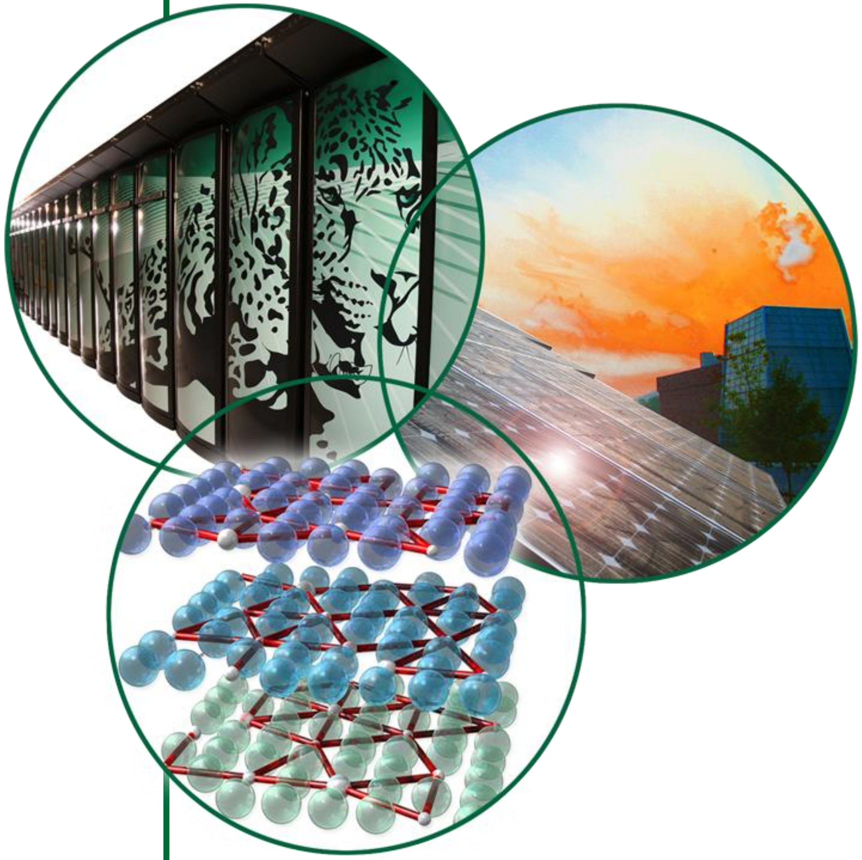
New Perspectives in Energy Storage Materials

Confocal Micro-Raman Microscopy



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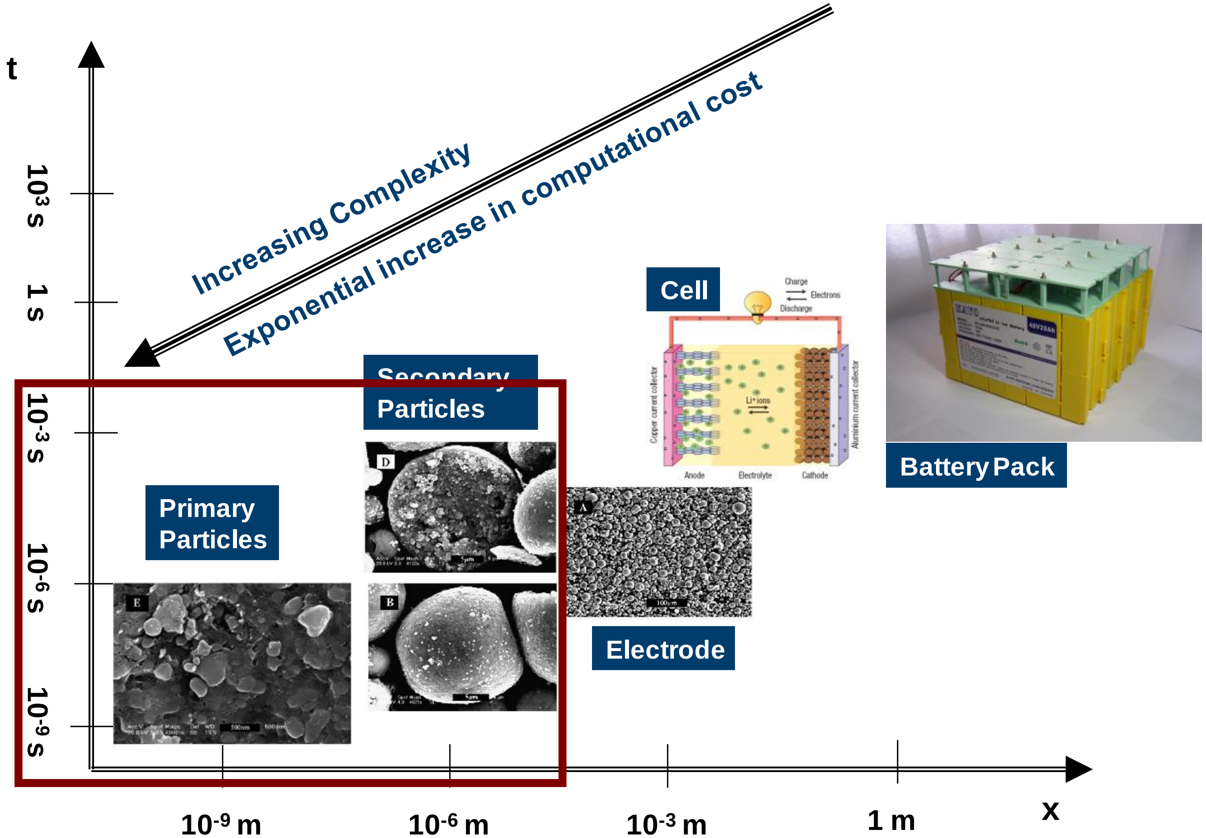
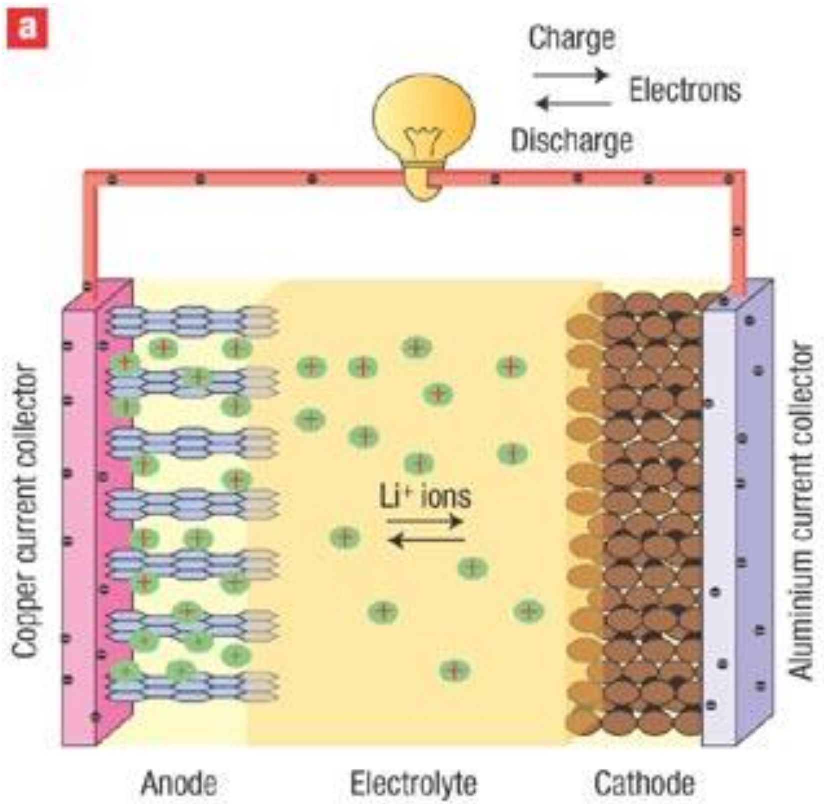
The Scale of Things

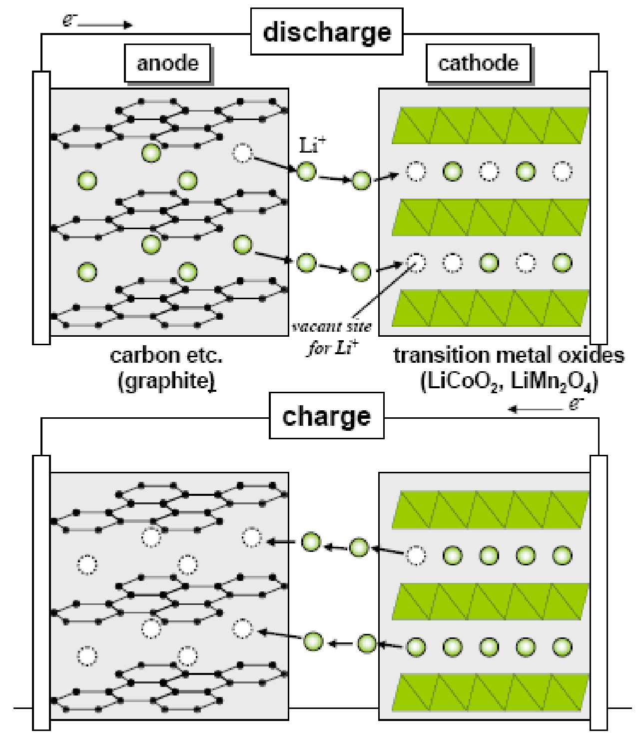


- Complex electrode assembly
- Multiple transport regime
- Spatio-temporal variation

Courtesy : Sreekanth Pannala

Working of a Li-ion full cell





Connecting Fundamental Material Properties to Macroscopic Parameters

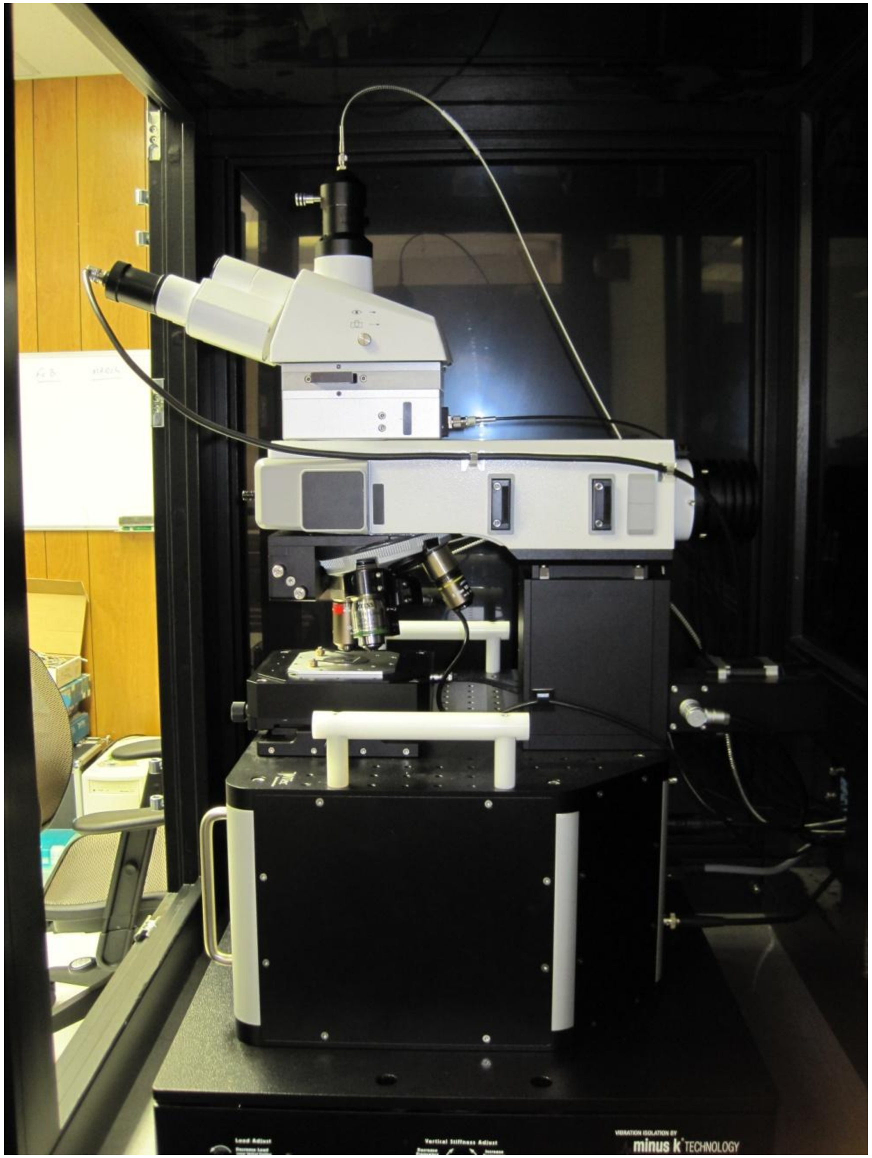
- Single particle "State of Charge" (SOC).

"Enabler for full capacity utilization"

- Observation of "Lithium Gradient" in an inhomogeneous medium.

" Transport in a complex electrode assembly"

Confocal Raman-AFM Setup



Spatial Resolution ~ 300 nm

Peizo driven mapping stage

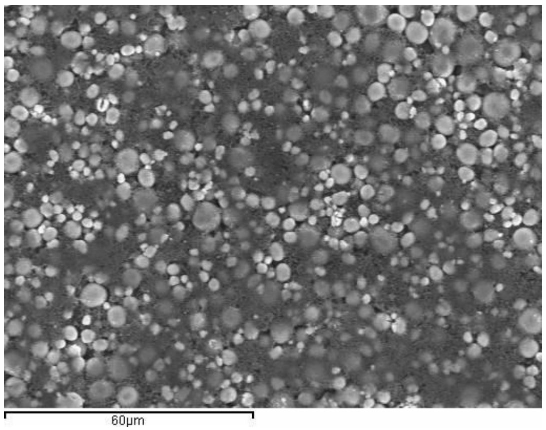
Multiple excitation wavelength

Raman Imaging plus topography

Support from Energy Storage, OVT, EERE DOE

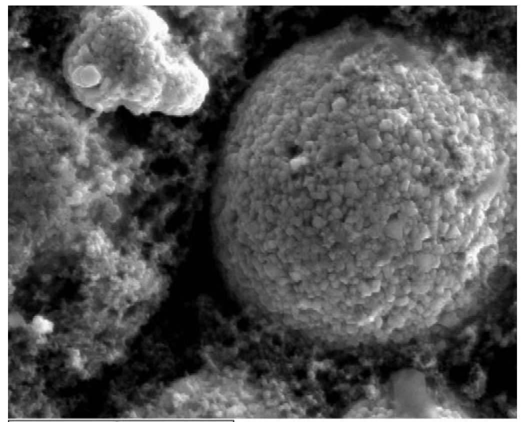
High Energy and Power Li-ion Electrodes

Electrode



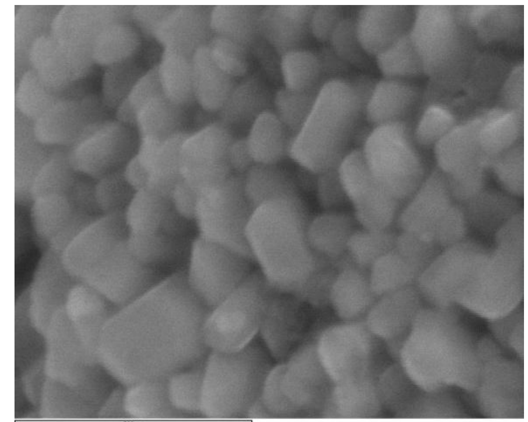
60 µm

Secondary particle



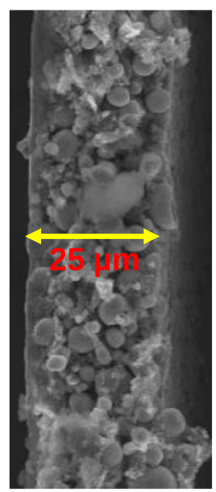
5 µm

Primary particle



700 nm

Edge

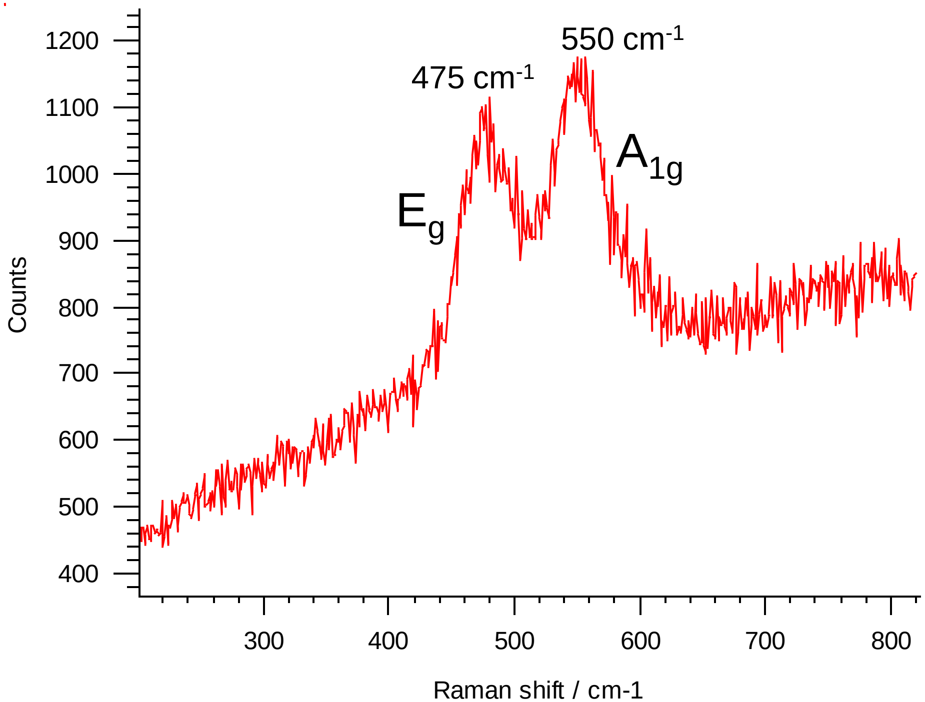


$LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA)

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

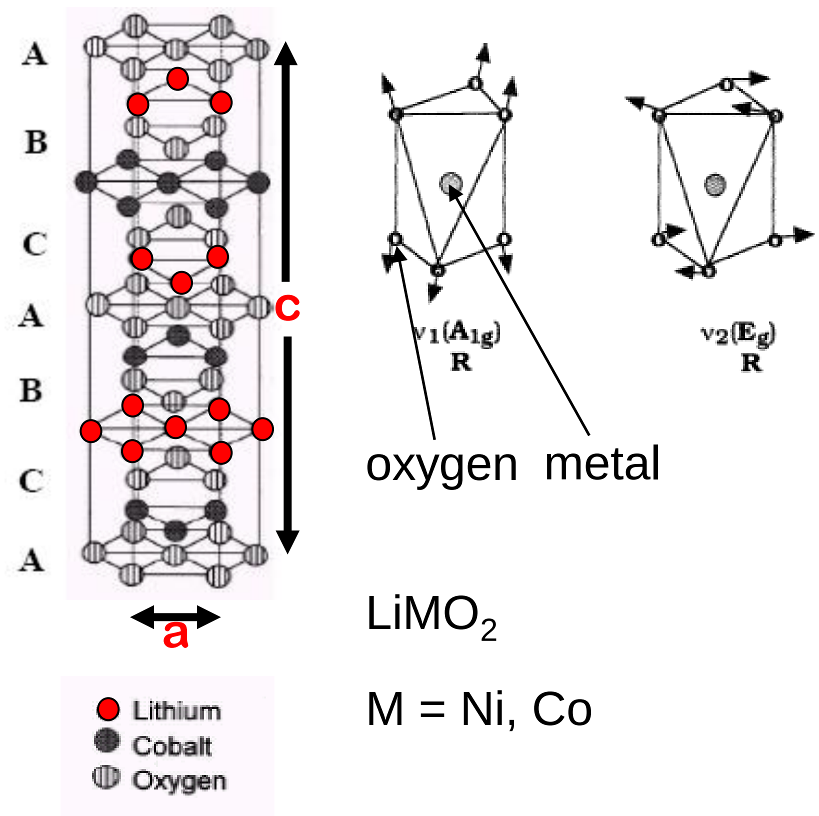
$xLi_2MnO_3 (1-x)LiMO_2$ (Excess Lithia compounds)

Origin of spectroscopic "SOC"



Charged NCA cathode (3.77V)

α - $NaFeO_2$ structure



$LiMO_2$

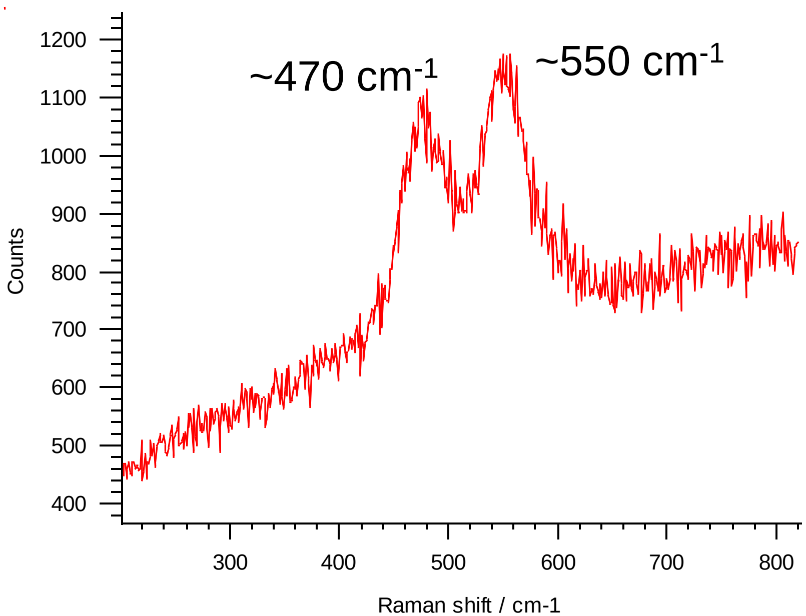
M = Ni, Co

- 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 $A_{475cm^{-1}} / A_{550cm^{-1}}$

Micro-Raman Technique

Positive Electrode

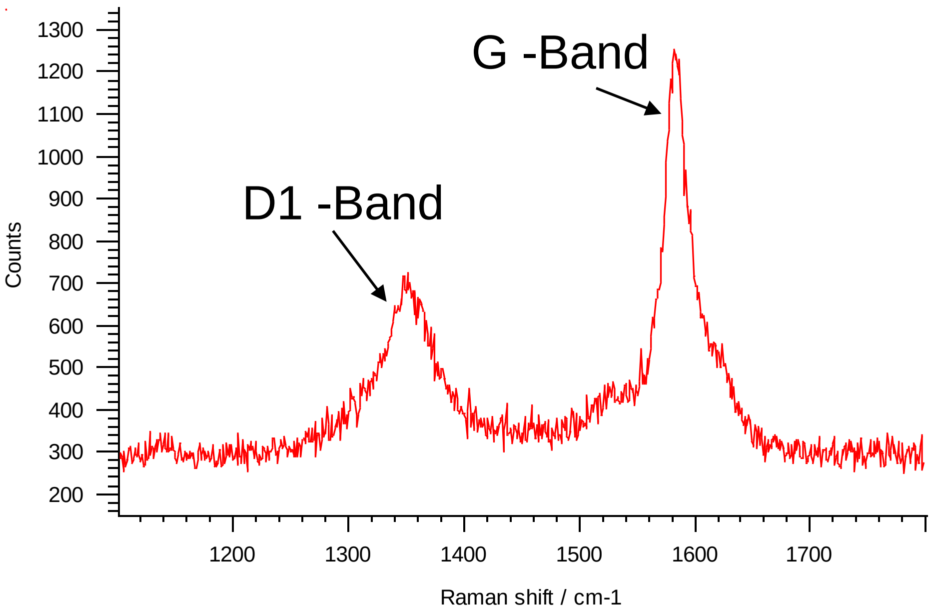
Raman spectrum of charged (3.77 V) NCA Cathode



A_{470}/A_{550} ~ to SOC

Negative Electrode

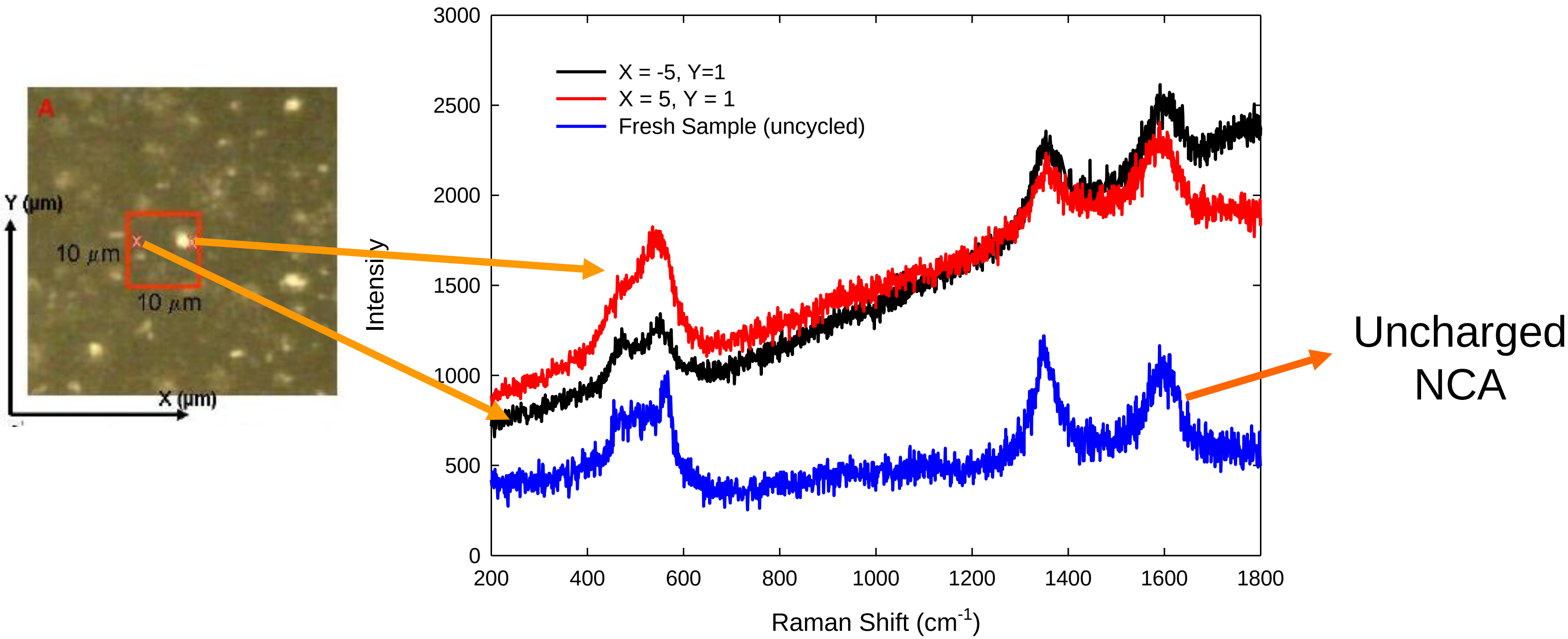
Raman Spectrum of Graphite Anode



A_{D1}/A_G ~ Disorder

Spectra can be obtained as a function of position on the surface and edge of the electrode material.

Carbon Coverage : Continued



Similar carbon coverage different particle “SOC”

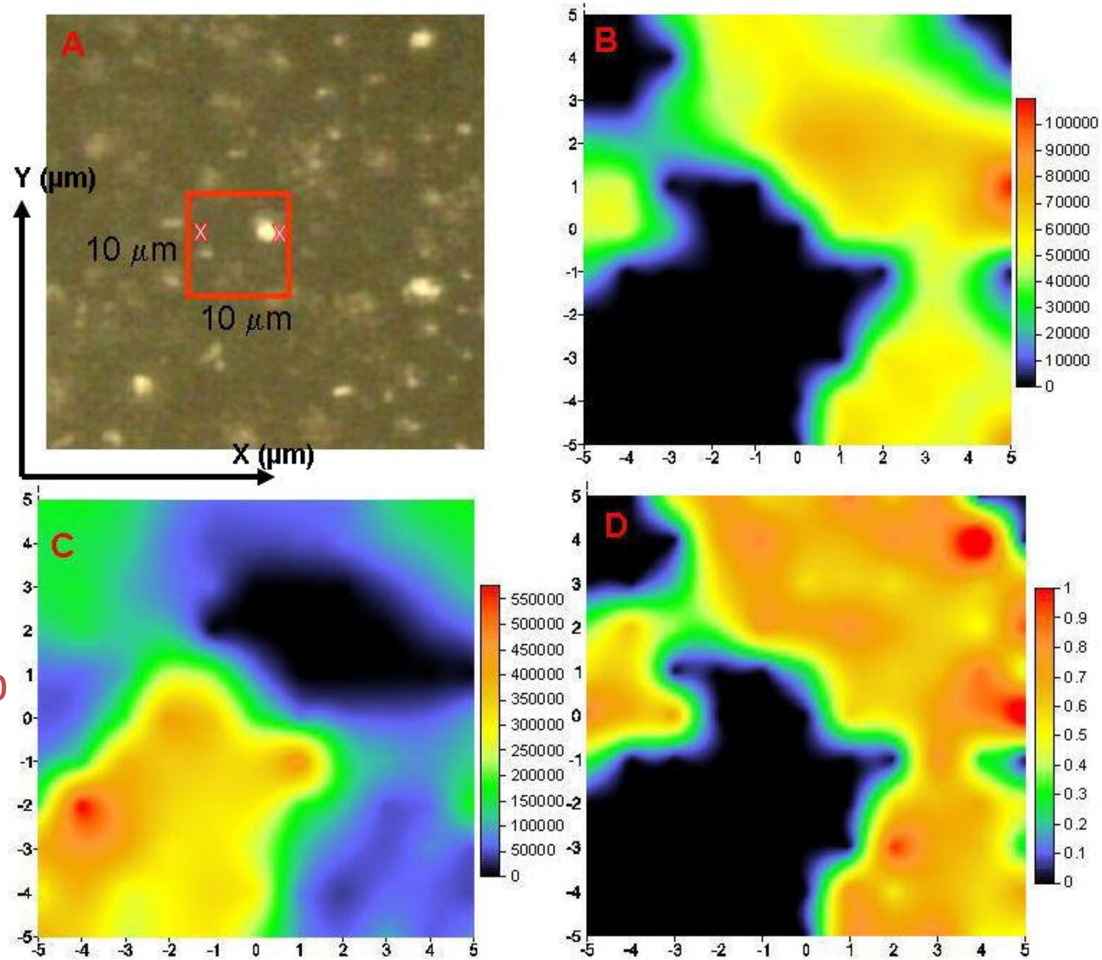
Raman Mapping : What it can do ?

Optical Micrograph

Intensity Map (NCA)

Intensity Map Carbon

SOC Map NCA



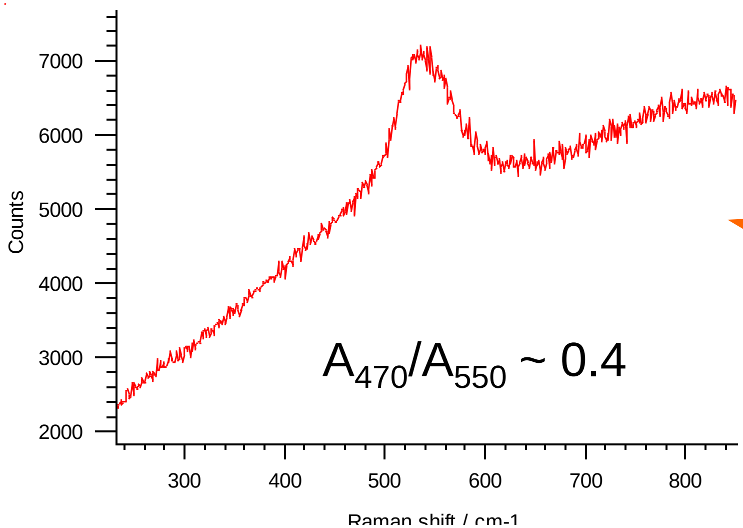
Micron

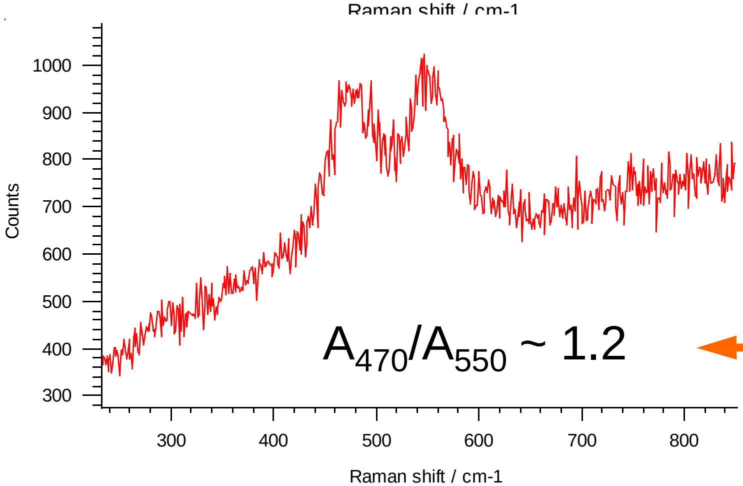
J. Nanda et al. 2010

State of Charge : $(A_{475} / A_{550}) \times (I_{475} / I_{550})$

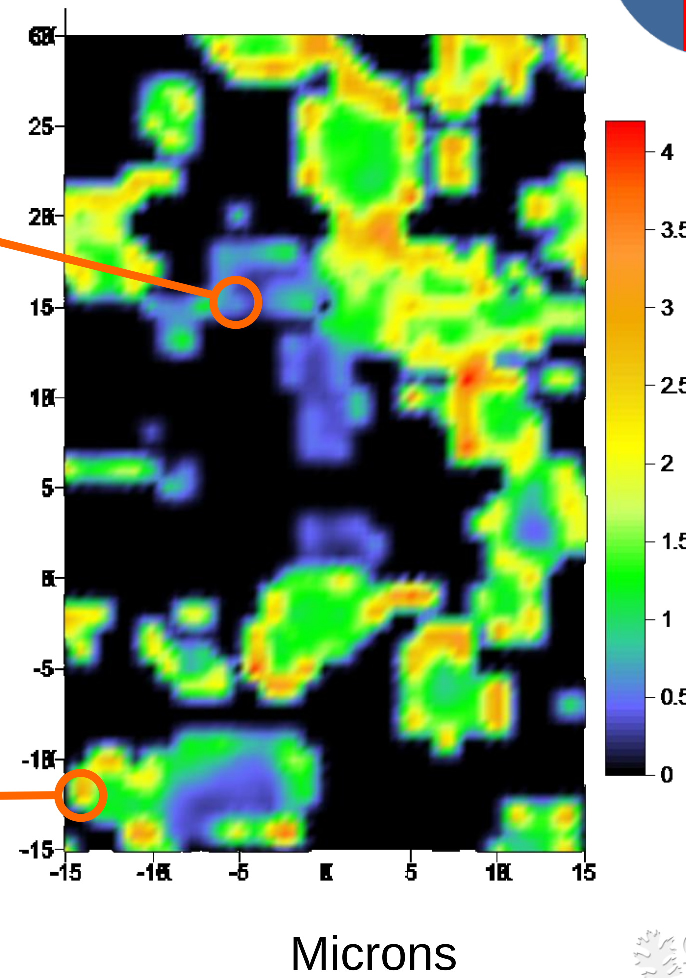
Mapping Lithium Deficiency Regions : $Li_{1-x}Ni_{0.80}Co_{0.20}Al_{0.05}$

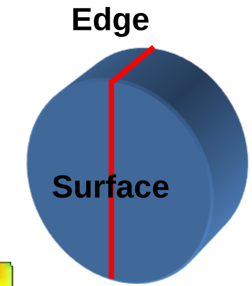
Spectroscopic Signature





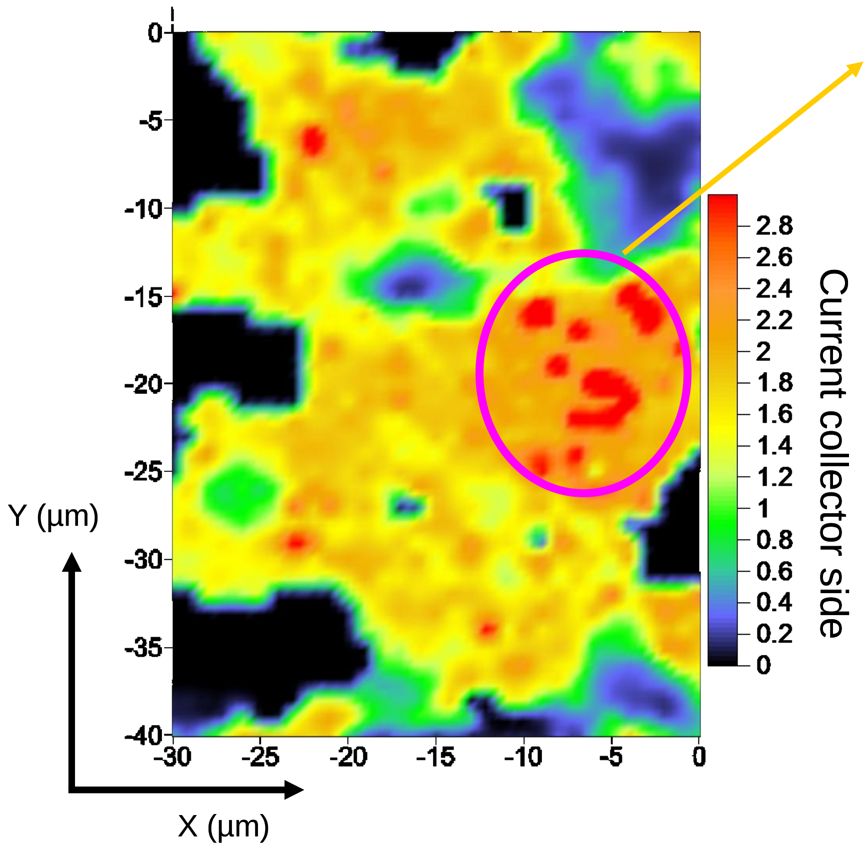
Mapping Pattern



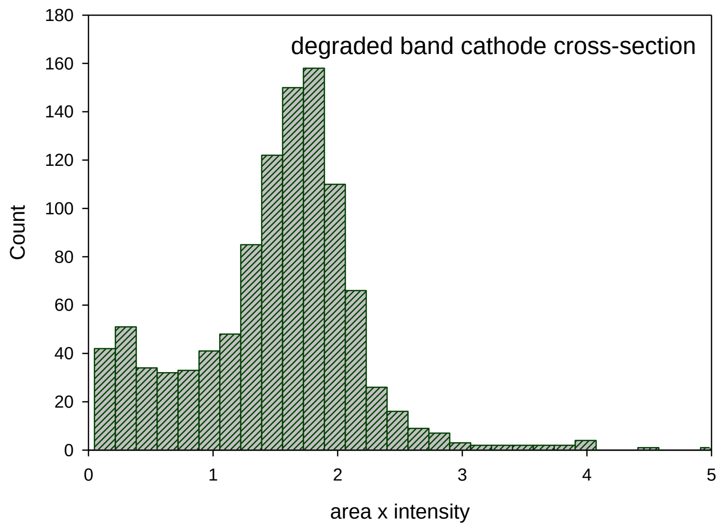


Severely degraded Sample

SOC Map

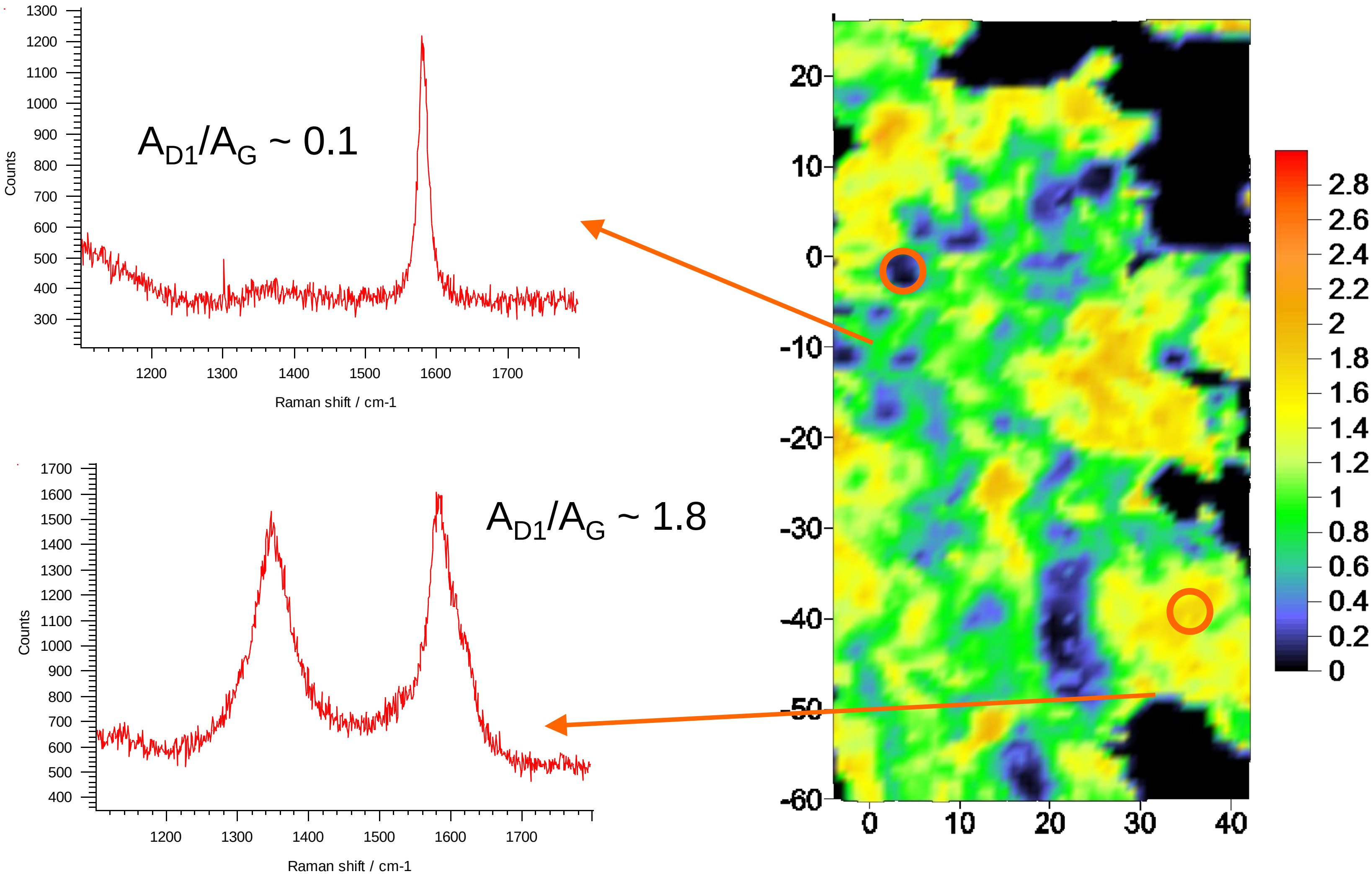


Extreme charged regions

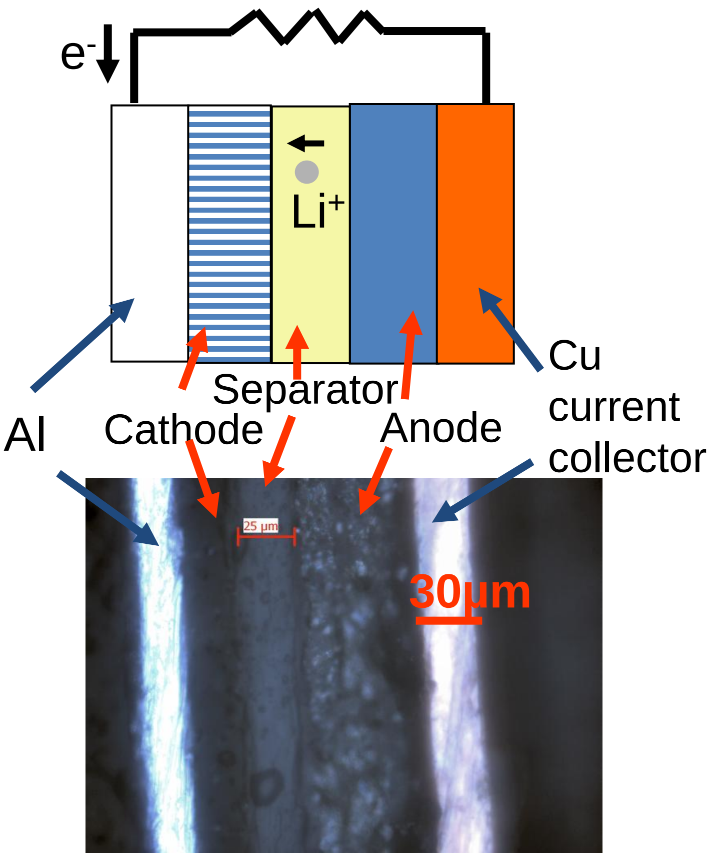


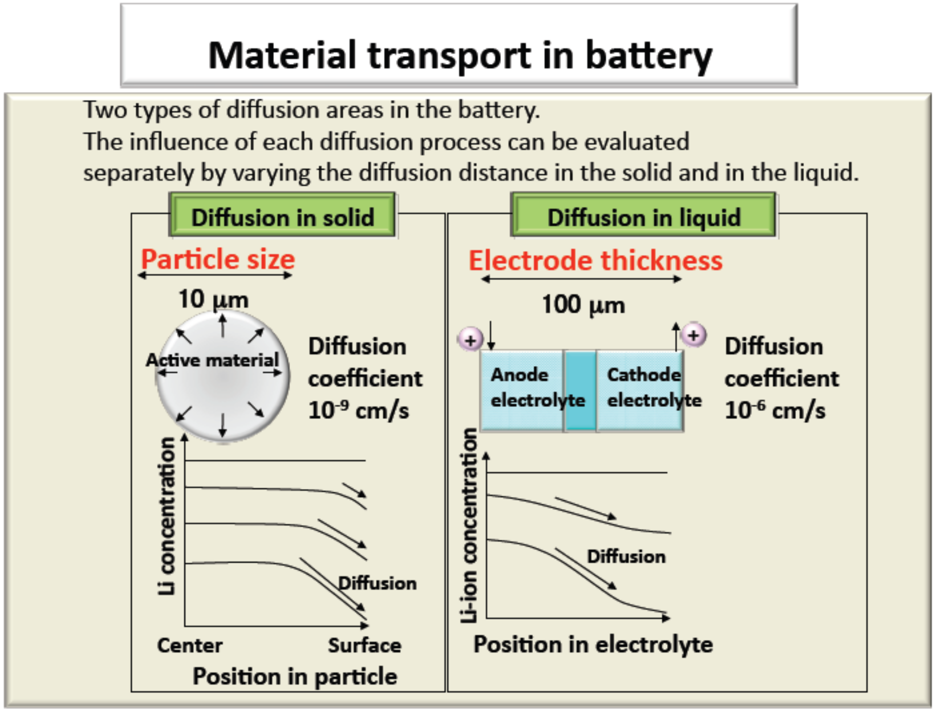
J. Nanda et al. Under reveiw 2010

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



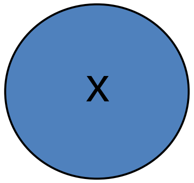
In situ Li-transport in Li-ion full cell



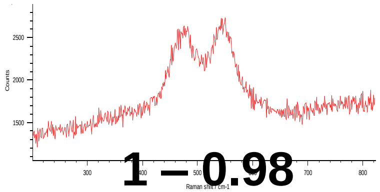


Single Particle Charge-discharge of an in situ edge cell

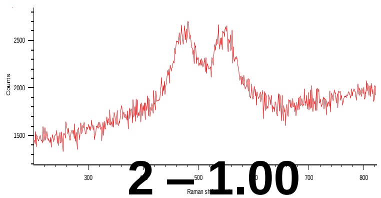
electrode



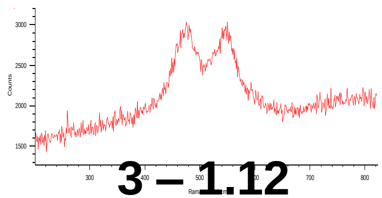
Cell voltage 3.7 V



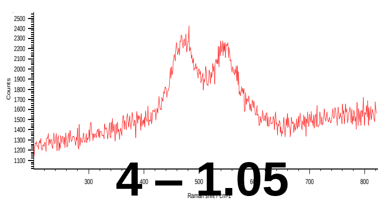
1 – 0.98



2 – 1.00

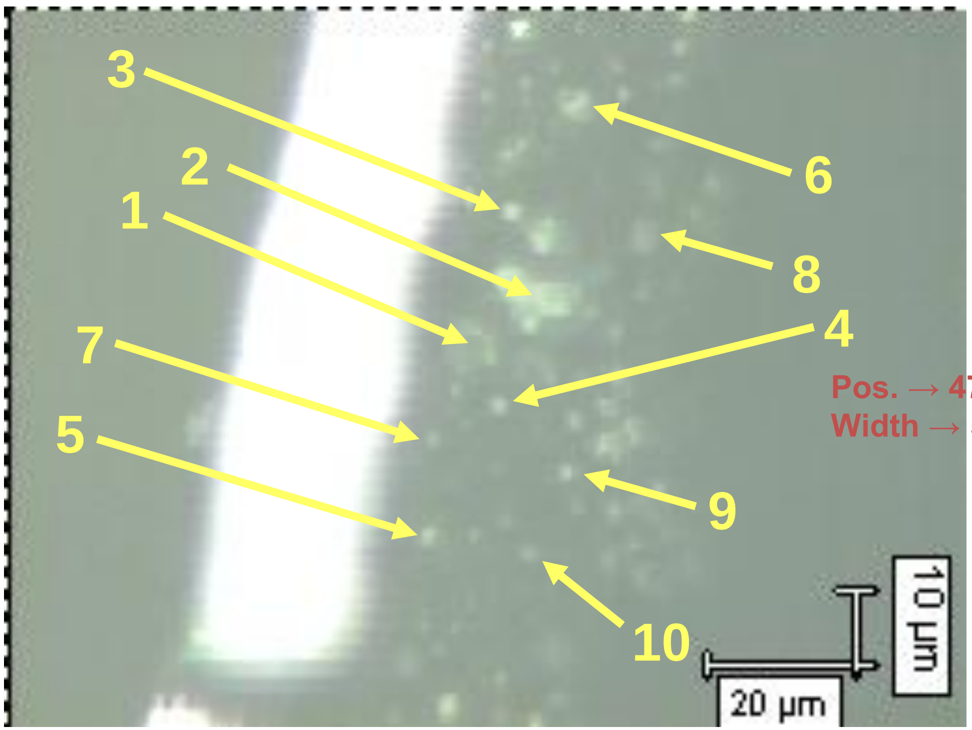


3 – 1.12



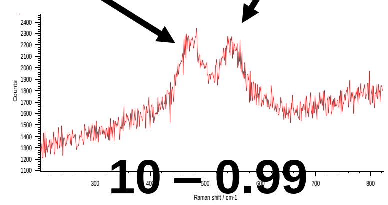
4 – 1.05

Avg. $Area_{474}/Area_{551}$ = 1.02 ± 0.10

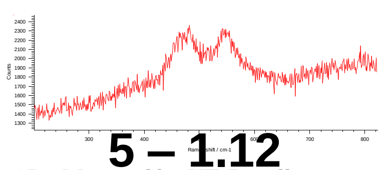


Pos. → 547.2 ± 0.91 cm^{-1}
Width → 56.9 ± 2.0 cm^{-1}

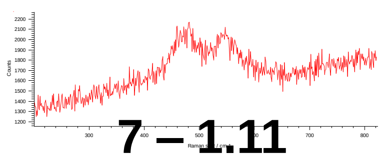
Pos. → 472.1 ± 0.76 cm^{-1}
Width → 56.4 ± 2.2 cm^{-1}



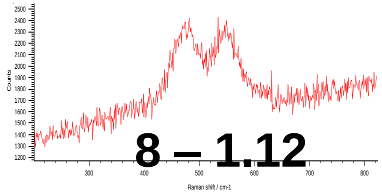
10 – 0.99



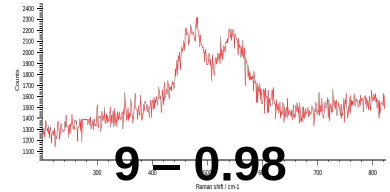
5 – 1.12



7 – 1.11

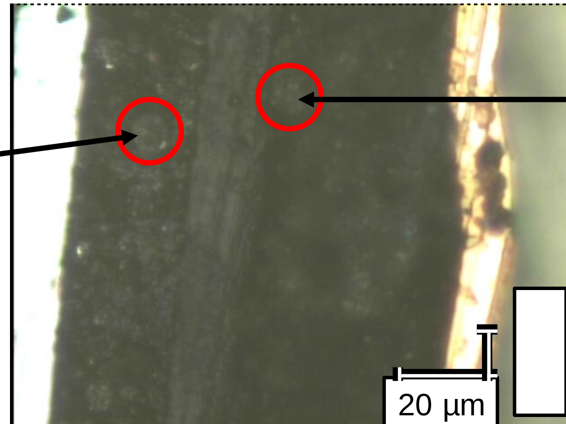


8 – 1.12



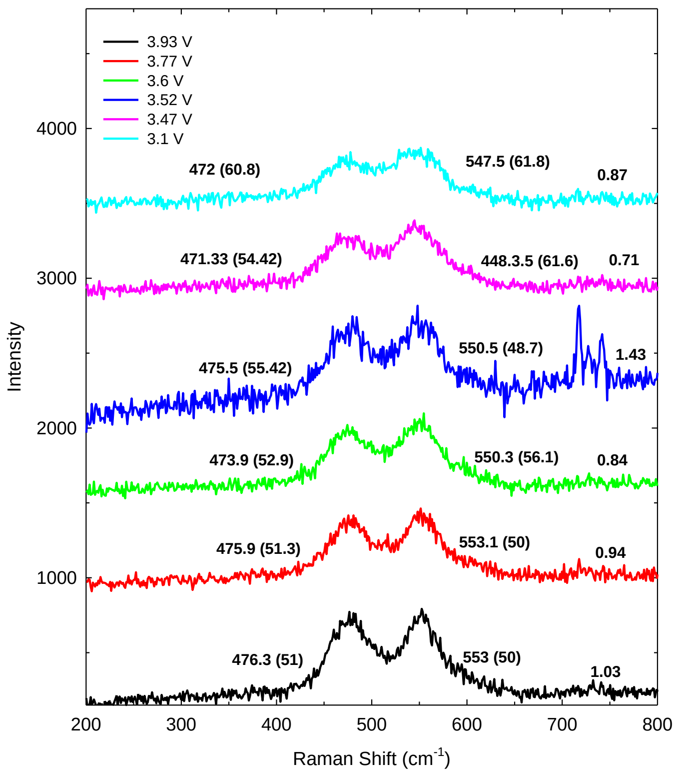
9 – 0.98

Observing "single particle" state of charge

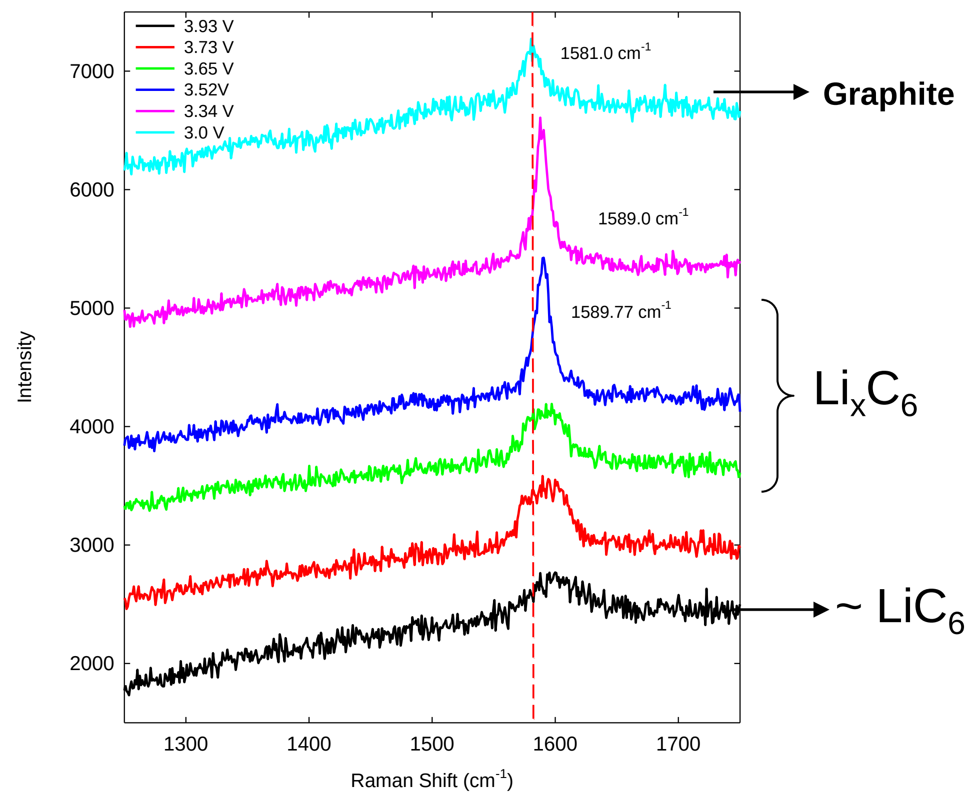


Galvanostatic at 1C rate

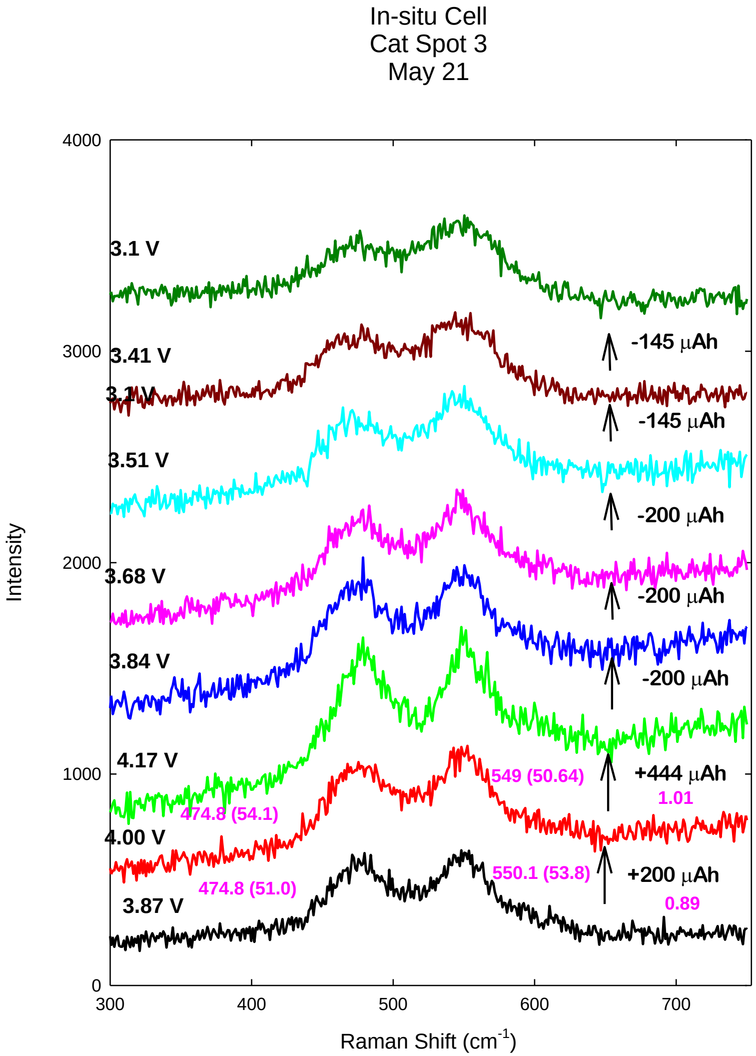
Cathode Particle 2
Near Separator

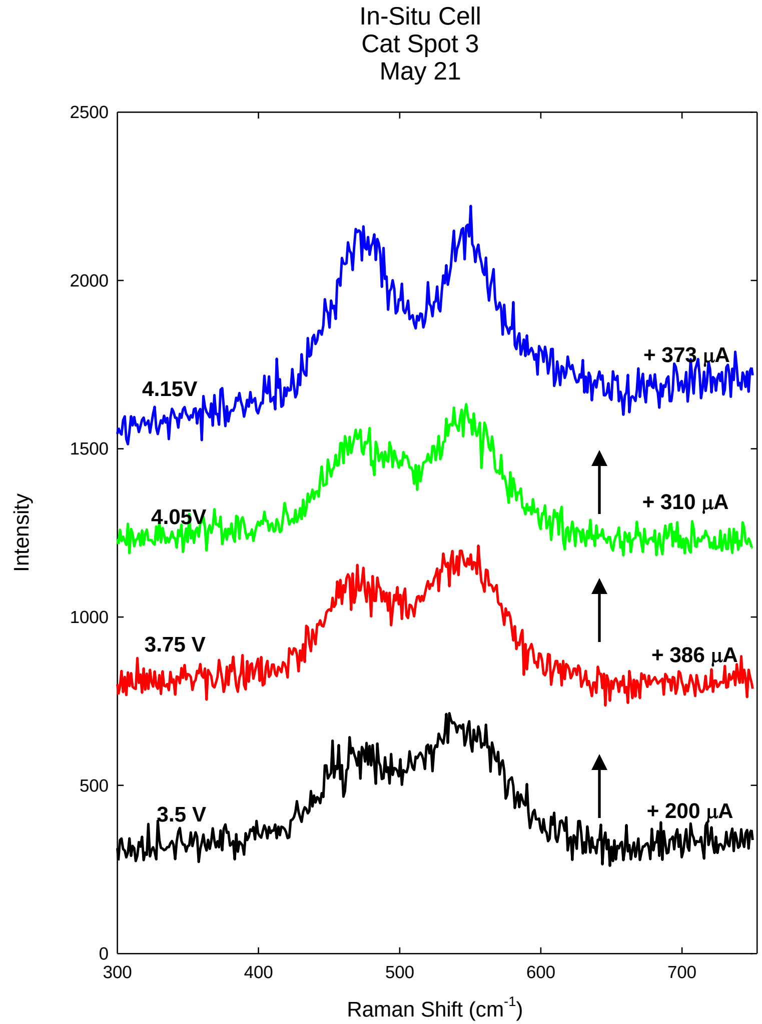


Anode Particle Near Separator



Dynamical Potentiostatic Condition



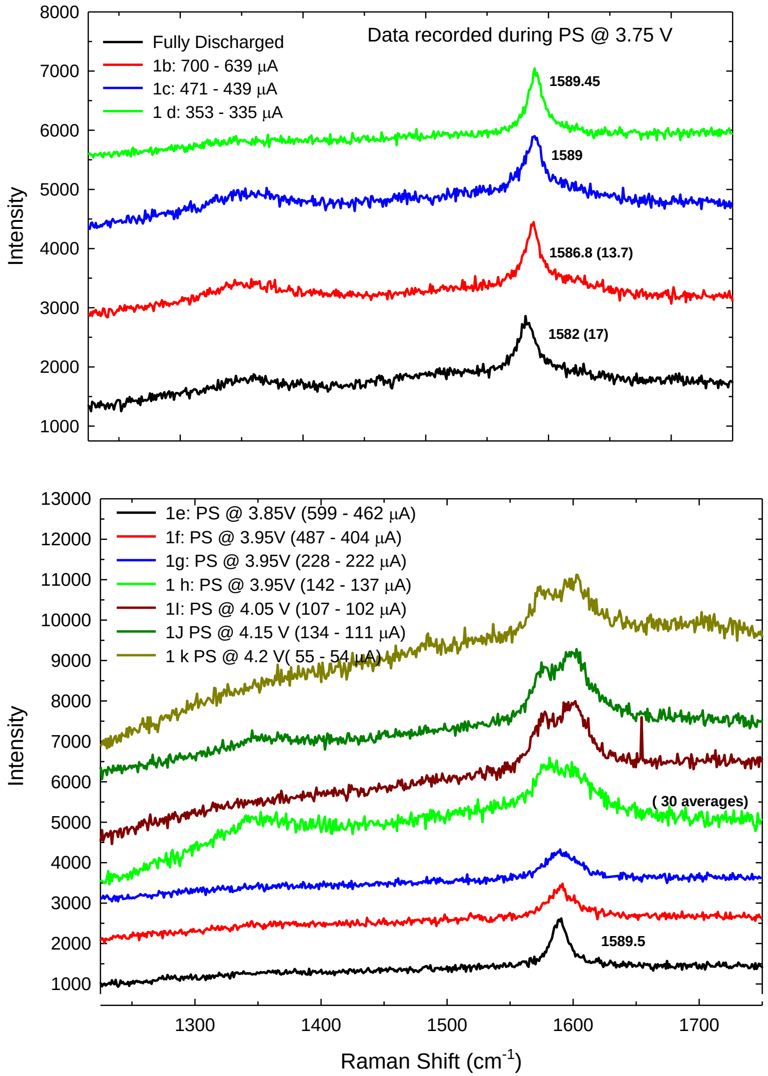


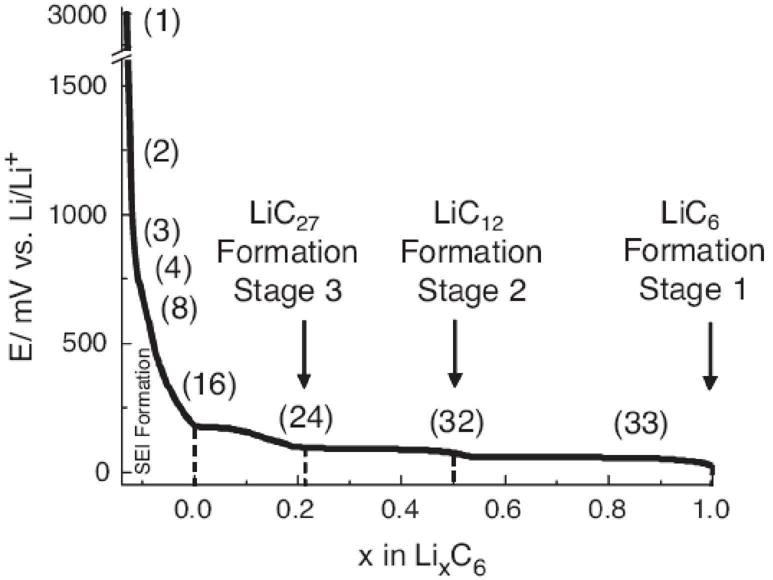
$$\text{SOC} \;\alpha\; A_{475cm^{-1}} / A_{550cm^{-1}}$$

J. Nanda et. al. Manuscript (2010)

Dynamical Potentiostatic Condition

Particle 1



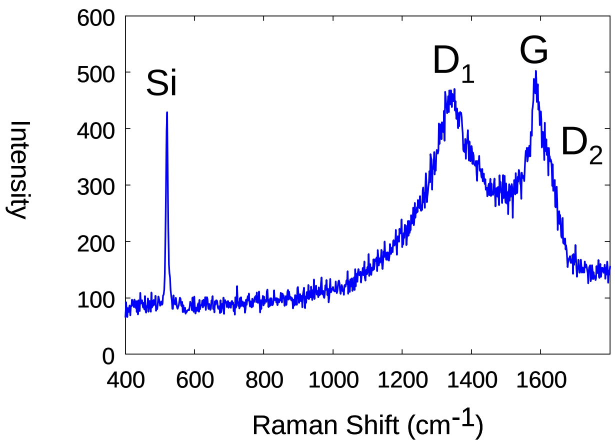


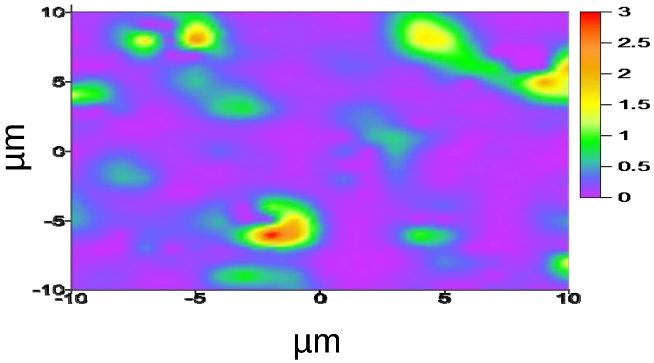
Hardwick et al. Solid State Ionics 177 (2006)

J. Nanda et al. (unpublished)

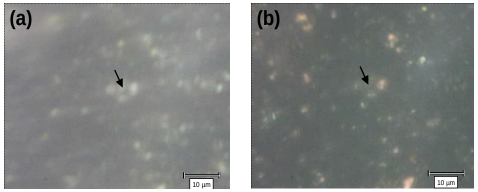
High Capacity Si-C Composite Anode

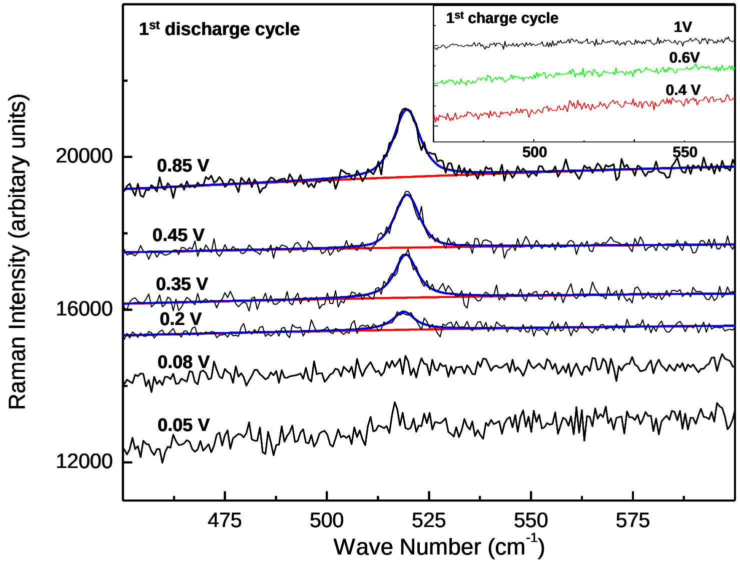
In-situ observation of lithiation of silicon-rich region in Si-C composite





Ratio of Si area to G-Band area





Nanda et al. Electrochem. Comm. (2009)

Conclusions

- Relative measure of spatial SOC distribution of cathode particle aggregates.
- Raman Intensity versus State of Charge : Skin Depth Effect.
- Micron level mapping of electrodes: Observation of Li-gradient.
- Kinetics of lithiation-delithiation at the primary-secondary particle interface