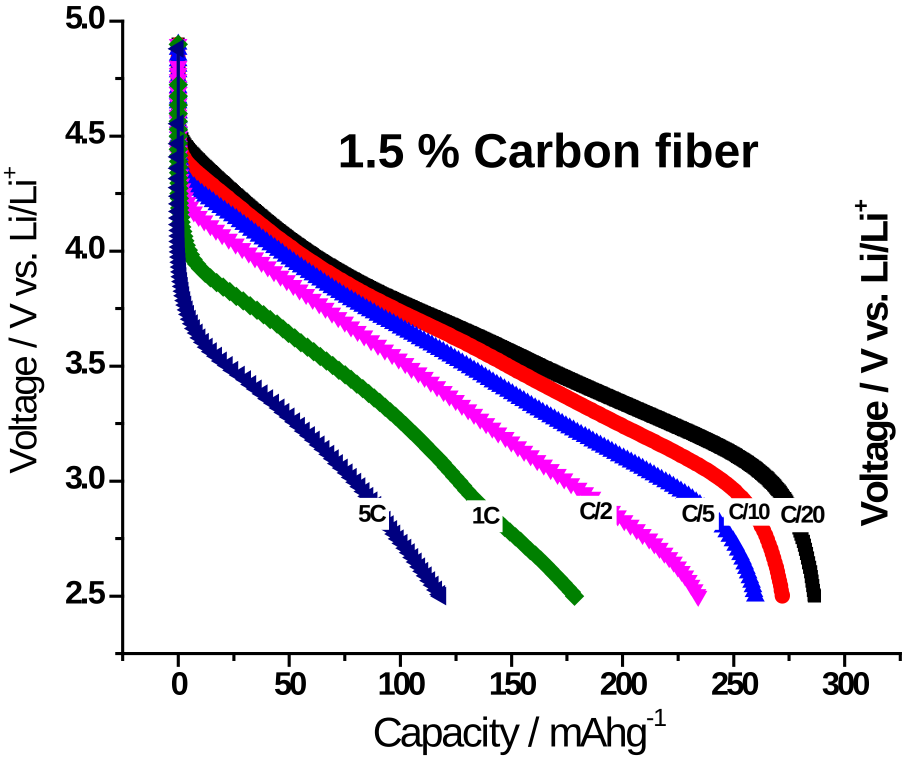
Rate Performance

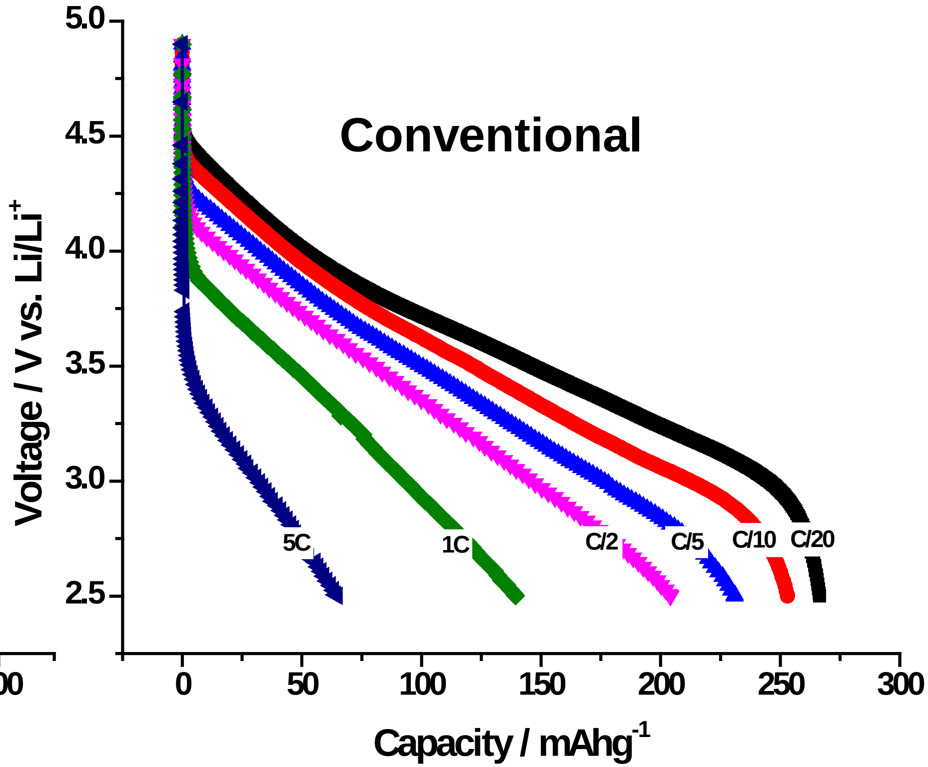




Materials Supplier Toda Inc.

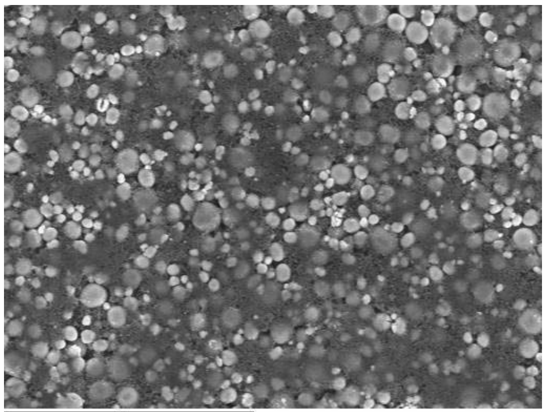
Discharge Capacity : Comparison





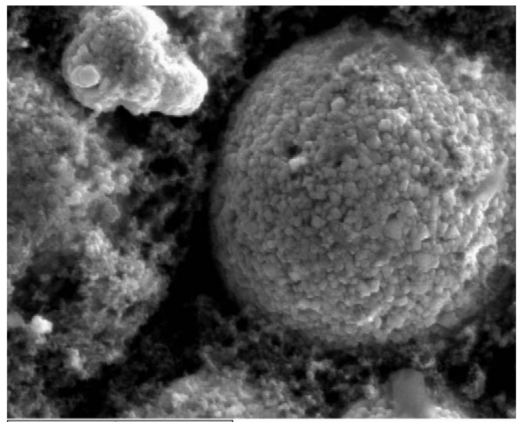
Task-2 Local State of Charge Concept

Electrode



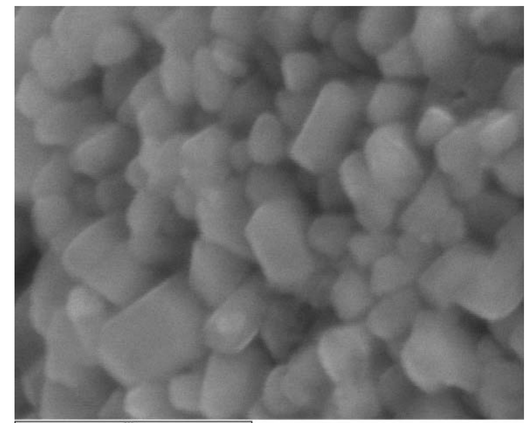
60 µm

Secondary particle



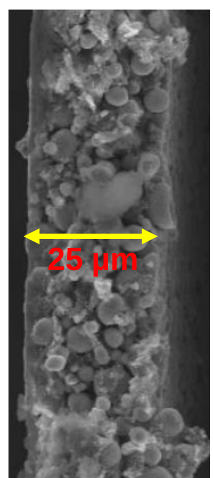
5 µm

Primary particle



700 nm

Edge

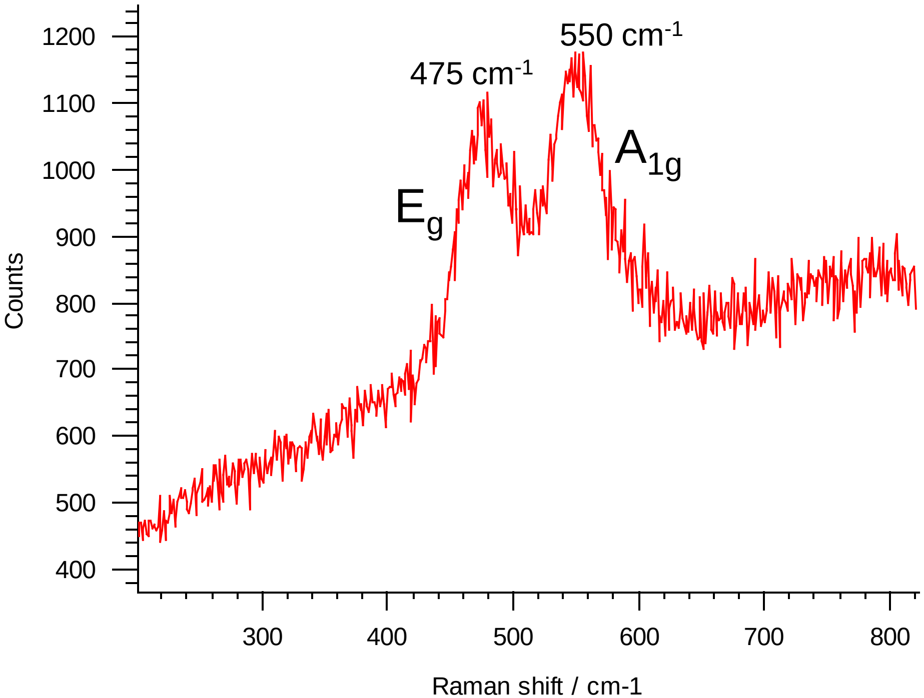


$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA)

$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM)

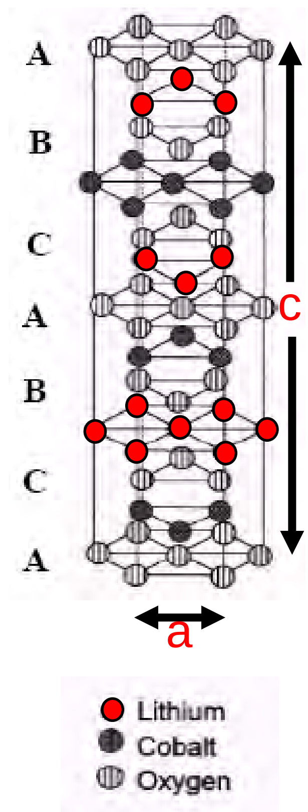
xLi_2MnO_3 (1-x)$LiMO_2$ (Excess Lithia compounds)

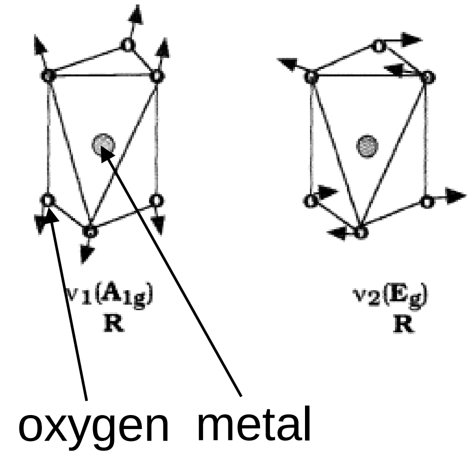
Raman Modes of $LiMO_2$ (M = Co, Ni, Cr)



Charged NCA cathode (3.77V)

α - $NaFeO_2$ structure

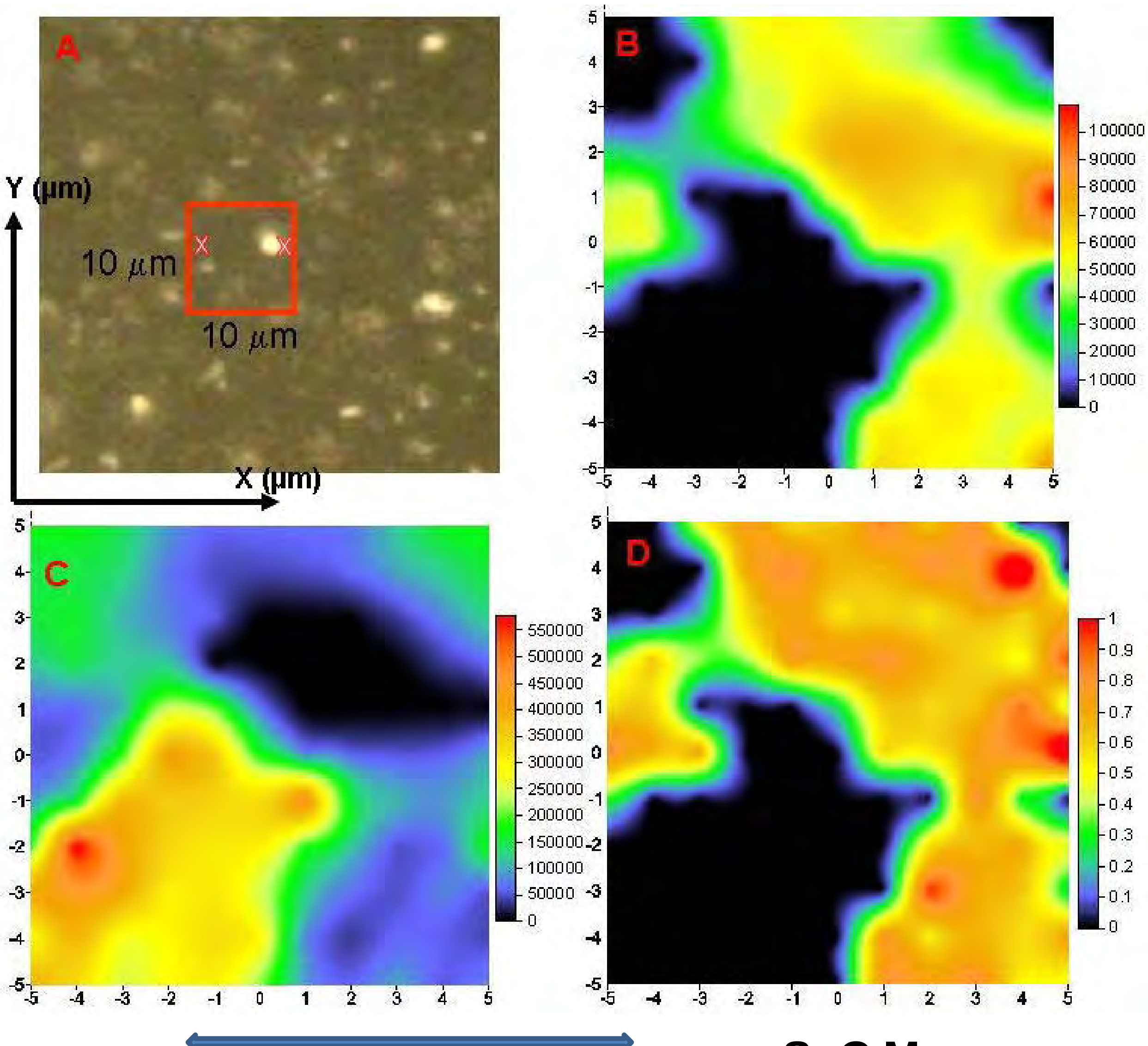




- A_{1g} – oxygen atoms vibrate in opposite directions parallel to c-axis
- E_g – oxygen atoms vibrate alternately in opposite directions parallel to Li and transition metal planes.
- SOC proportional to $A_{475\,cm^{-1}} / A_{550\,cm^{-1}}$ (Kostecki)

Micro-Raman Mapping

NCA

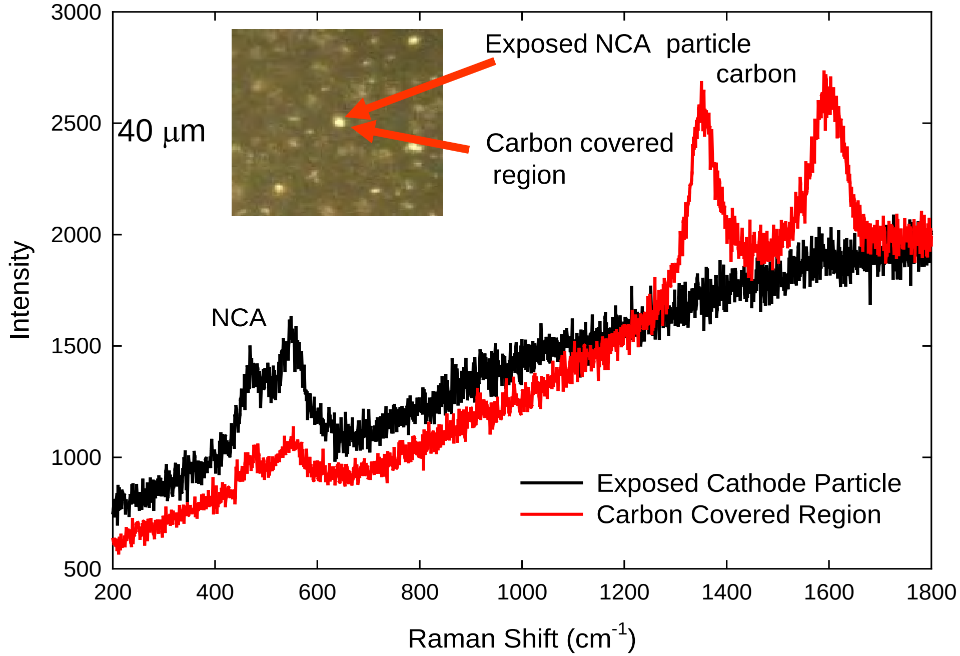


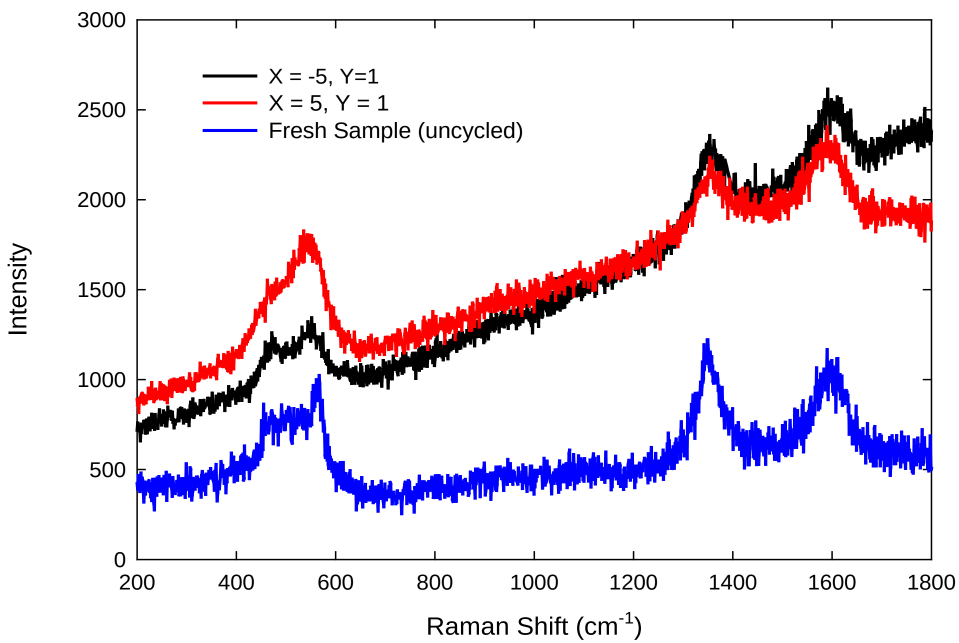
Carbon

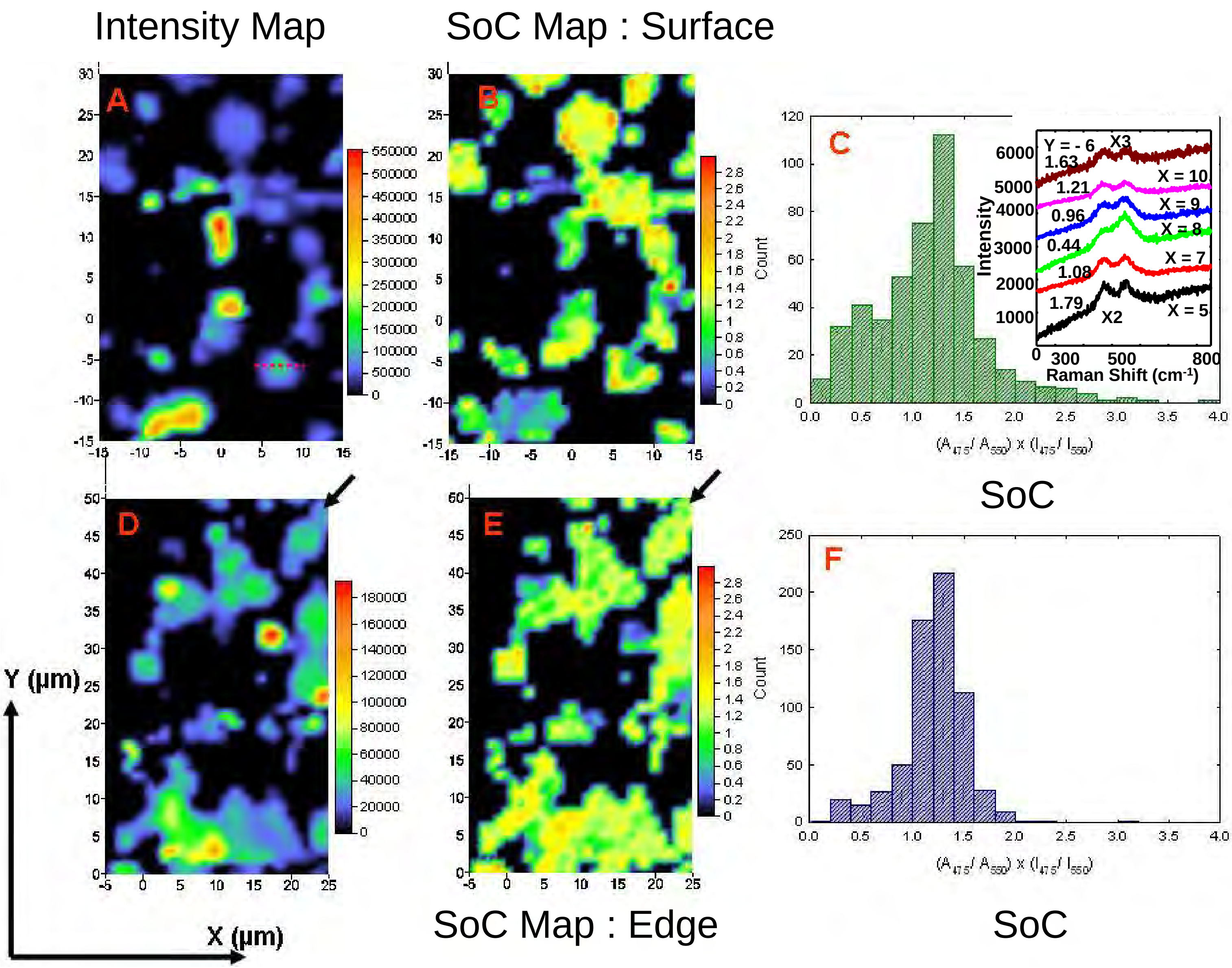
SoC Map

Micron

Carbon Coverage

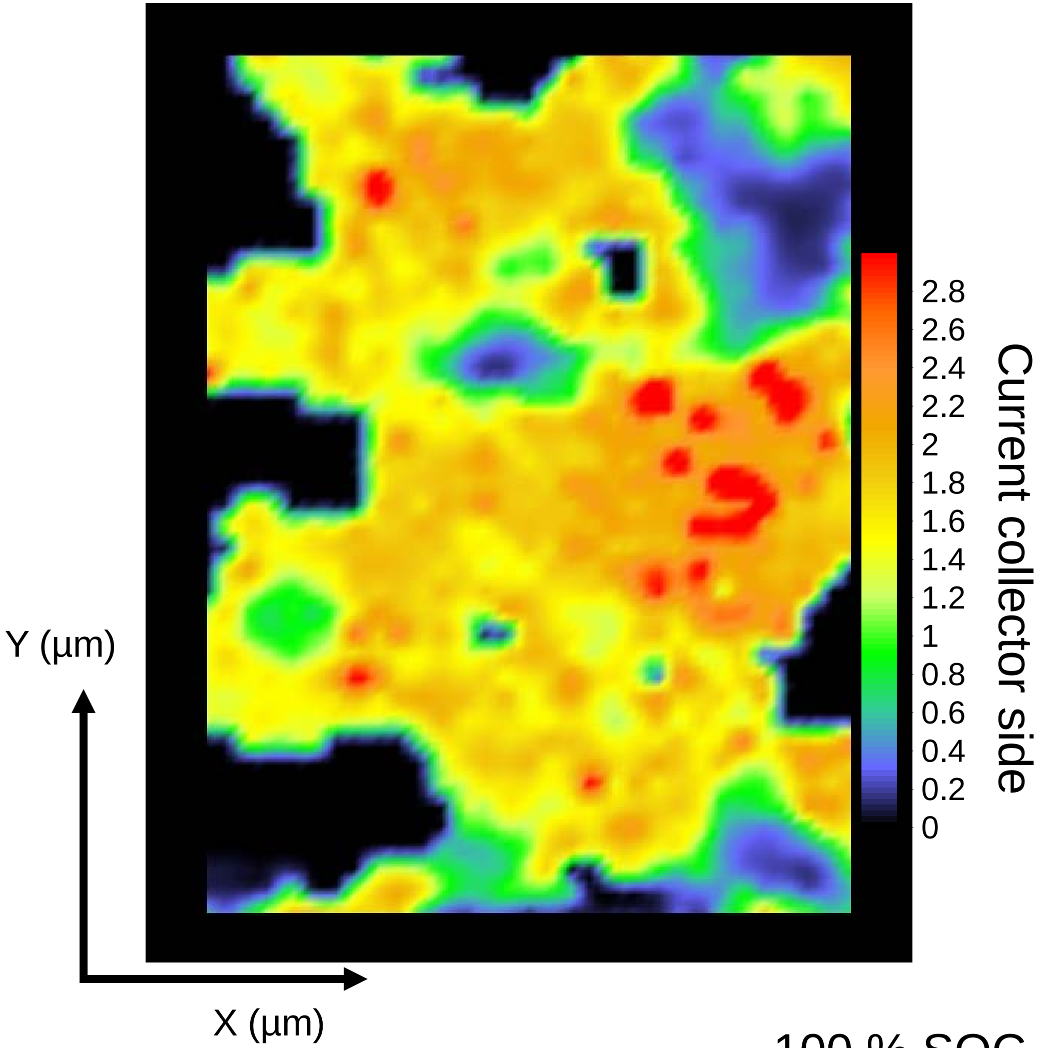






Intensity Map
SoC Map : Surface
A
B
C
D
E
F
Y = - 6
X3
X2
X = 10
X = 9
X = 8
X = 7
X = 5
1.63
1.21
0.96
0.44
1.08
1.79
Intensity
Raman Shift (cm-1)
Count
$(A_{475}/A_{550}) \times (I_{475}/I_{550})$
SoC
Y (μm)
X (μm)
SoC Map : Edge
SoC

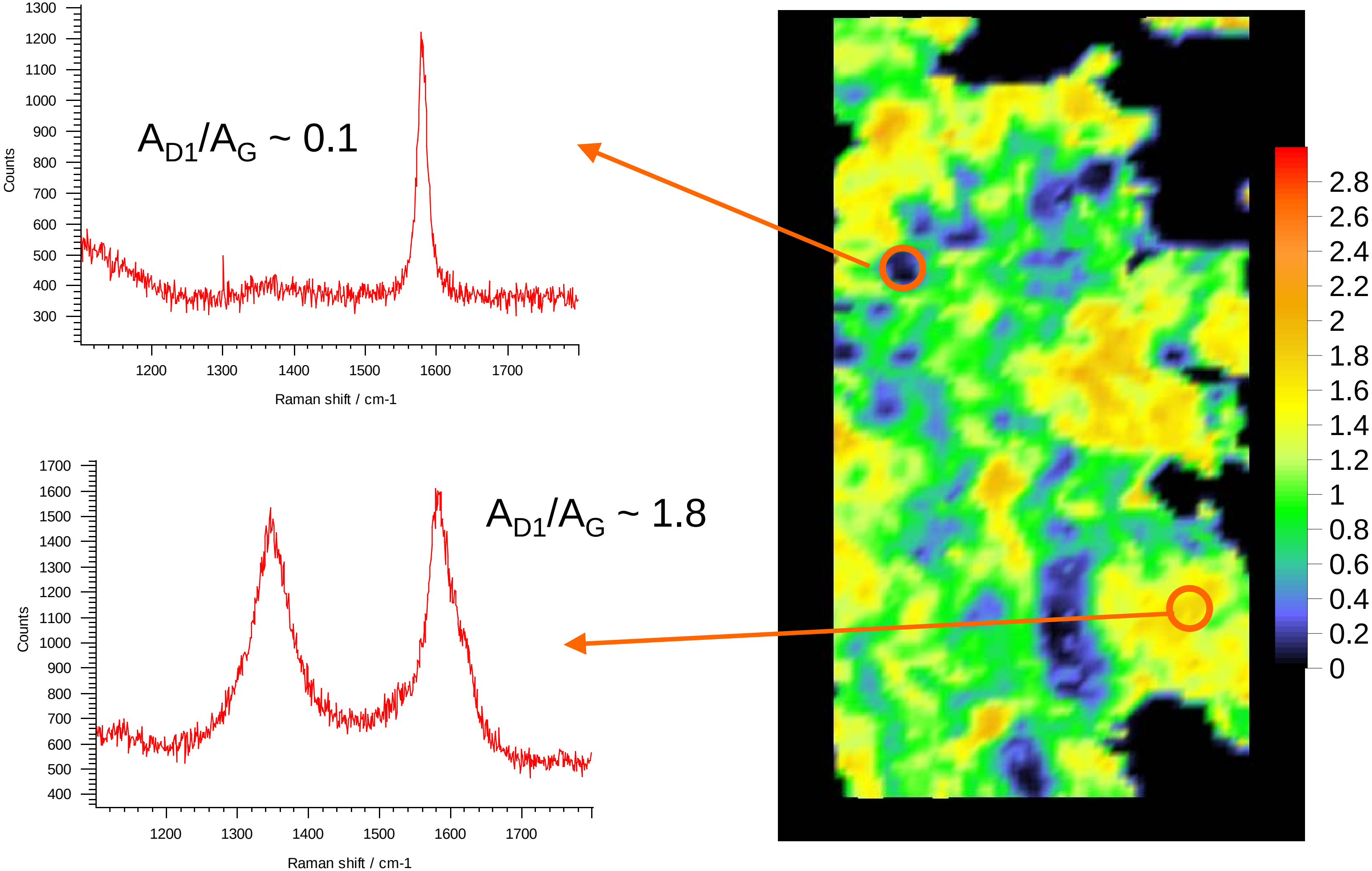
Severely Degraded Electrodes



100 % SOC

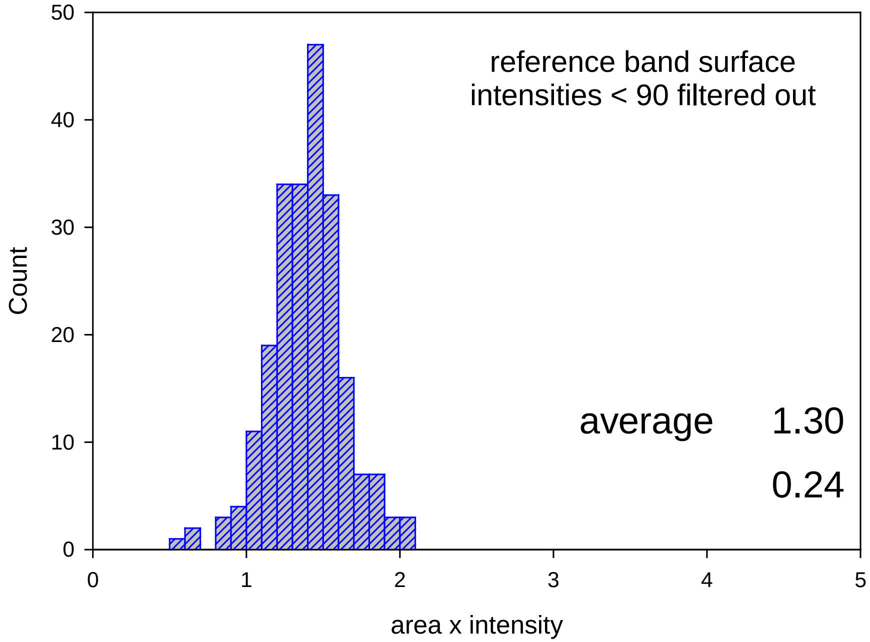
45 ^{o}C; 22% SOC swing

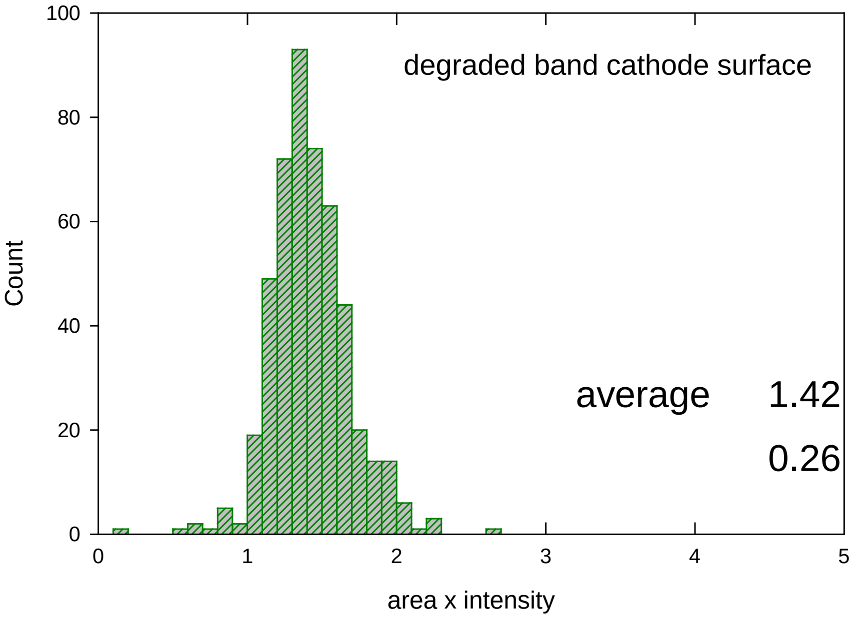
The Anode Story

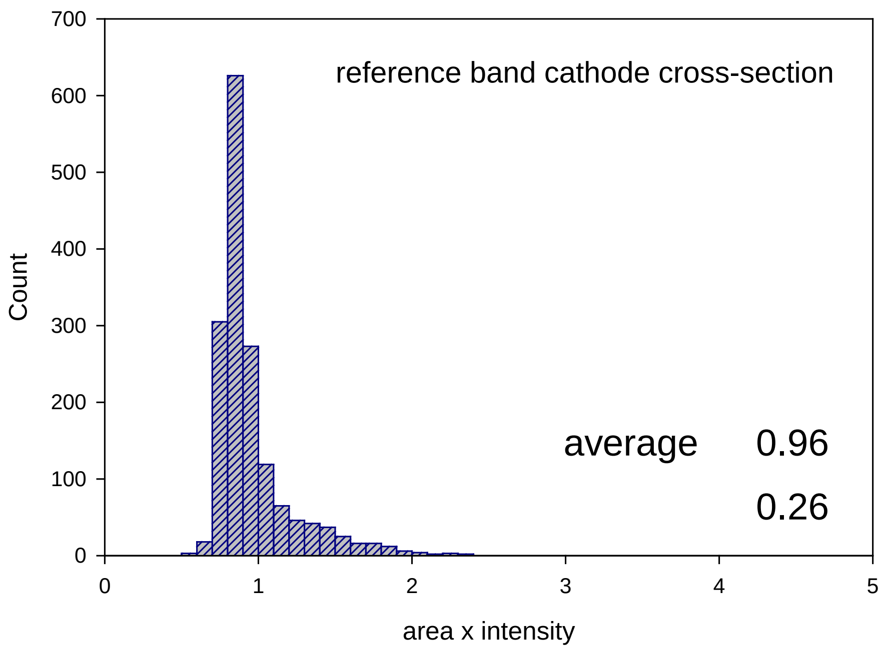


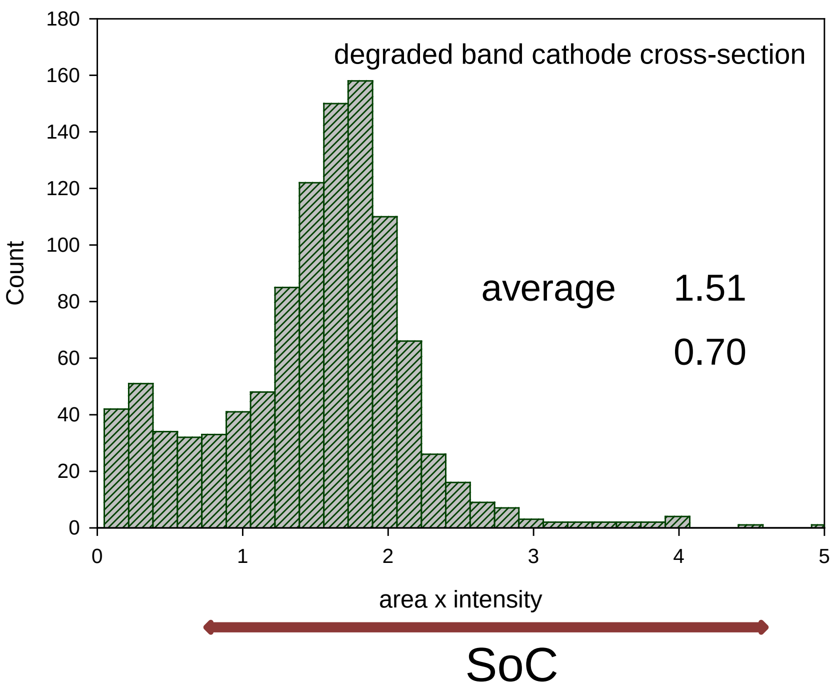
Spatial anode maps of A_{D1}/A_G --
greater value, more graphite disorder (damage)

Histogram Analysis : SoC

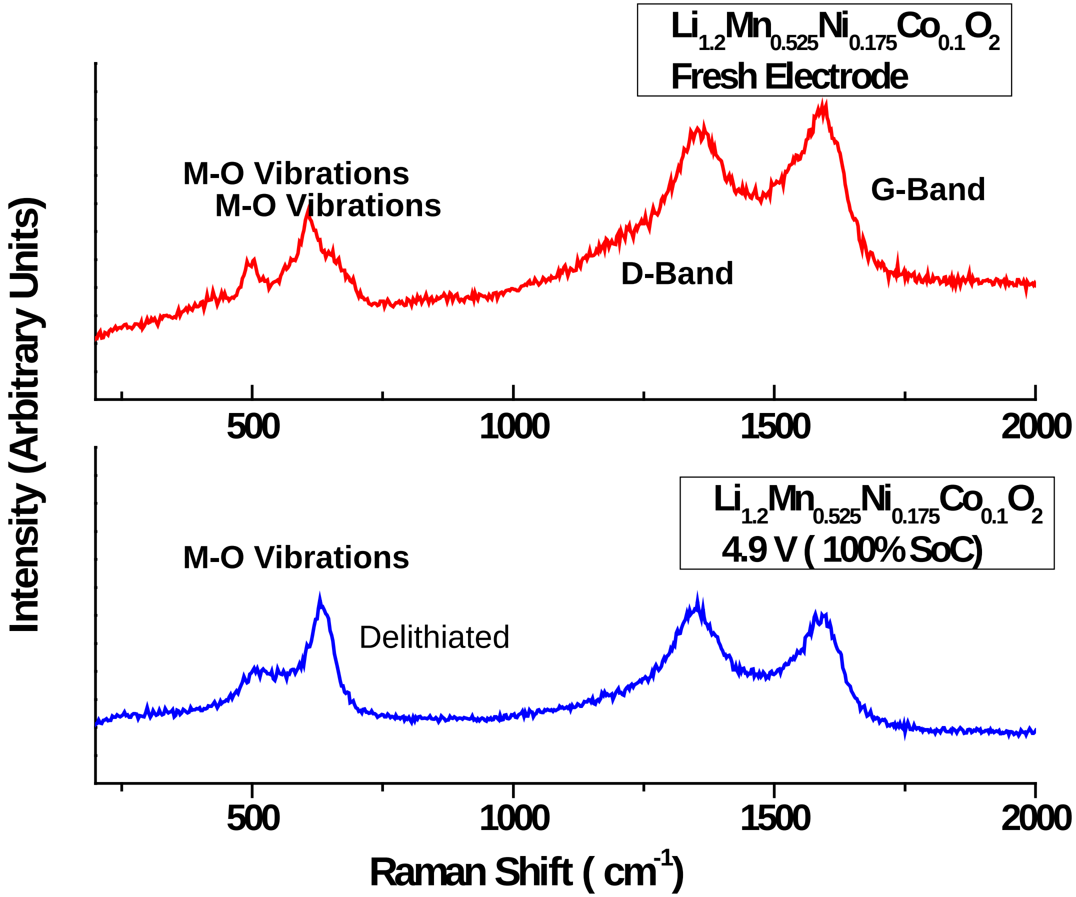






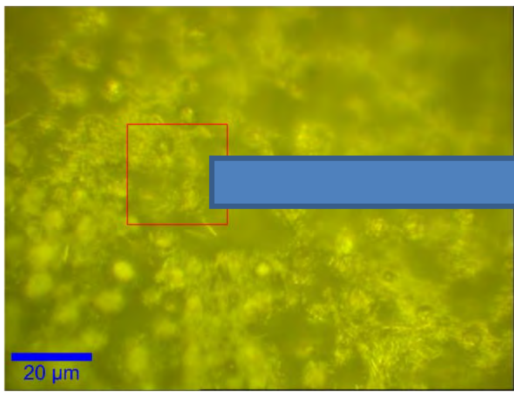


Ex-situ Raman Spectra of $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$

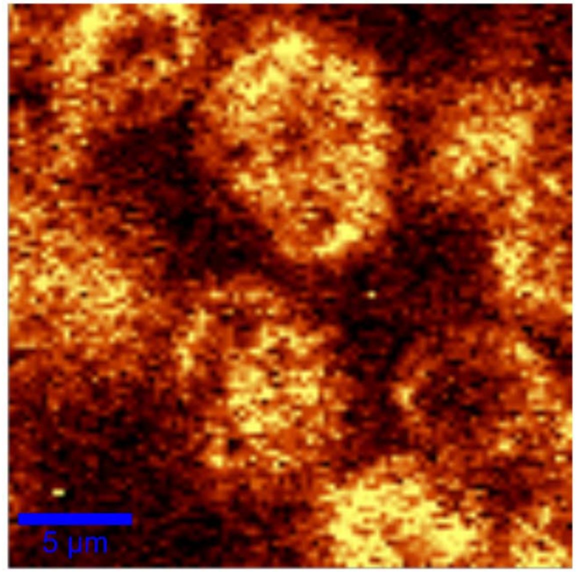


Ratio of Raman peaks of M-O vibrations changes upon lithiation/delithiation

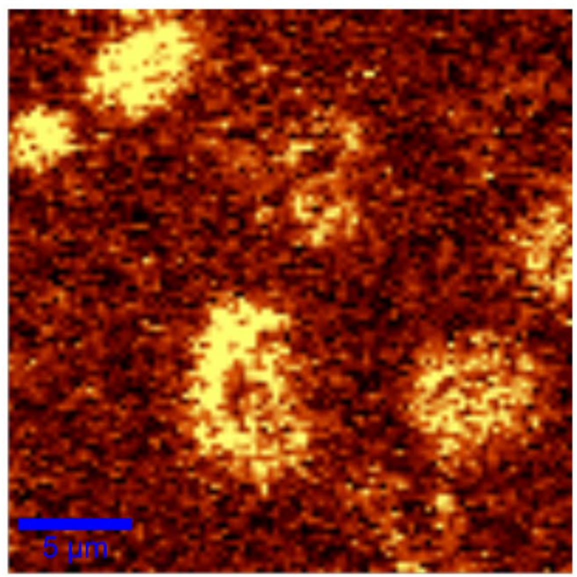
Micro Raman Imaging of Pristine $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$



Video Image

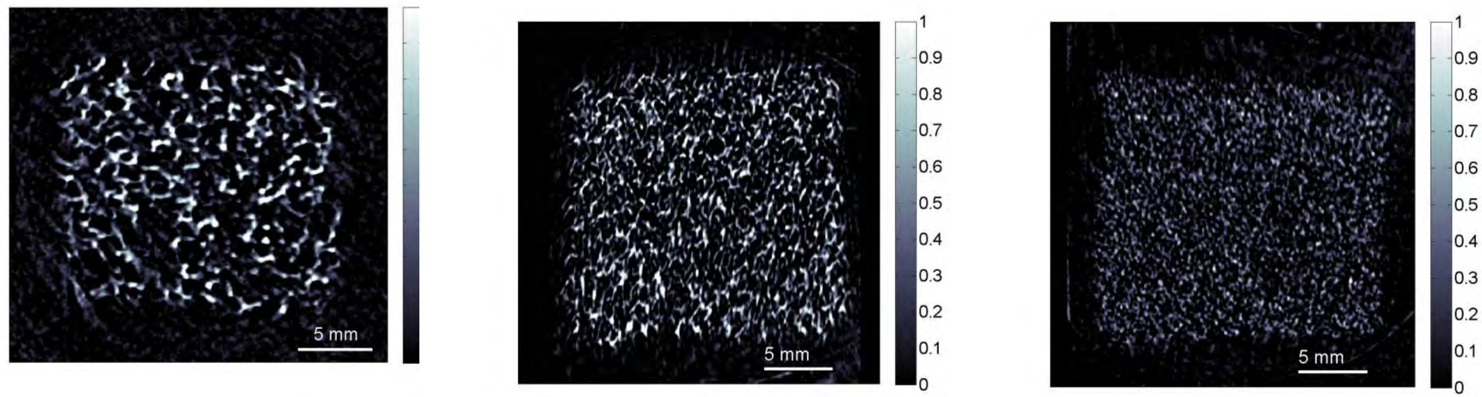


Integrated Carbon Peaks



Integrated M-O Peaks

3D Imaging of Lithium in porous Carbon Electrodes : Neutron Radiography



2D Neutron Imaging Reconstructed Radiographs of Li distribution (Li_2O_2) in Foam Matrices (from coarse to thin matrix)

3D Li distribution (Li_2O_2) in coarser carbon foam matrix

Nanda, Bilheux *et. al.* Unpublished 2011

Summary and Conclusion

• Good columbic efficiency and capacity of $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}$

• Stable cycling (> 100 cycles) without high voltage additives and

• Addition of graphitic fibers improves the capacity retention and rate.

• Raman analysis provides spatial information about the electrode SoC

at various cycling conditions.

• Statistical analysis of degraded electrodes.

Work in Progress

• *In situ* Raman studies of Excess Lithia compositions
• High Resolution Electron Microscopy of Excess Lithia compositions at various lithiation stages (SoC).

Acknowledgments

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ORNL Team/Collaborators
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