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Raman Spectroscopy
Particle Characterization

Analysis Techniques for Modern Battery Design and Manufacture

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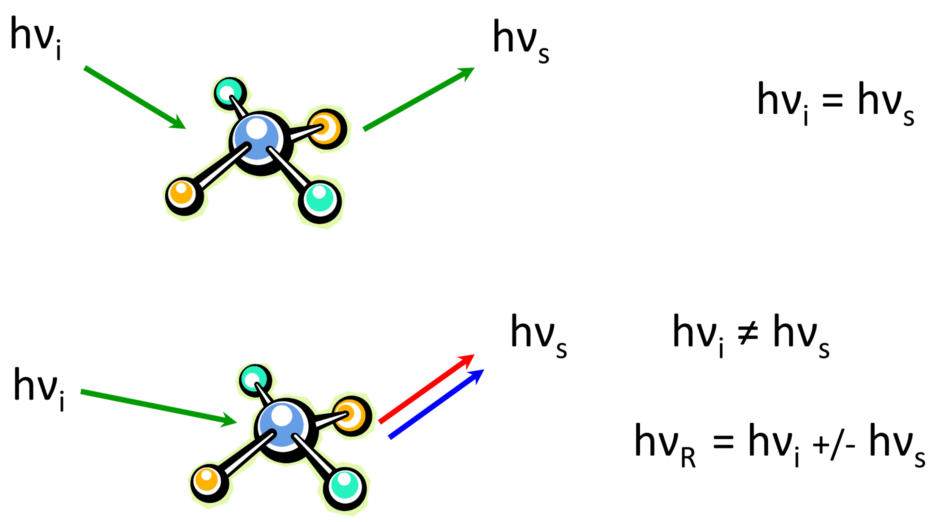
Overview

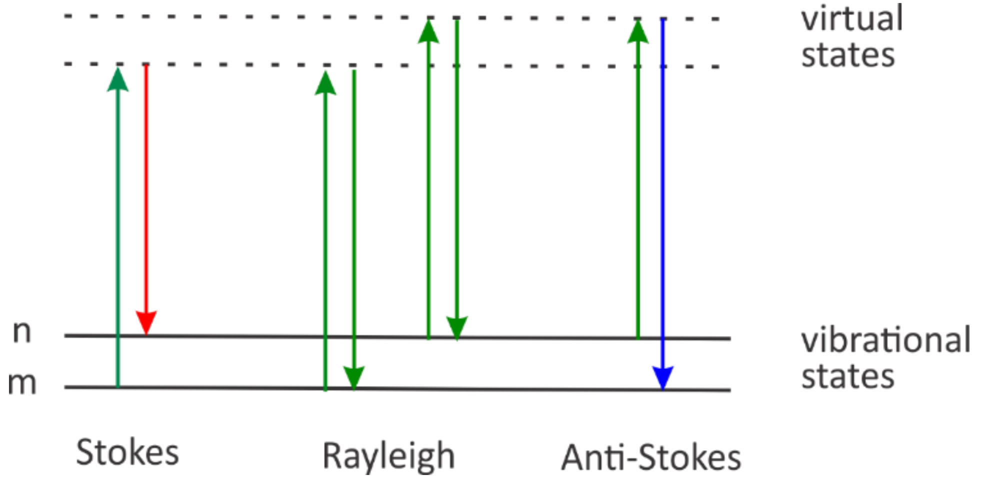
- ✓ ***Basics of Raman spectroscopy***
- ✓ ***Raman spectroscopy of mixed metal oxides: NCM***
- ✓ ***A few examples of chemical analysis of Li-ion batteries***
- ✓ ***Beyond: applications of micro-XRF in Li-ion batteries industry***

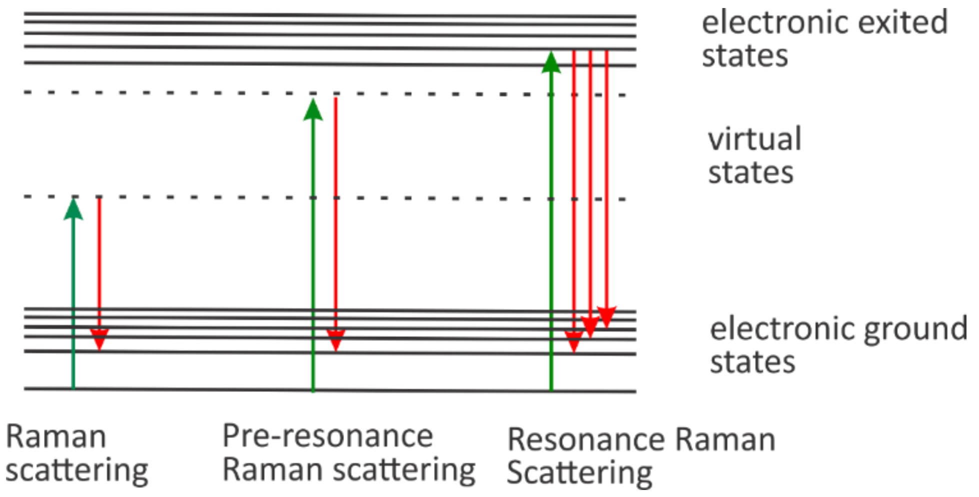
What is the Raman Effect?

When light hits molecules, the predominant mode of scattering is ***elastic scattering***, called **Rayleigh scattering**. It increases with the fourth power of the frequency and is more effective at short wavelengths.



It is also possible (approximately ***1 in 10^7 photons***) for the incident photons to interact with the molecules in such a way that energy is either *gained* or *lost* so that the scattered photons are shifted in frequency.
Such ***inelastic scattering*** is called **Raman scattering**.





Raman Effect

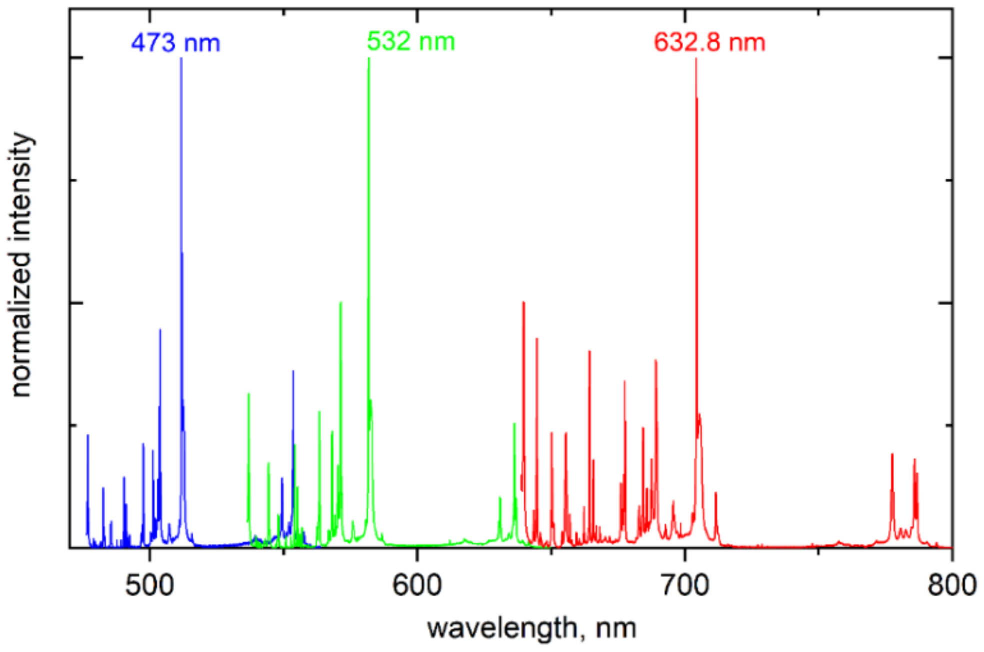
Raman observes laser energy changes as it excites a molecular vibrations.

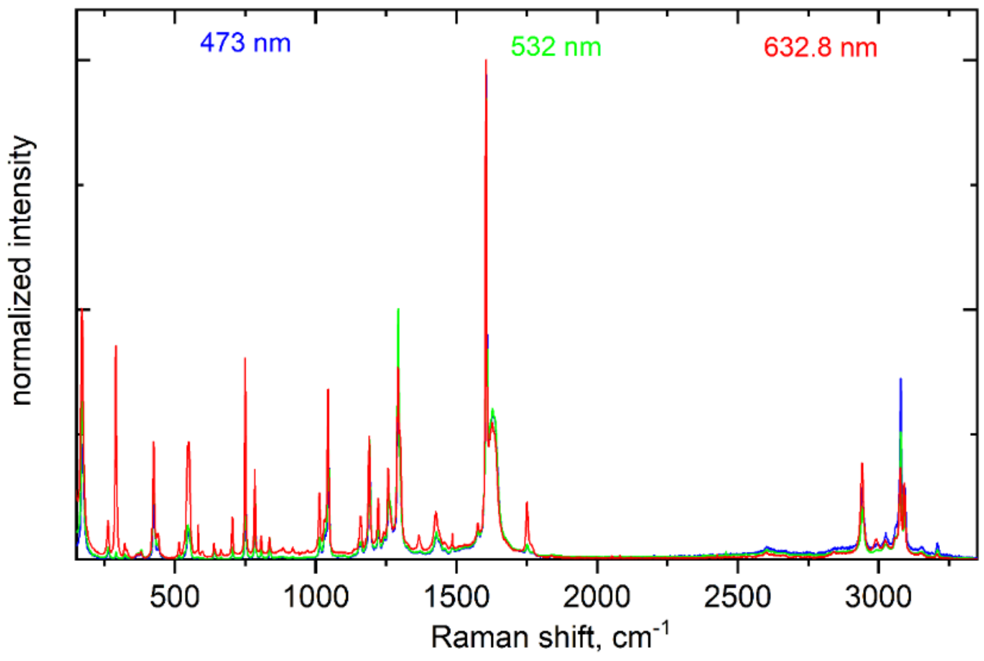
The unit used is relative to the energy ω $\omega\ (cm^{-1}) = 1/\lambda\ (cm)$ $\omega_{raman} = [\ 1/\lambda_{laser} \pm 1/\lambda_{peak}]$

Laser – 473 nm = 21141.6 cm^{-1}
21141.6 cm^{-1} – 520.6 cm^{-1} = 20621.0 cm^{-1}
20621.0 cm^{-1} = 484.94 nm
λ = 11.94 nm

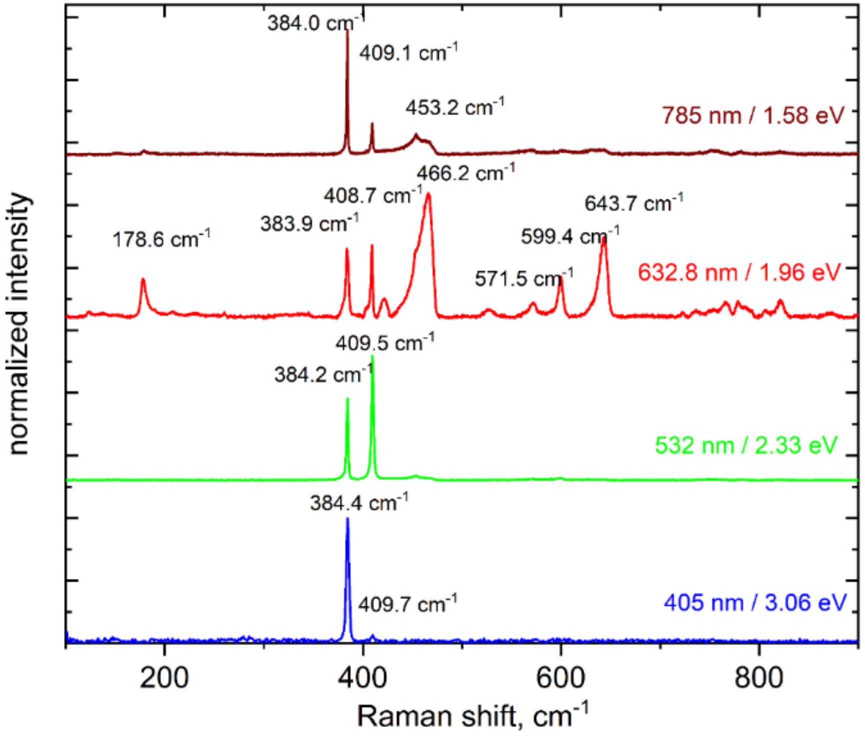
Si band — 520.6 cm^{-1}/64.6 meV

Laser – 632.8 nm = 15802.8 cm^{-1}
15802.8 cm^{-1} – 520.6 cm^{-1} = 15282.2 cm^{-1}
15282.2 cm^{-1} = 654.36 nm
λ = 21.56 nm

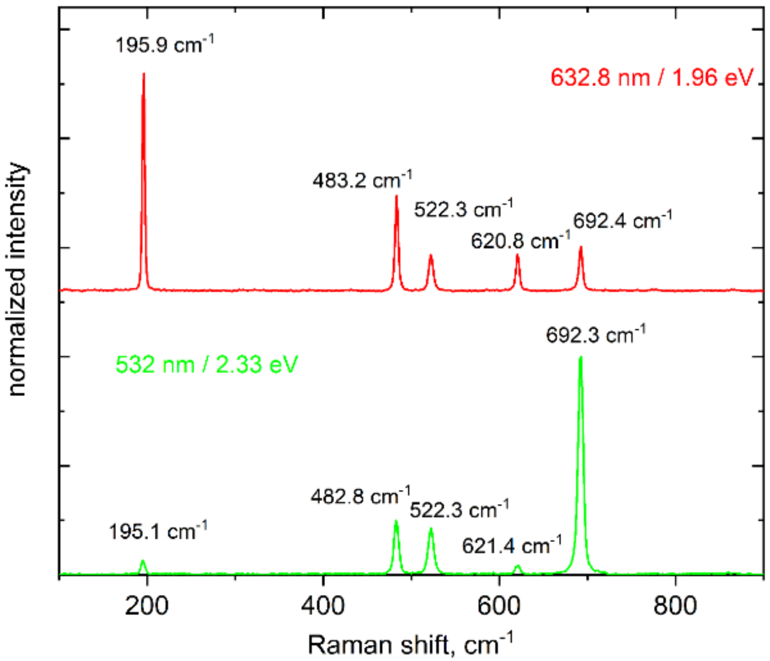




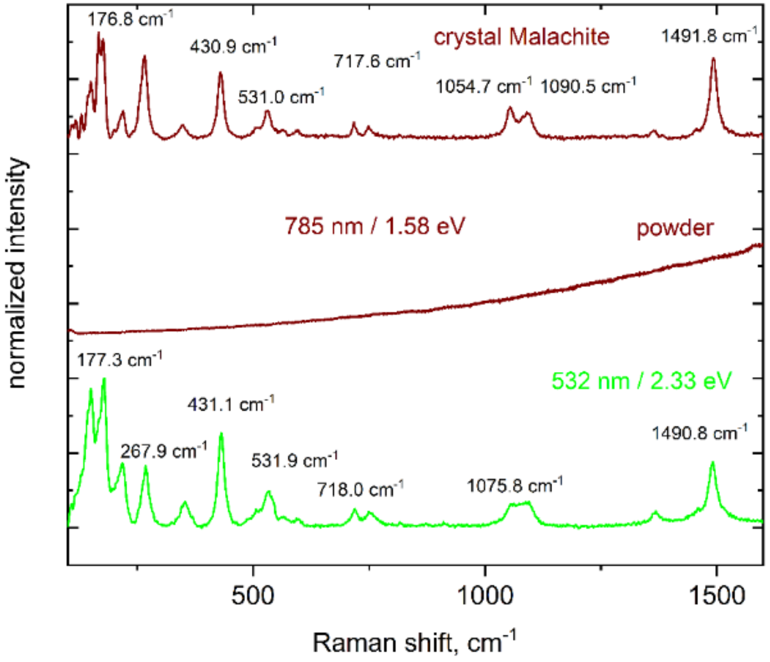
Raman Effect



MoS_2- indirect gap: 1.23 eV
direct gap – 1.80 eV



Co_3O_4 - direct gap: 0.6 eV/0.75 eV



$Cu_2CO_3(OH)_2$ - direct gap 2.2-2.4 eV

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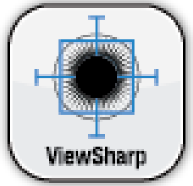
Instrumentation and Software

LabRam Evolution

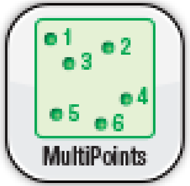
Focal length 800 mm
Laser: 532 nm
Grating: 600 gr/mm
CCD Synapse 1024 x 256 pixels
100x objective
LabSpec 6 Spectroscopy Suite

View Sharp



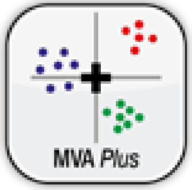
Nav Sharp

Multi-Points



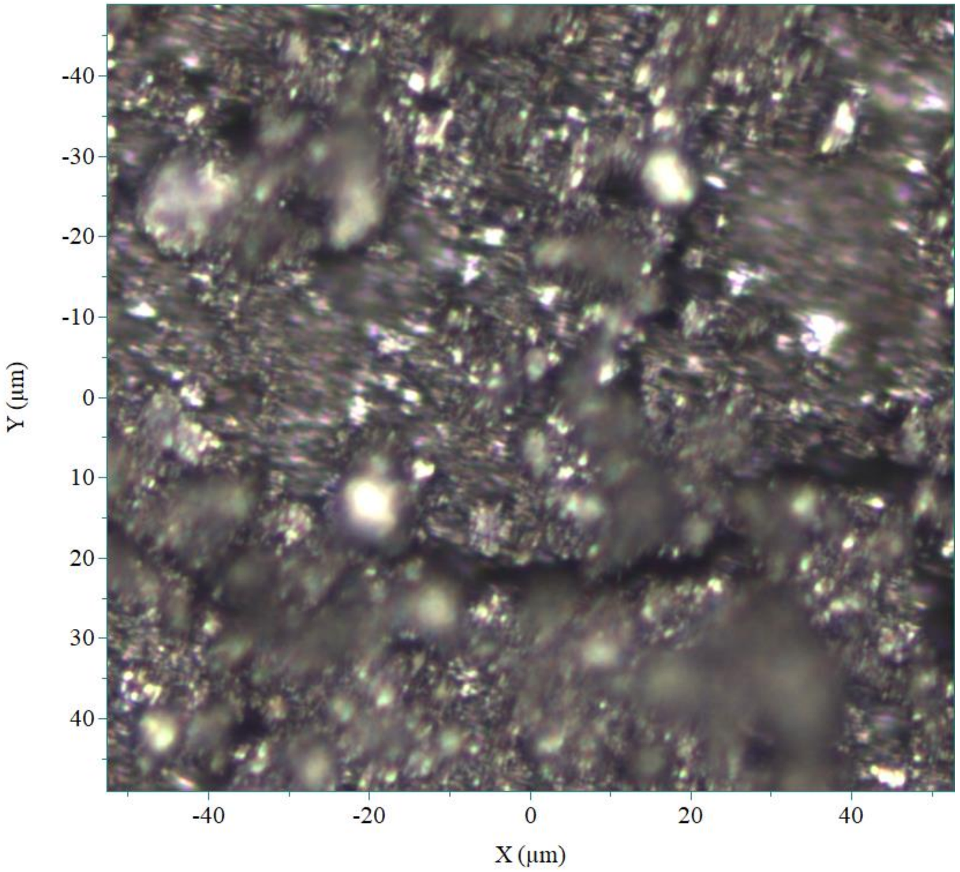
Particle Finder

Multivariate analysis

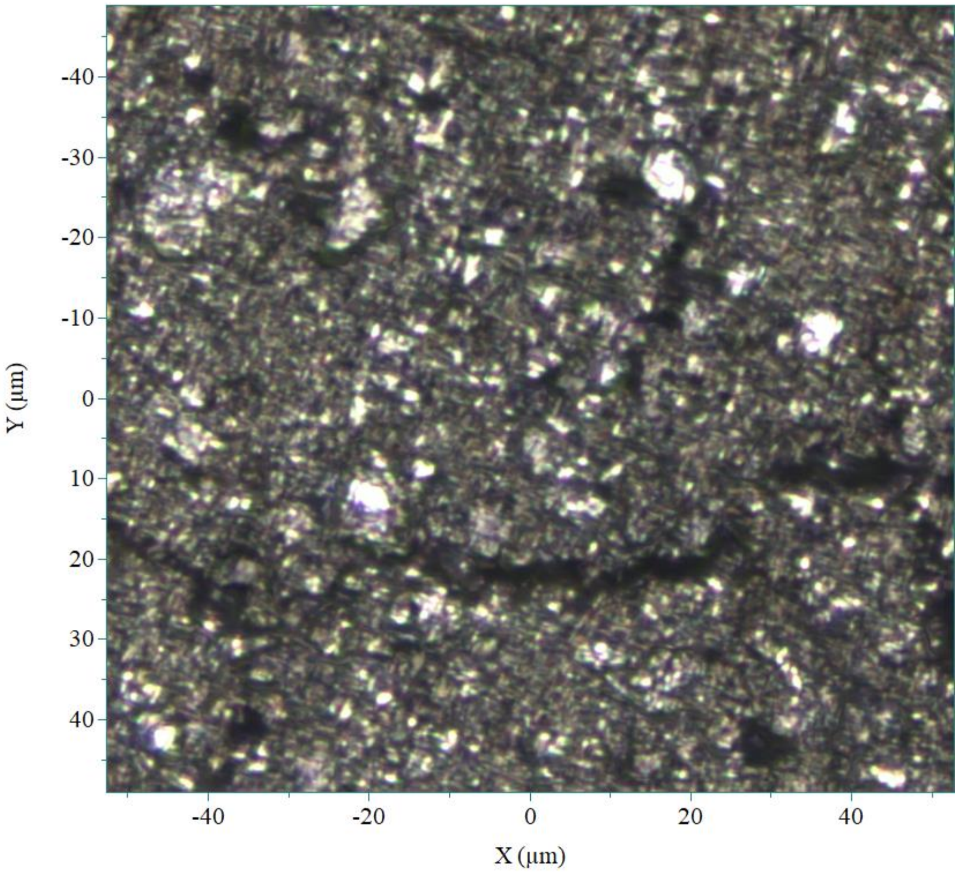


View Sharp

Optical image



View Sharp Optical image



ViewSharp

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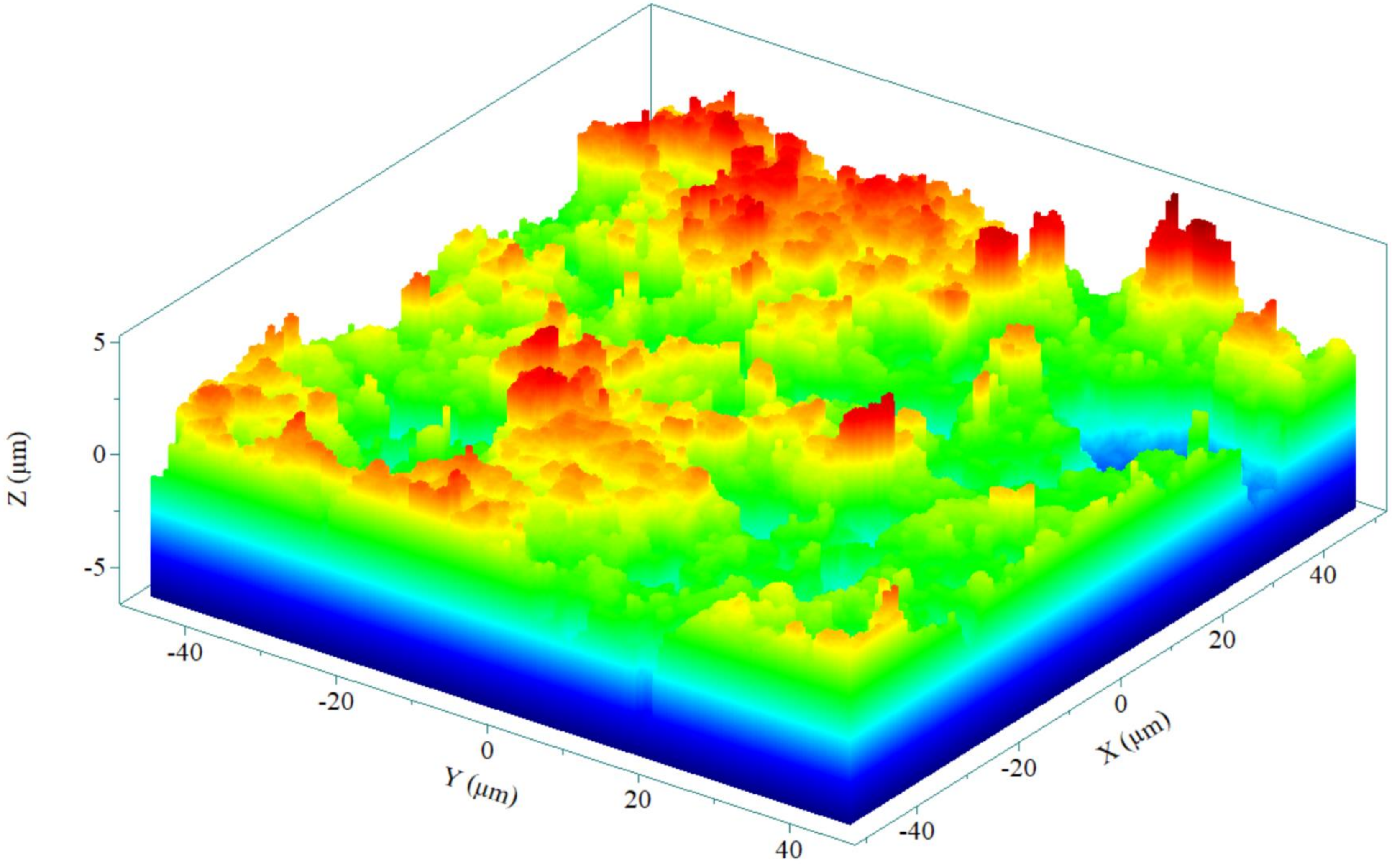
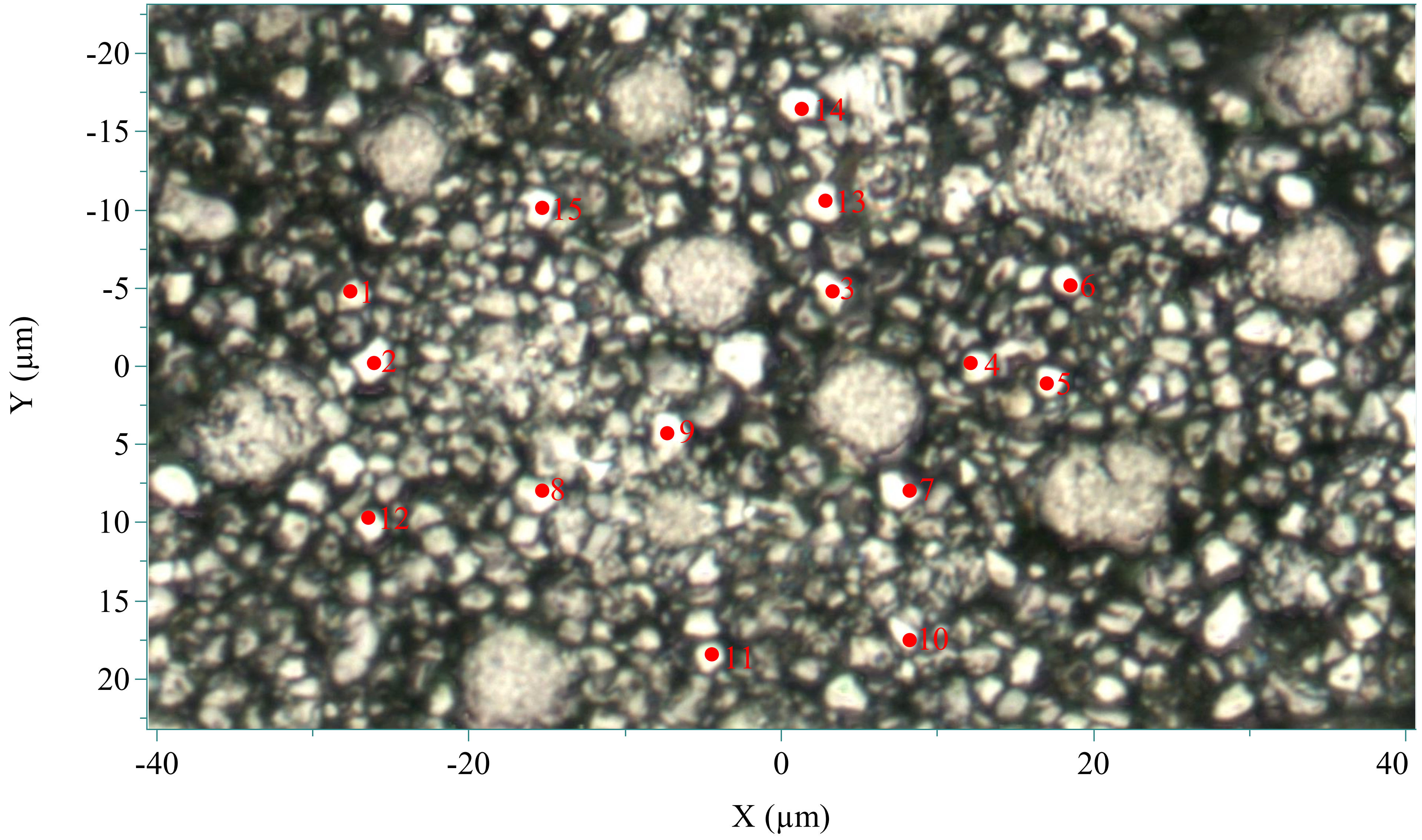
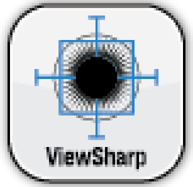
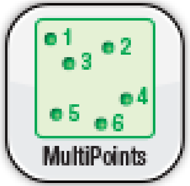
View Sharp – Z-profile = Topology



View Sharp – Particle Finder – Multi Points







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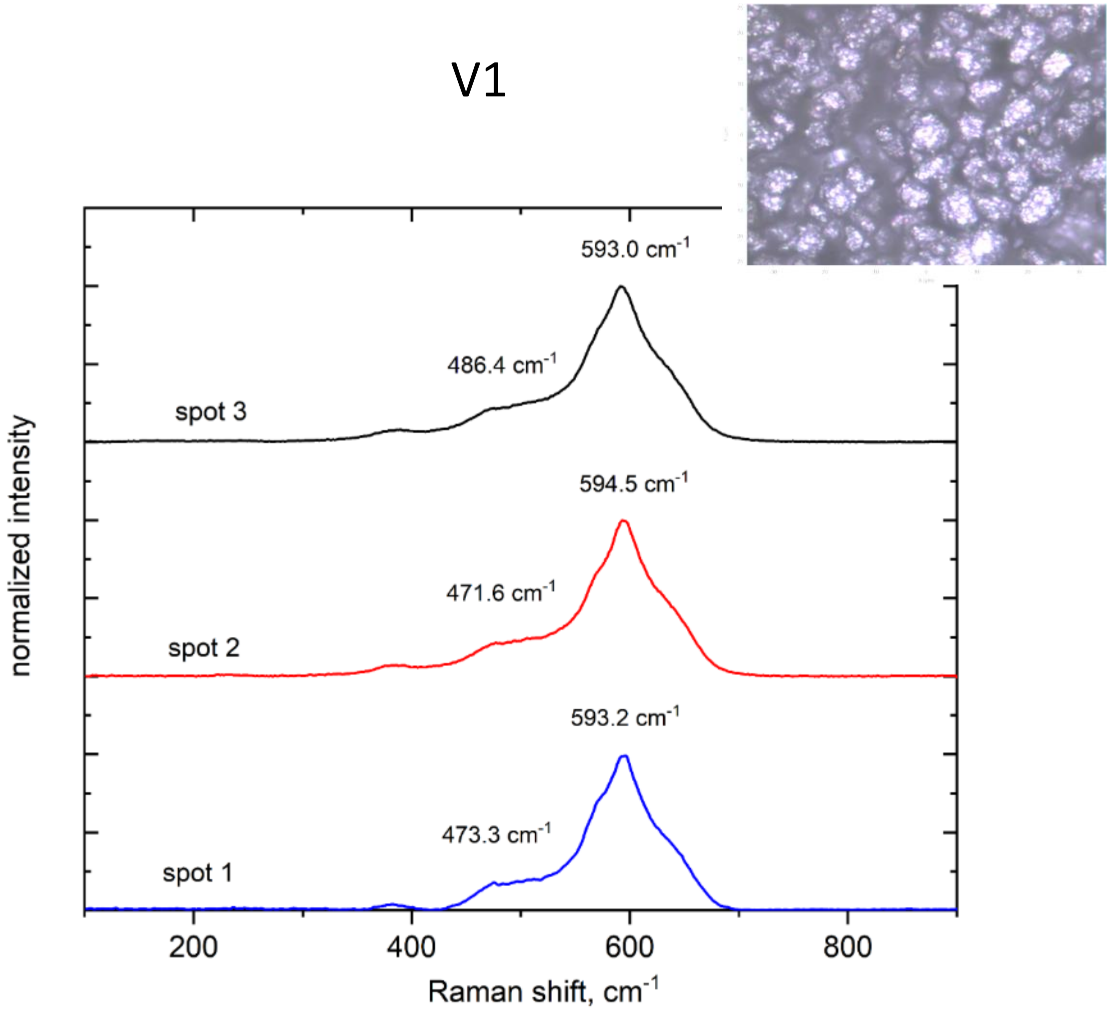
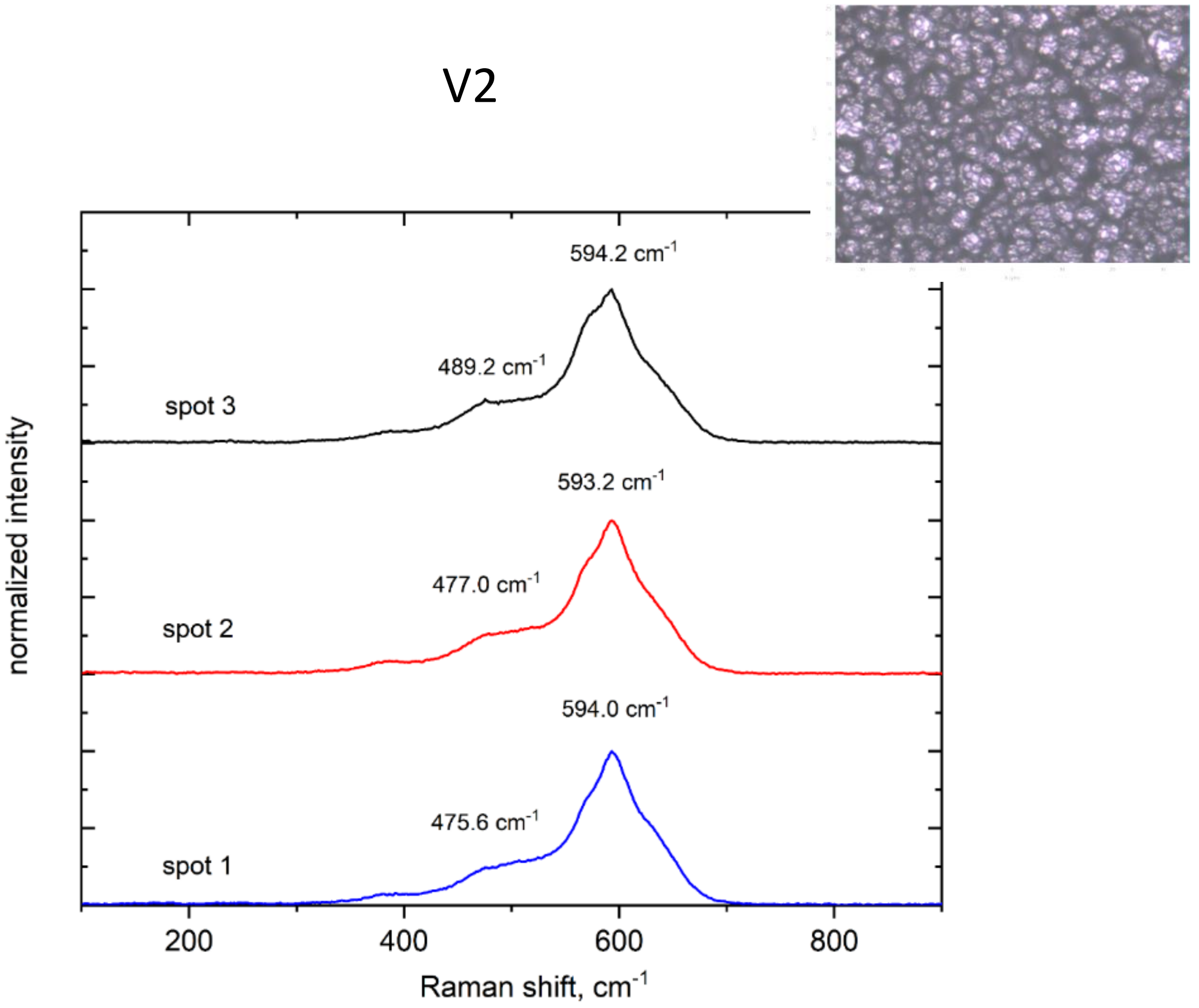
Raman spectroscopy of NCM 1:1:1





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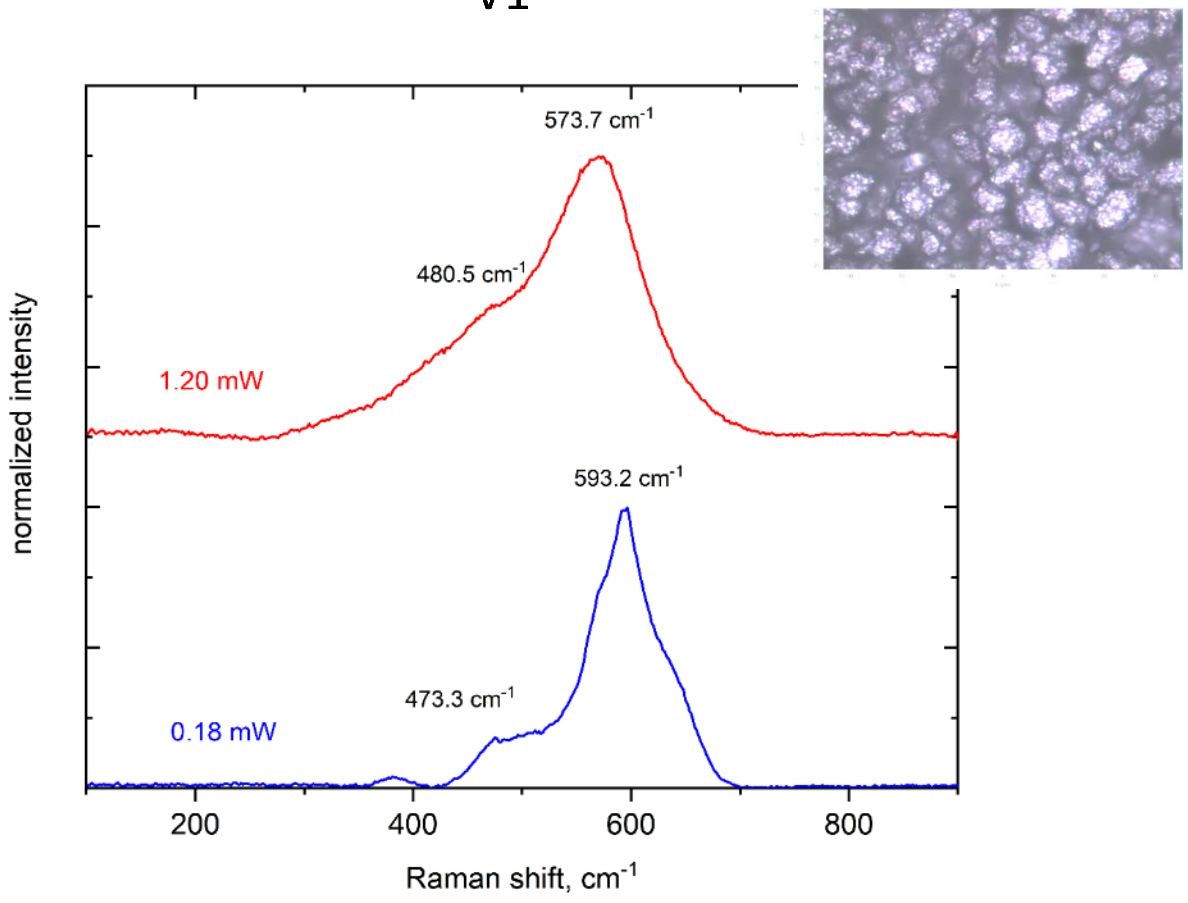
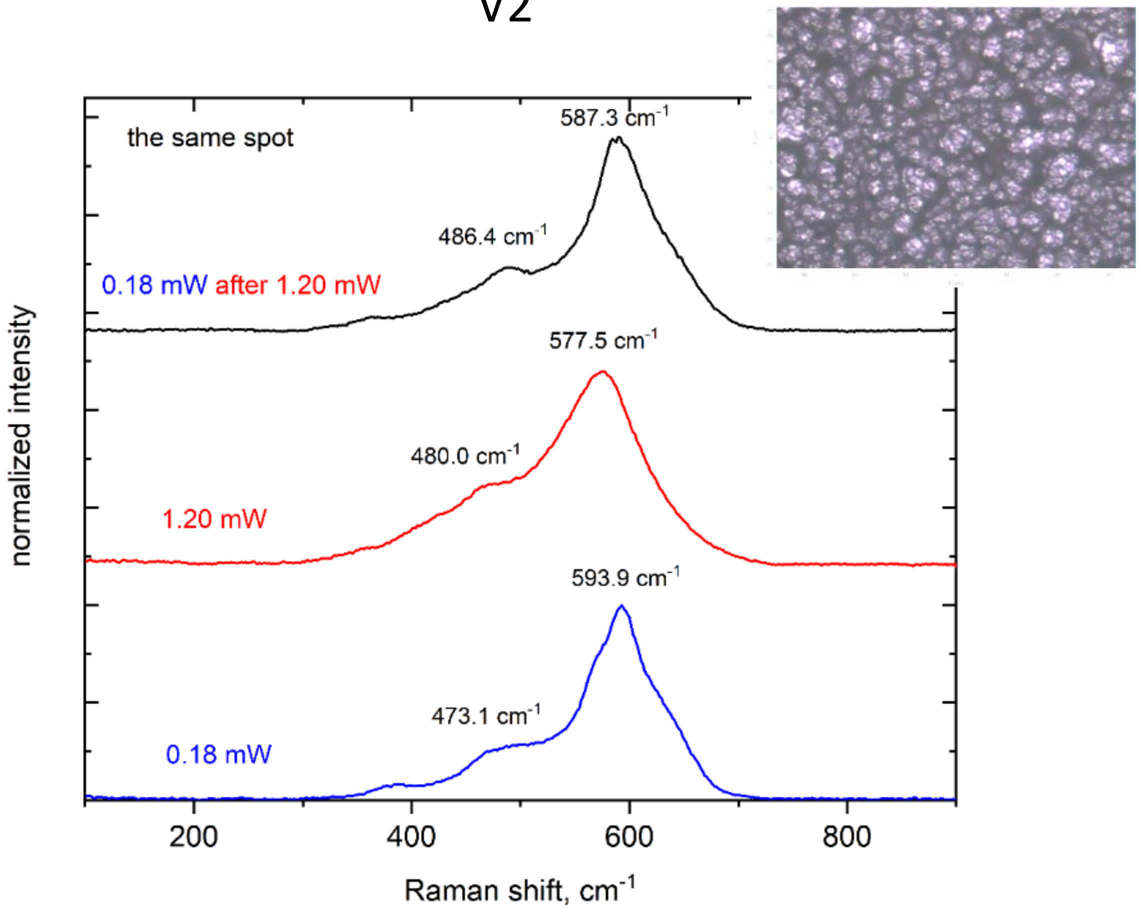
Raman spectroscopy of NCM 1:1:1

V1



V2



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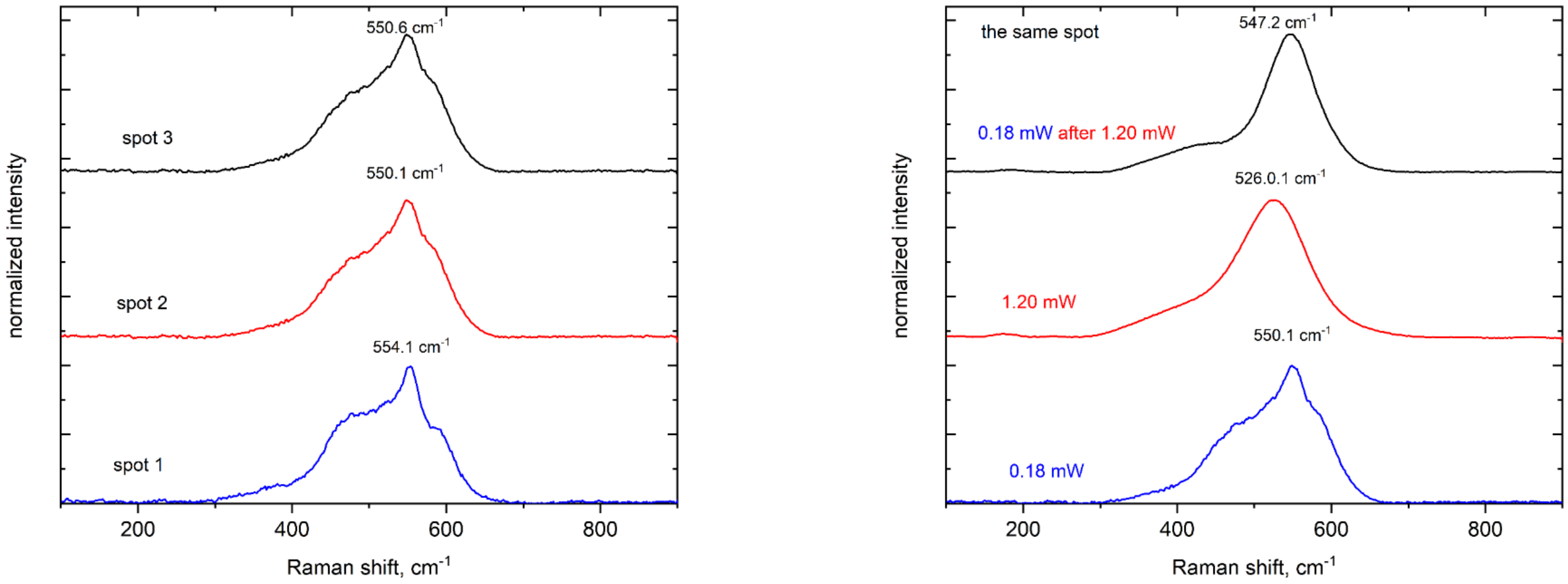
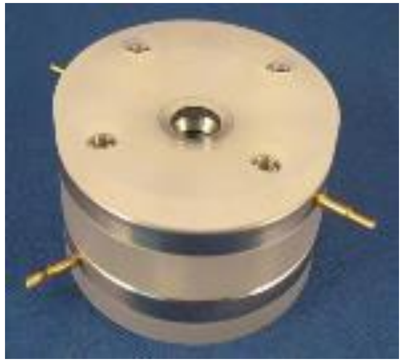
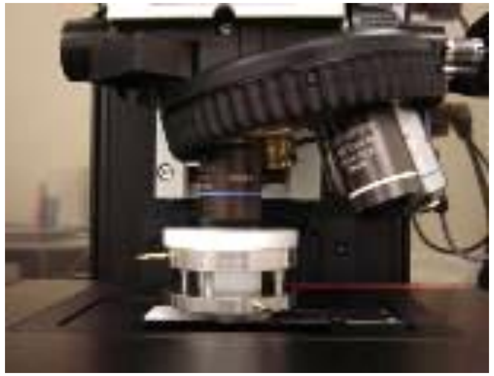
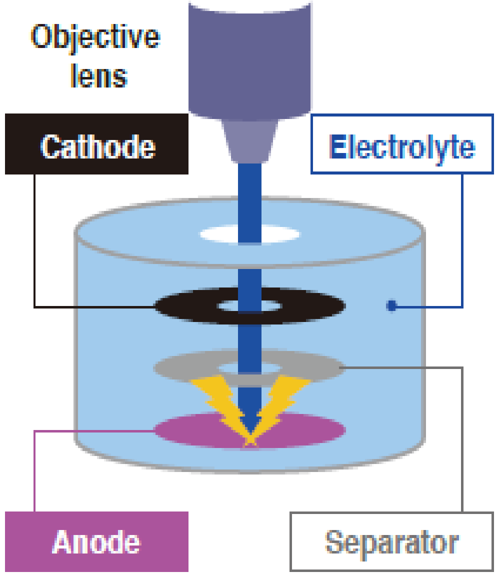
Raman spectroscopy of NCM 8:1:1

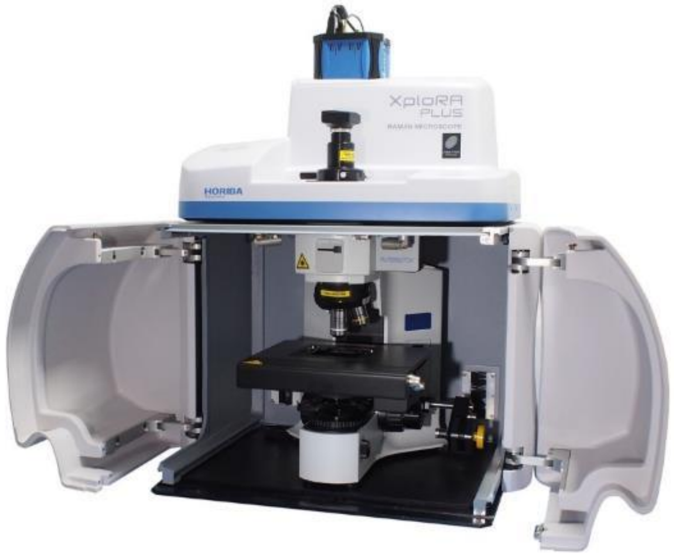


Instrumentation



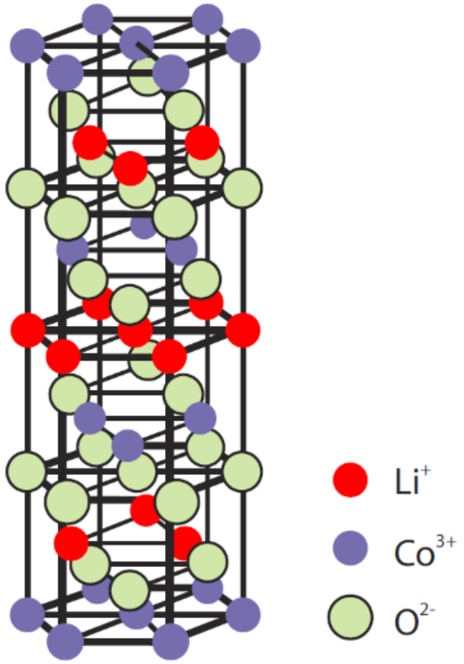






$LiCoO_2$ cathode

$LiCoO_2$ Crystal structure



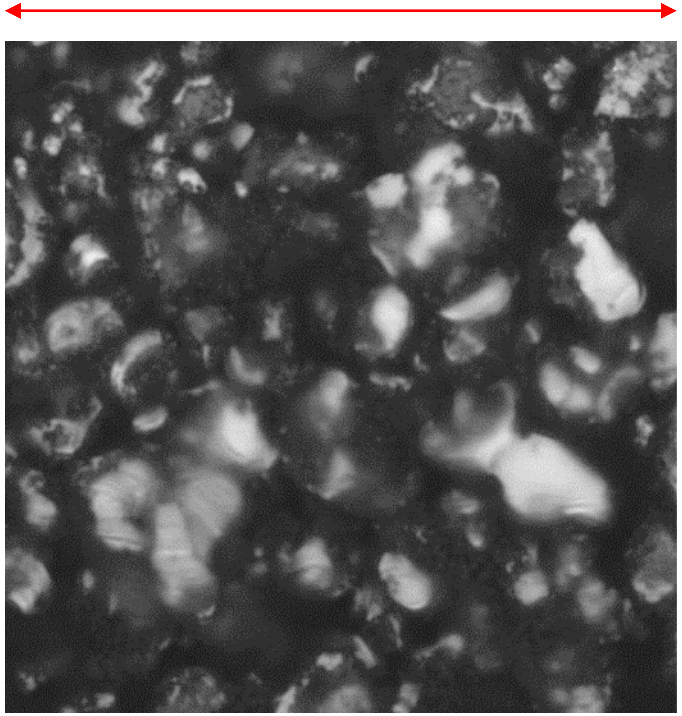
$$LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+ + xe^-$$

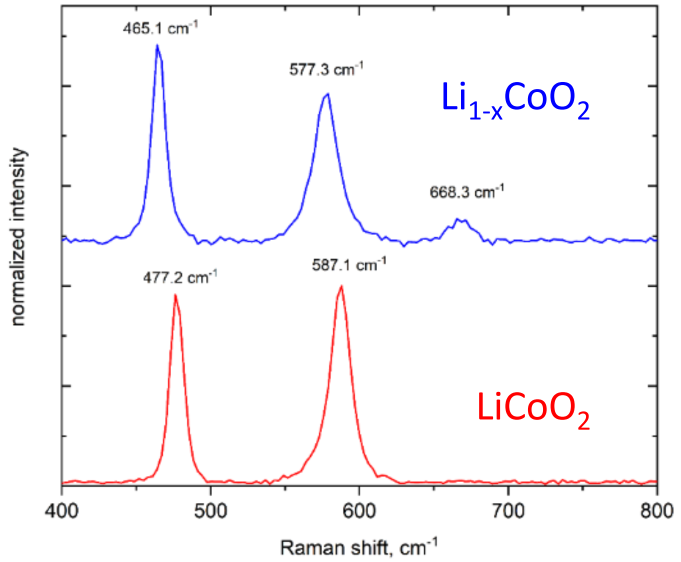
$$3LiCoO_2 + Li^+ + e^- = Co_3O_4 + 4Li_2O$$

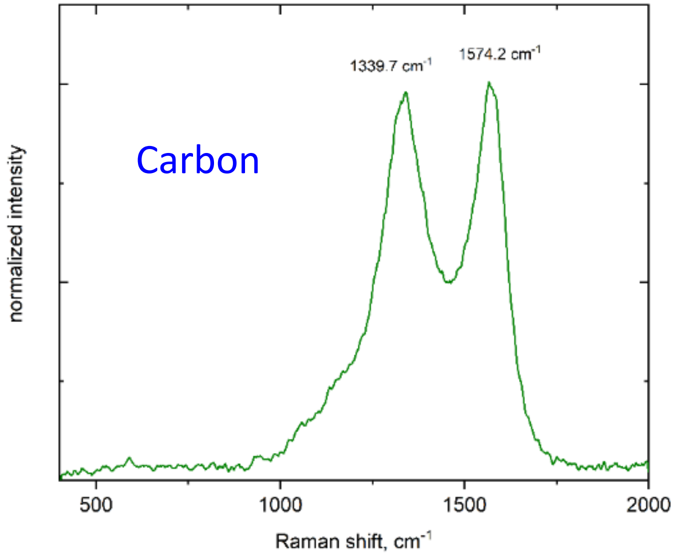
$LiCoO_2$ cathode

Ideally, charging - discharging processes are reversible. However, degradation = irreversible changes occur in cathode or anode.

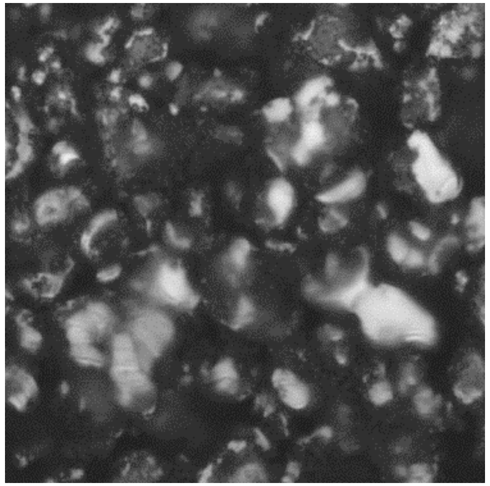
50 microns

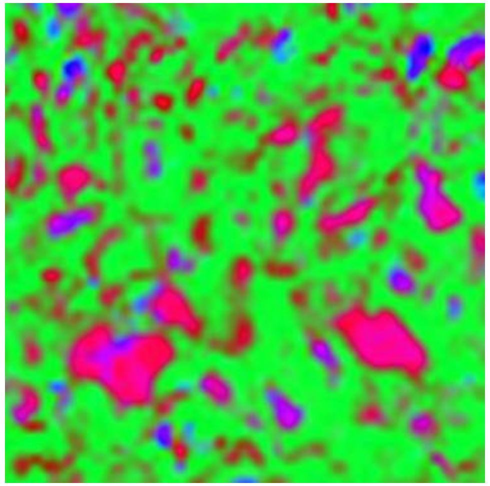


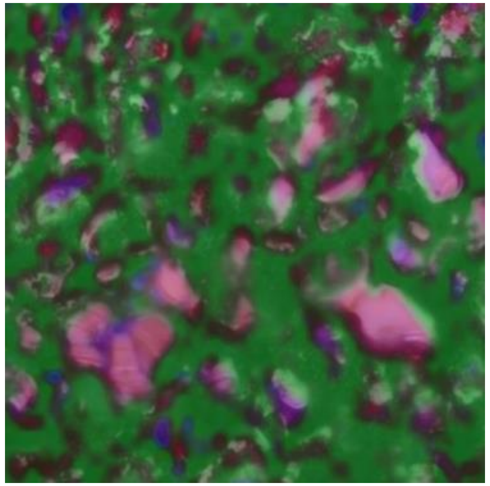




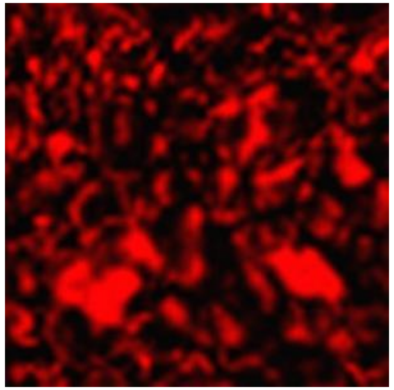
$LiCoO_2$ cathode



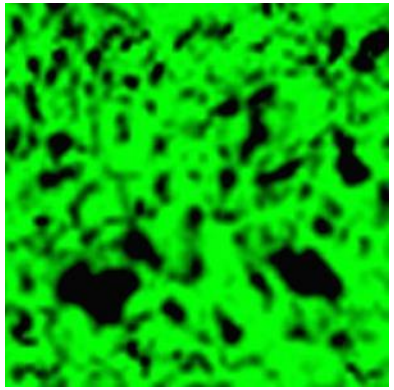




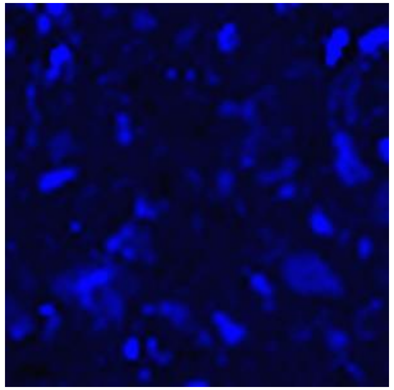
$LiCoO_2$



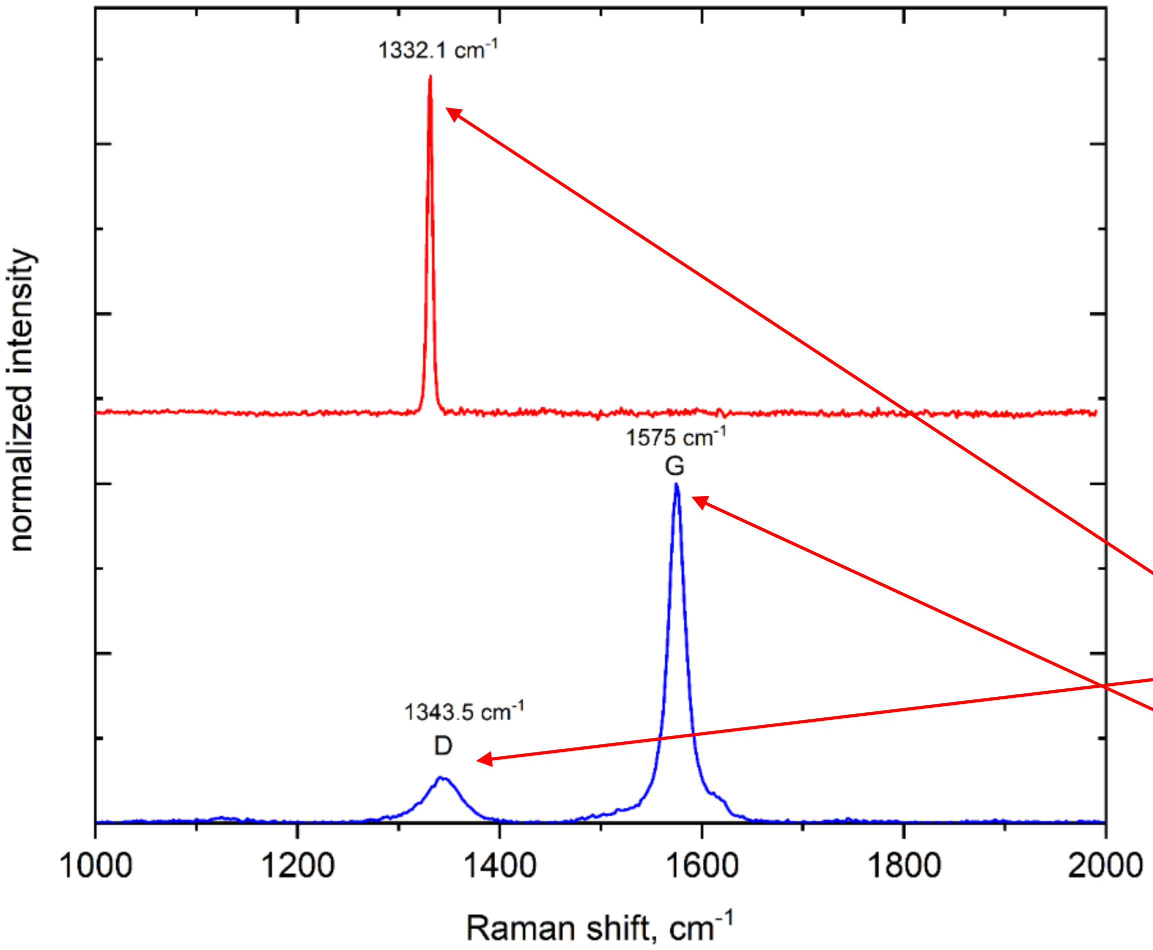
Carbon



$Li_{1-x}CoO_2$



Carbon based anodes

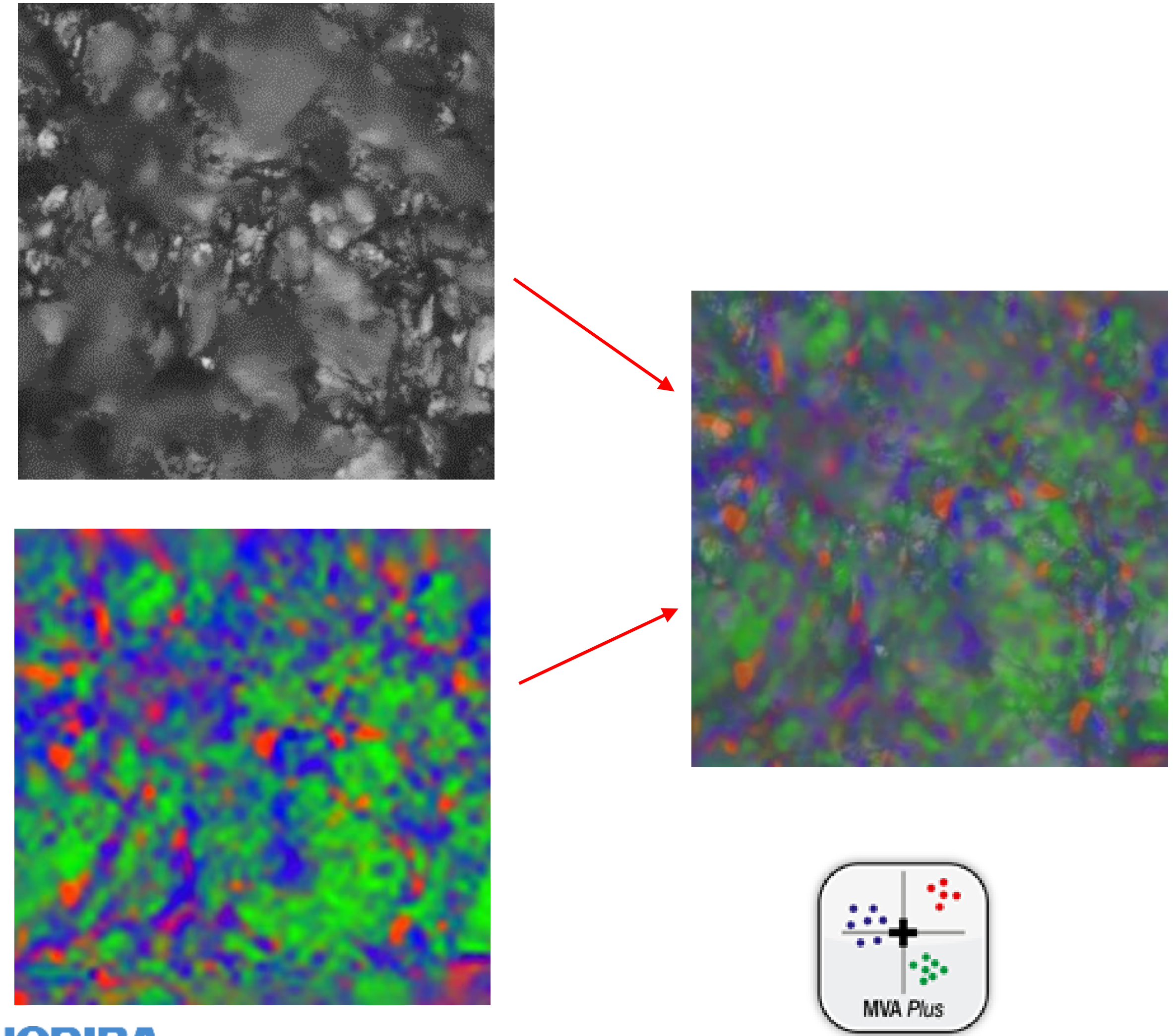


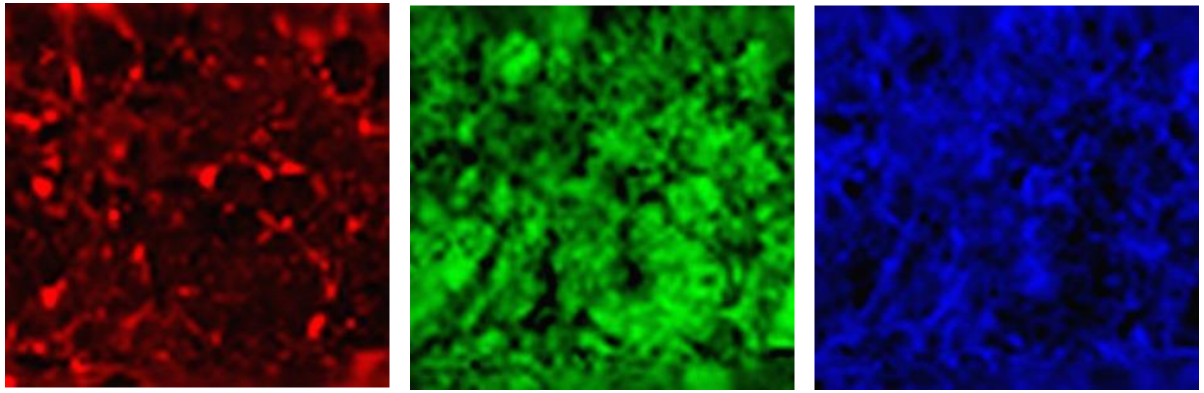
I_G/I_D ratio is a measure of disorder

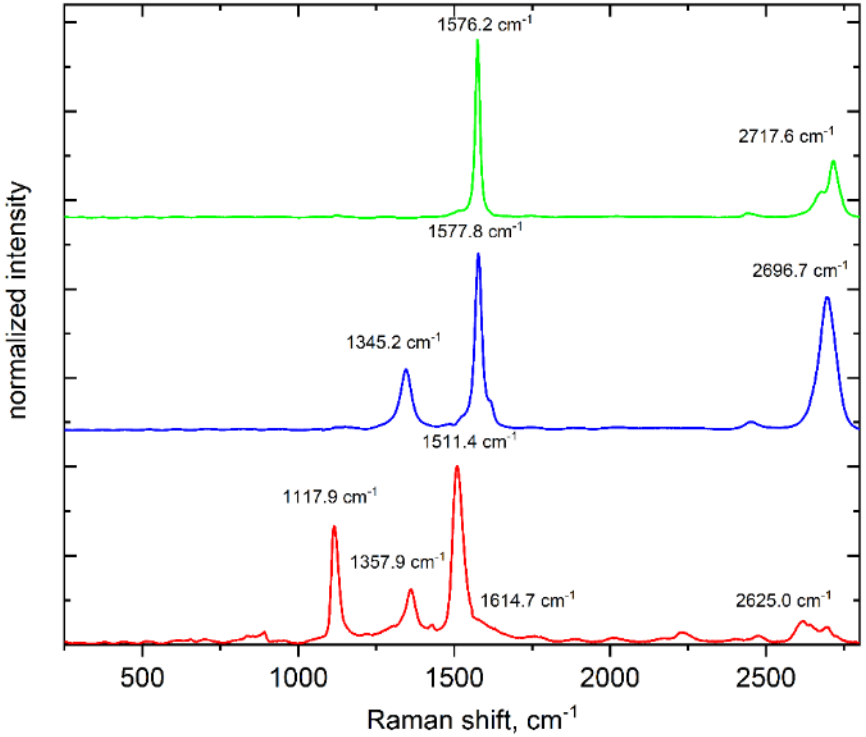
Nature of vibrations	Mode frequency (cm^{-1})	FWHM (cm^{-1})	Scattering cross section relative to the 1332 cm^{-1} mode	Depolarization ratio
sp^3 or sp^2[a]	~1150	80	1 or 57[b]	0.24
a-C[c]	1200	152	233[d]	0.24
a-C[c]	1300	132	233[d]	0.23
sp^3	1332	7	1	0.26
D[c]	1345	250	176	0.24
a-C[e]	~1470	80	233[d]	0.23
G[c]	1560	110	57	0.23

R. Ramamurti at all, *J. Vacuum Science and Technology, 2006, A24, 179.*

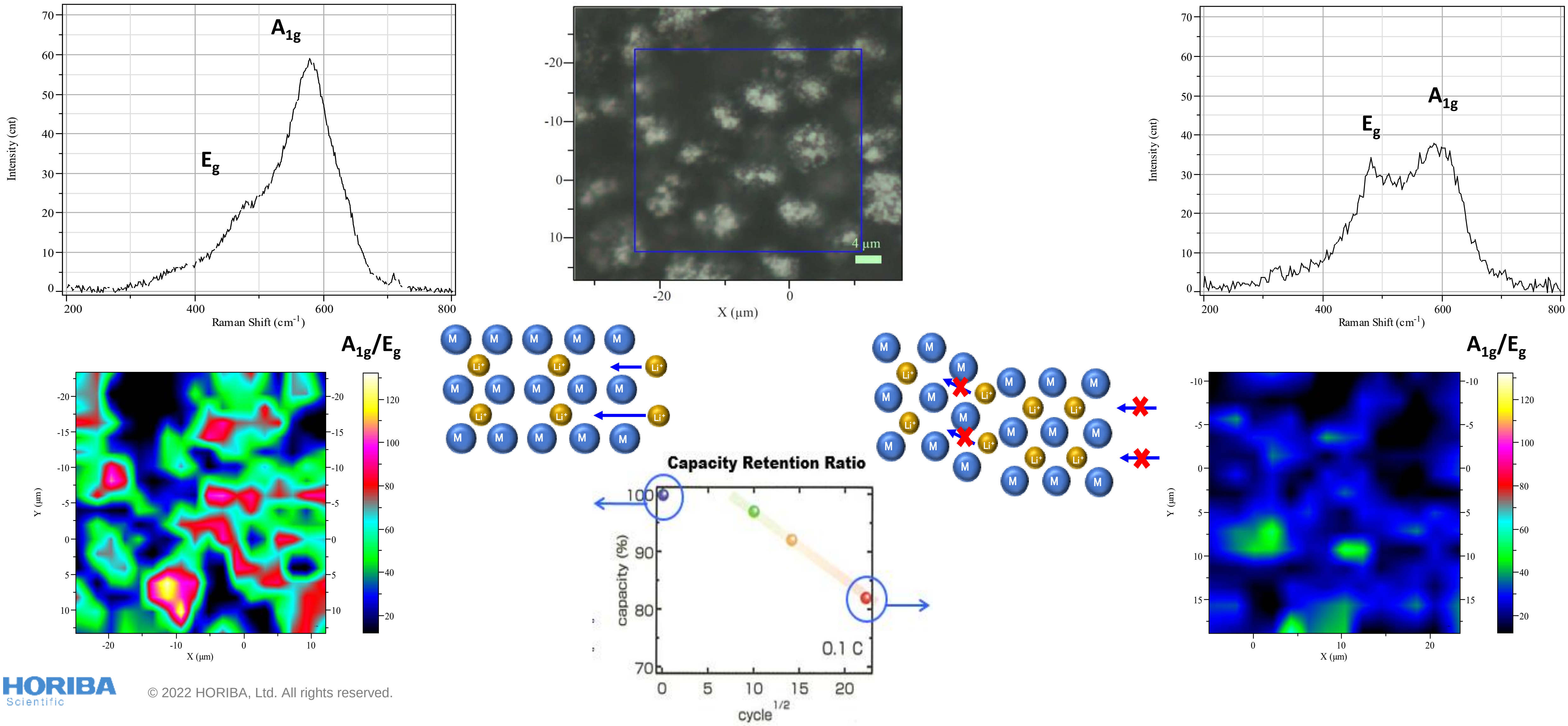
Carbon based anode





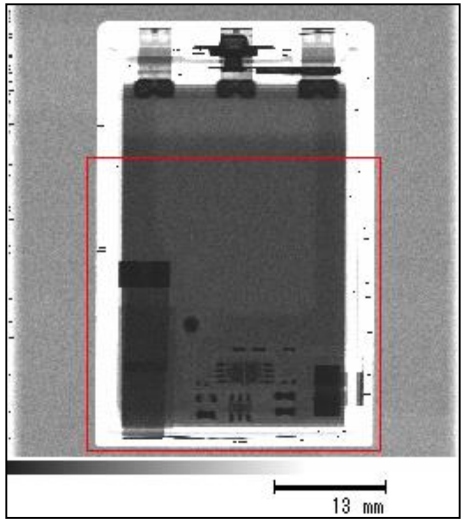


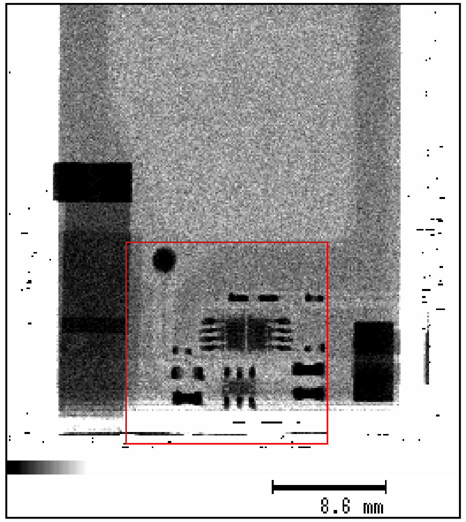
NMC cathode

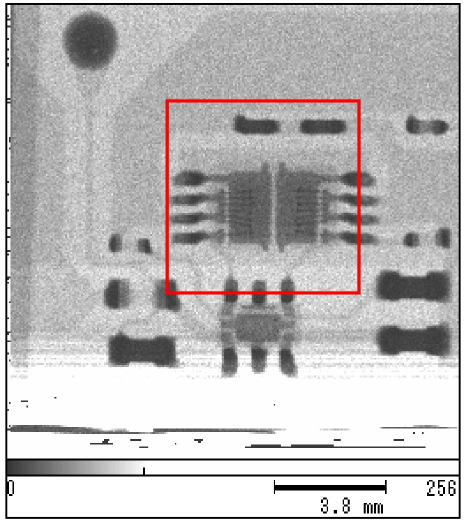


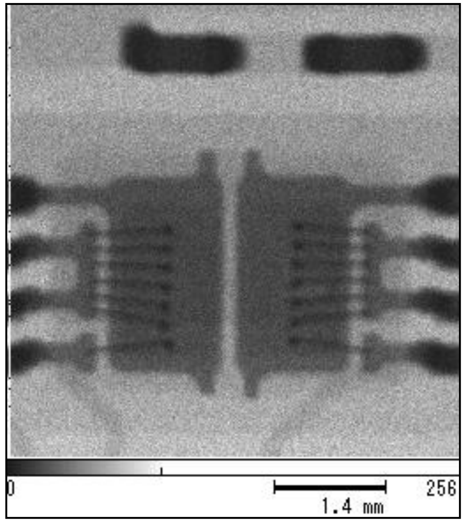
A1g
Eg
Intensity (cnt)
Raman Shift (cm-1)
X (µm)
4 µm
A1g/Eg
Y (µm)
Capacity Retention Ratio
capacity (%)
cycle1/2
0.1 C
M
Li+

Micro-XRF – Li-ion batteries



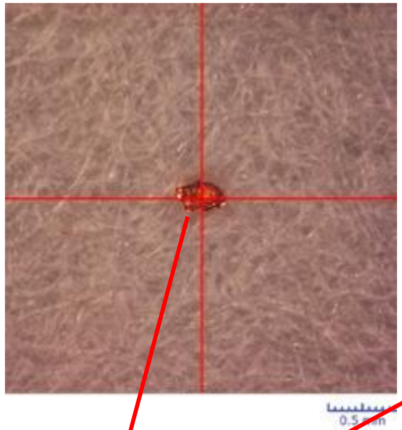


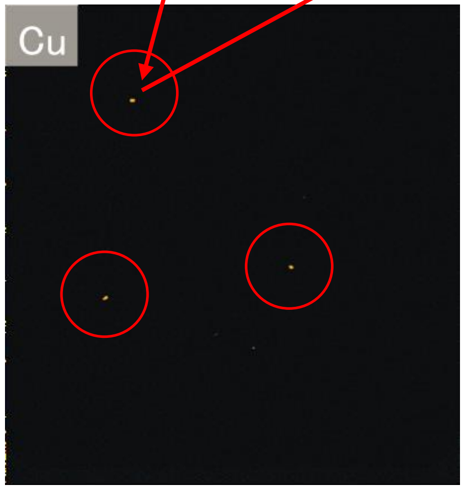


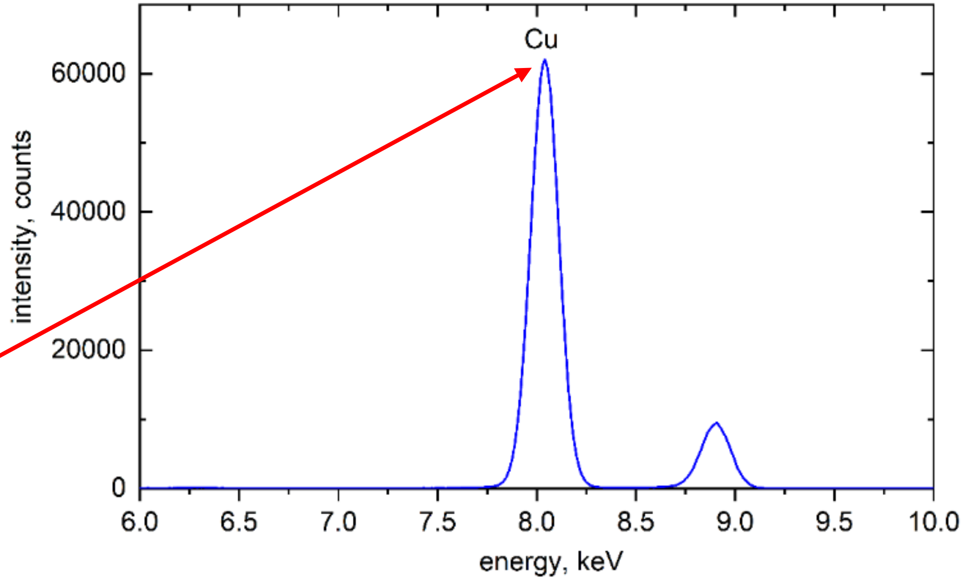


Micro-XRF – Li-ion batteries

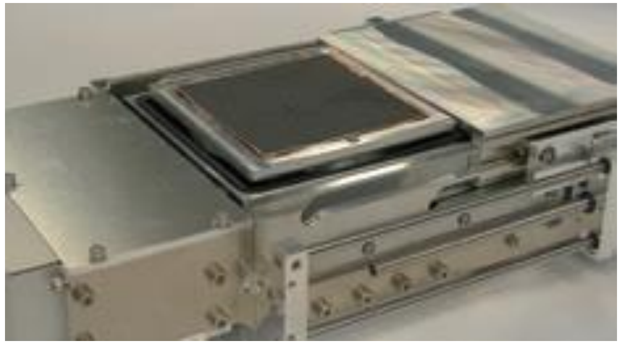
Contamination on separators is causing short circuits, which lead to malfunction.







The transfer vessel controls the environment between a glove box and a device.

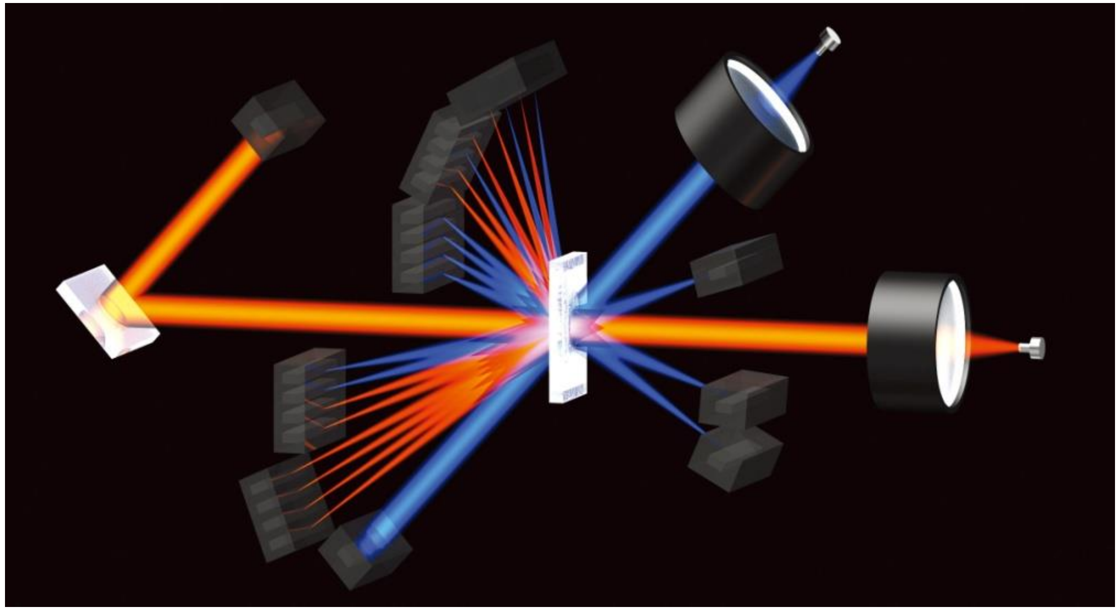


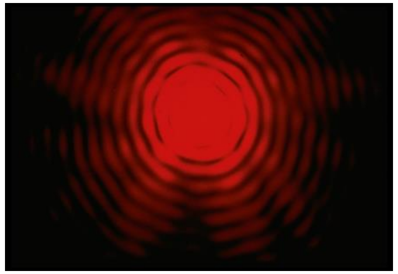
XGT-9000

Particle Characterization (Jeff Bodycomb)

The LA-960 and laser diffraction

- Converts scattered light to particle size distribution
- Quick, repeatable
- Powders, suspensions
- Most common technique



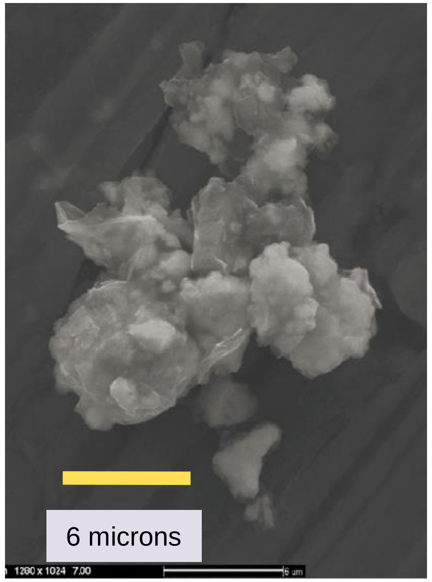


But my battery is solid!

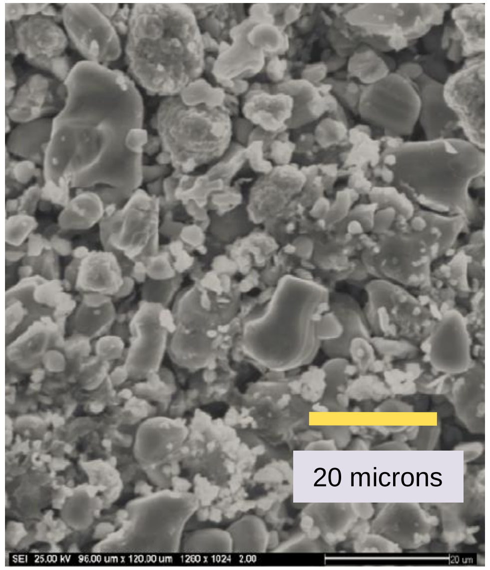
A battery is usually solid and quite durable.

But what if we look inside a Li-ion battery?

Anode

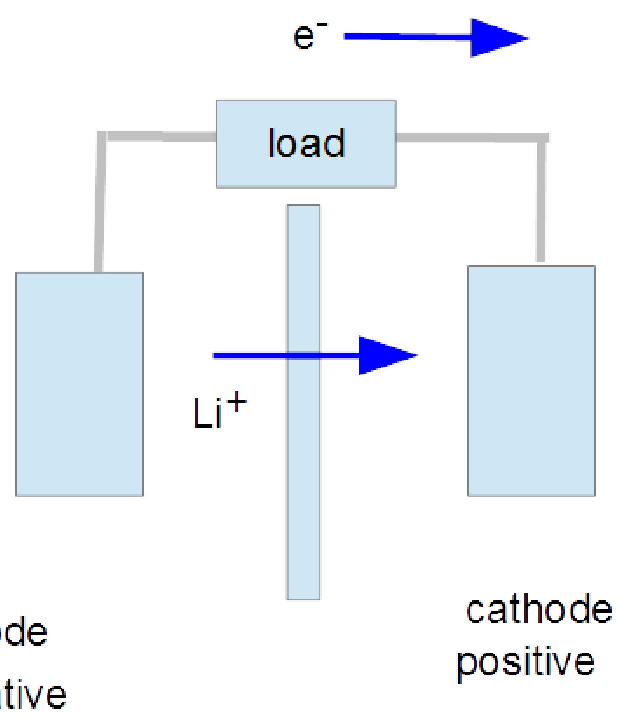


Cathode



Particles!

Battery Basics



$CLi \leftrightarrow Li^+ + e^-$

$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$

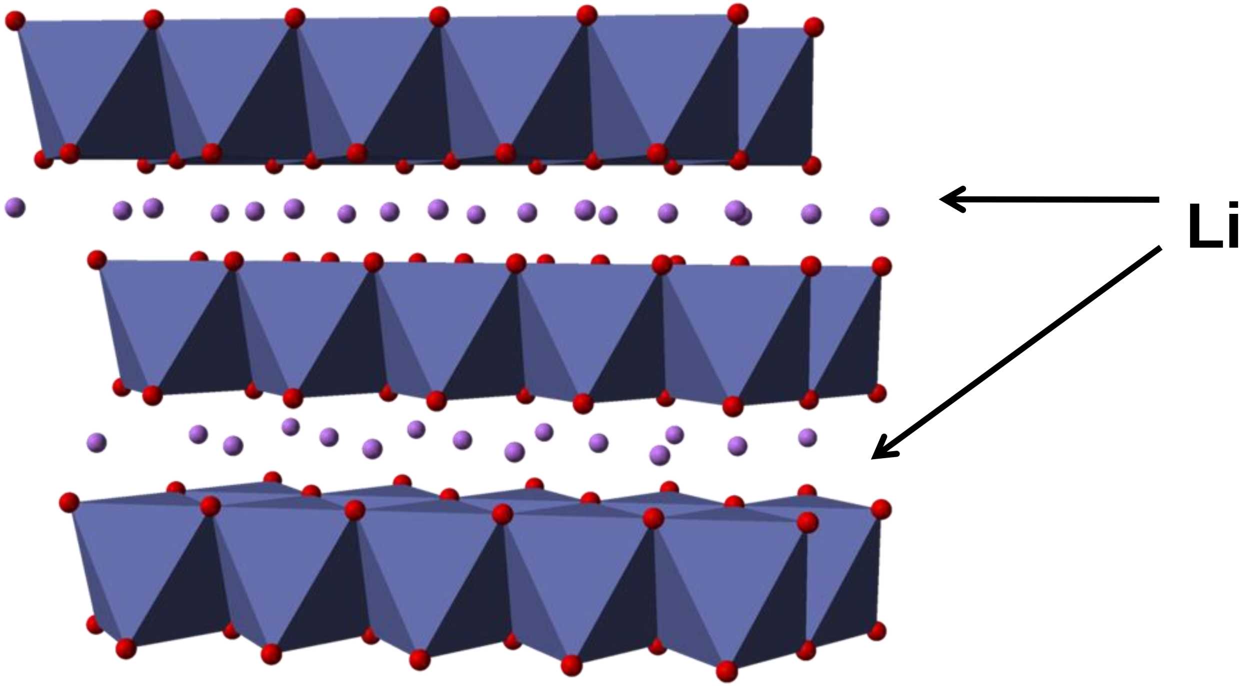
Chemistry sets potential (voltage)…
But the voltage drops due to resistance (electrical and ionic).

Microscopic View

$LiCoO_2$

Li moves into CoO_2 octahedra slabs

How fast can the LI get in there?

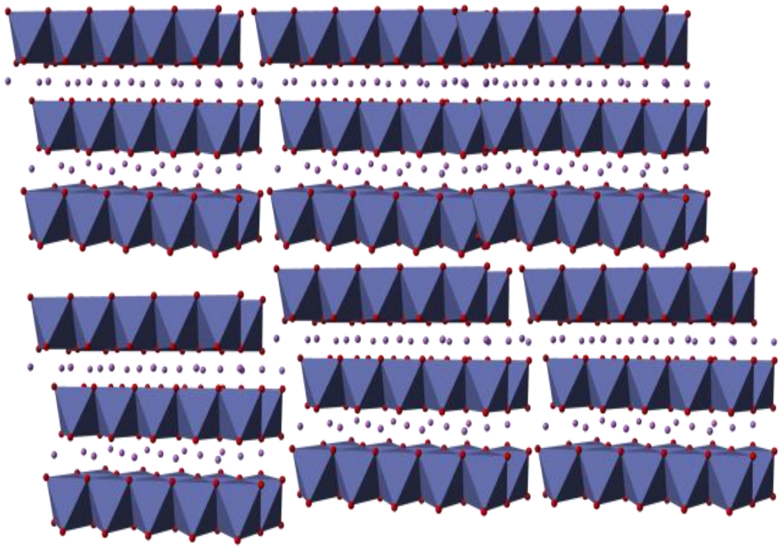


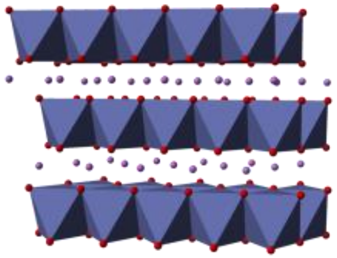
Particle Size!

Need to consider diffusion of Li+ into CoO_2 when considering charge/discharge rate (or power, not energy)!

As particles get smaller, area for diffusion increases

Also, area for undesirable side reactions increases





See M. Park, et al., J. Power Sources (2010), doi:10.1016/j.jpowsour.2010.06.060

Alkaline battery

Graphite particle size

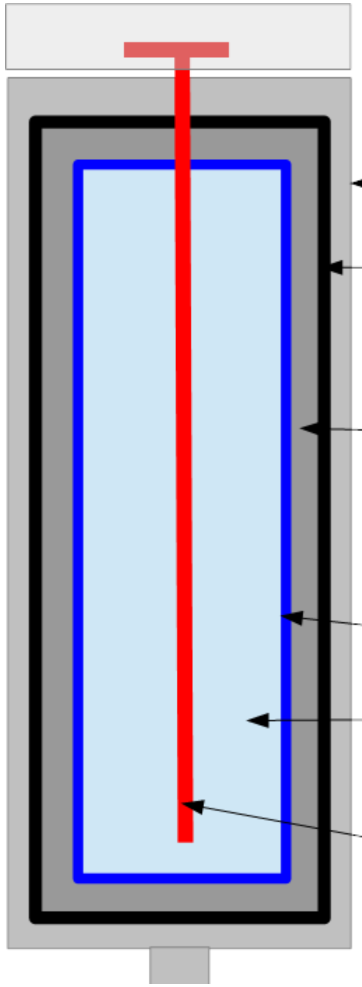
- Smaller particles

  lower resistivity at low loadings (5%)

  lowers flex strength
- D90's from 10 to 100 microns

MnO_2 powder is ~100's of microns

Anode is Zn powder (D50 of 50~200 microns) in gel



Measuring graphite

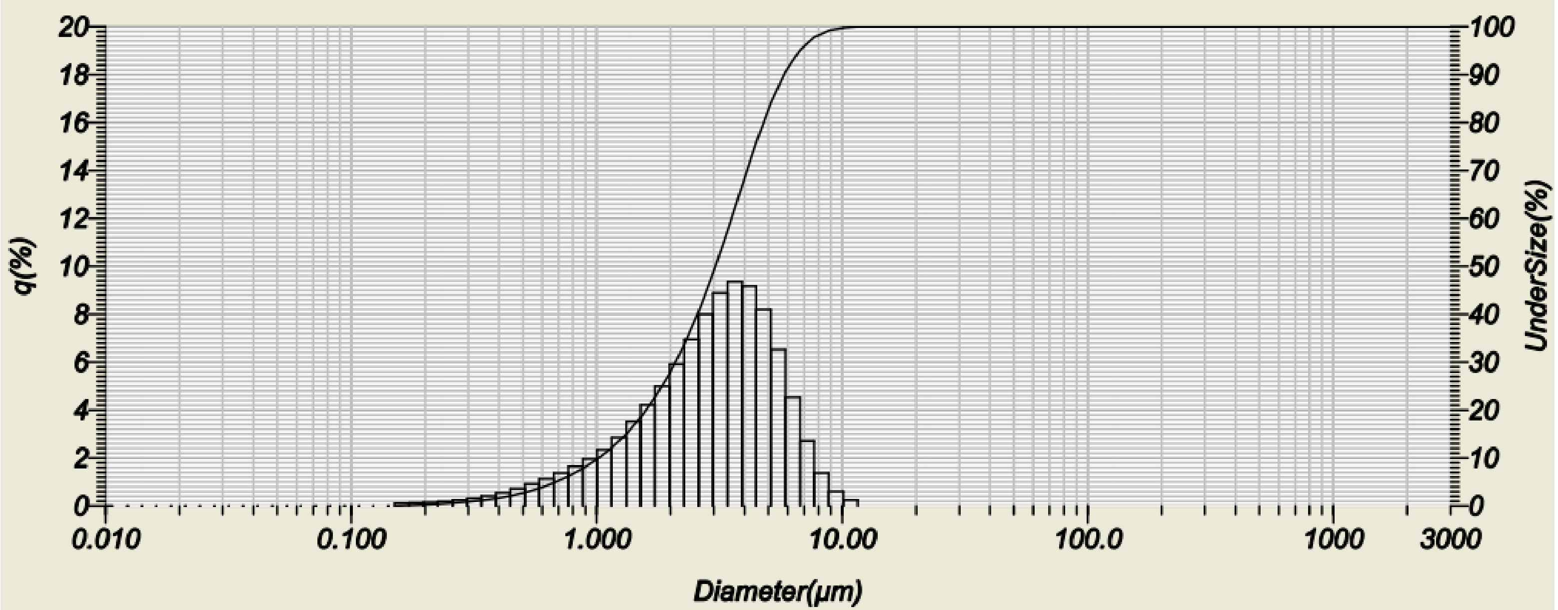
Laser diffraction

Dispersed in 0.01% Tween 20

10 minutes ultrasonic

D50: 3.05 micron

D90: 5.80 micron



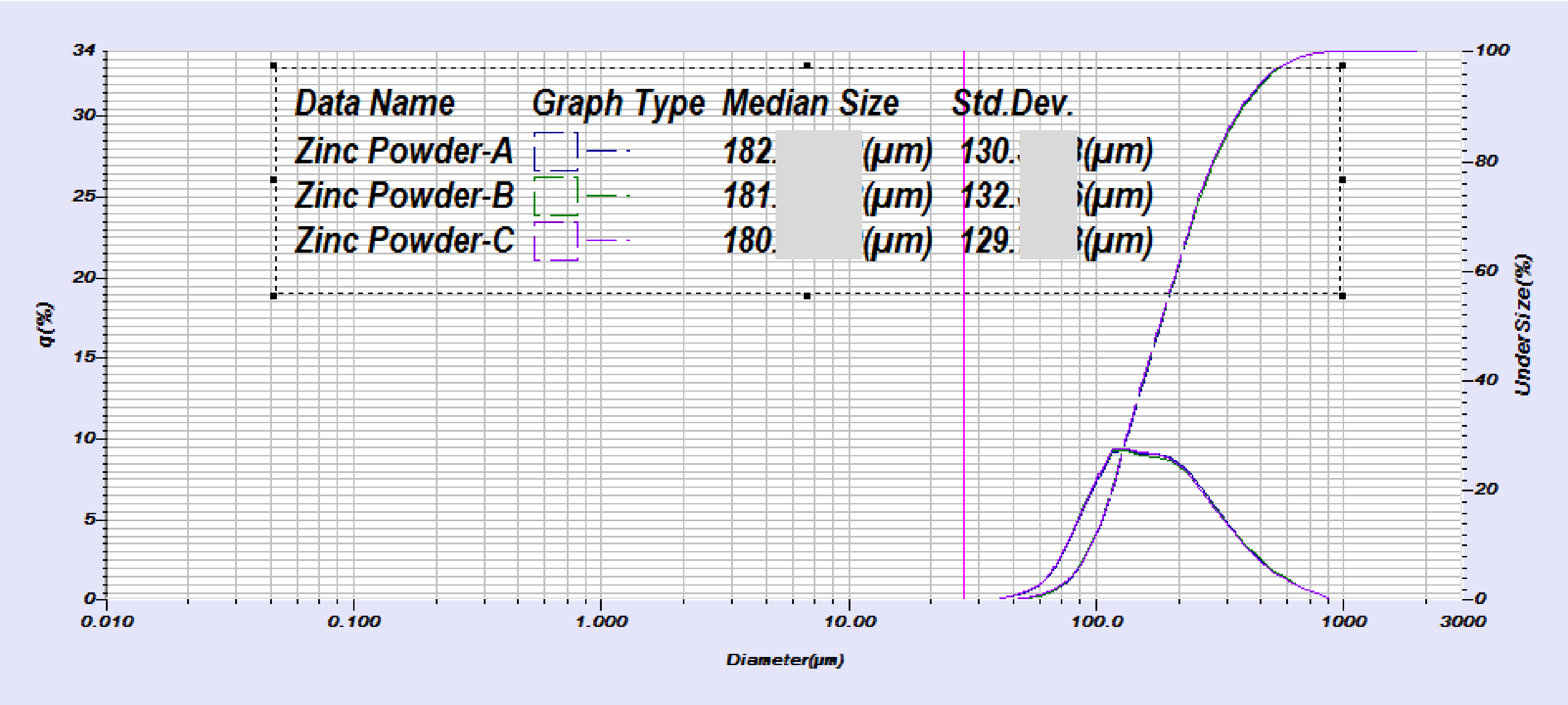
Small for imaging

Large for dynamic light scattering (DLS)

Diffraction and the LA-960 is your friend

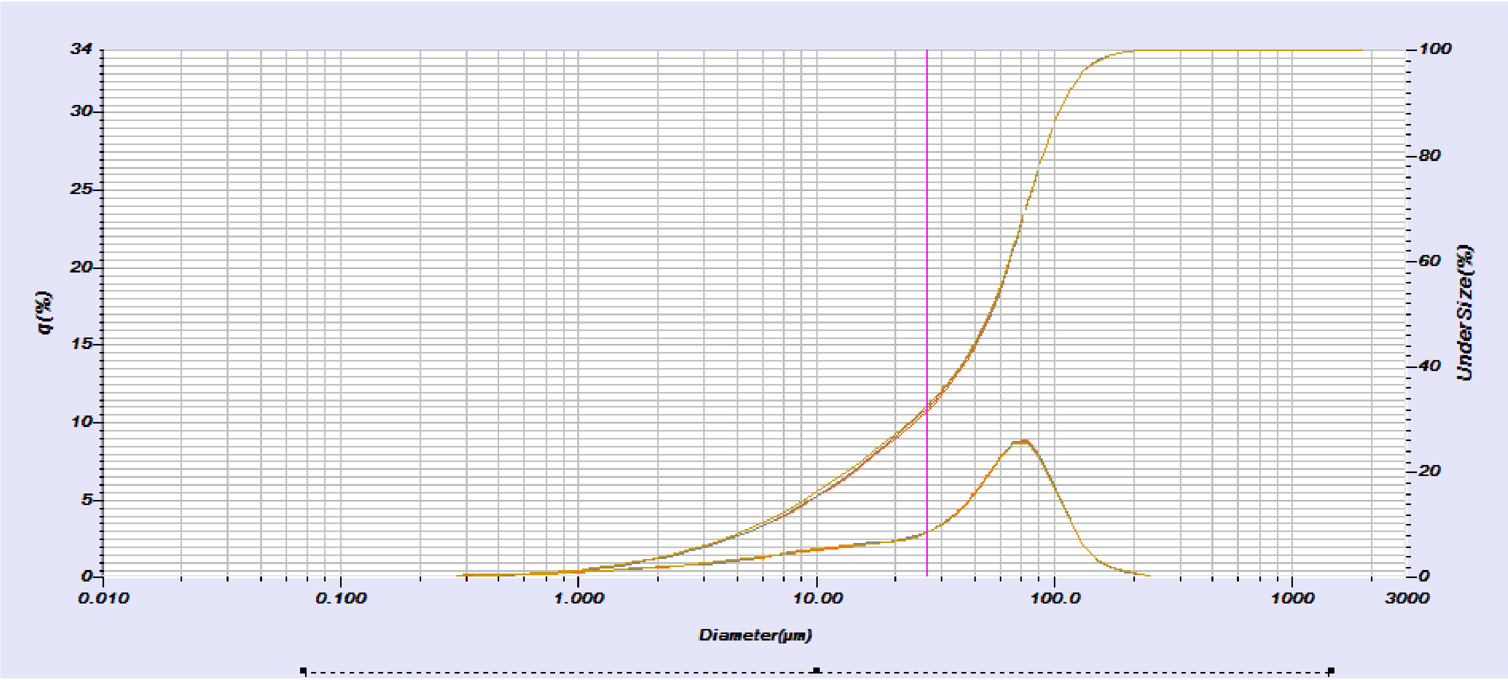
Measuring Zinc Powder

This sample was measured dry by laser diffraction…there is no need to disperse it in liquid.

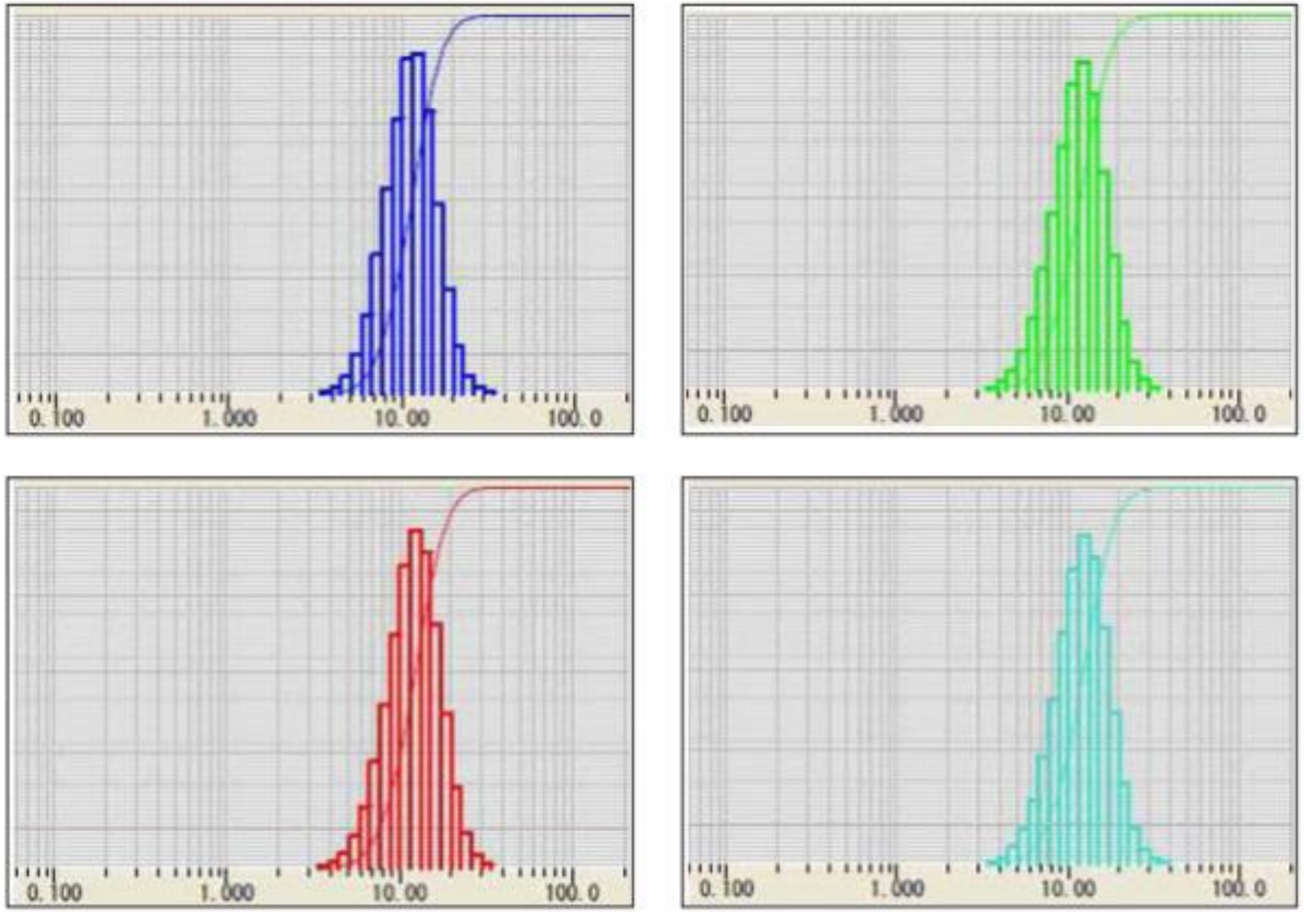


Measuring MnO2

Yes, laser diffraction works here as well.



$LiCoO_2$

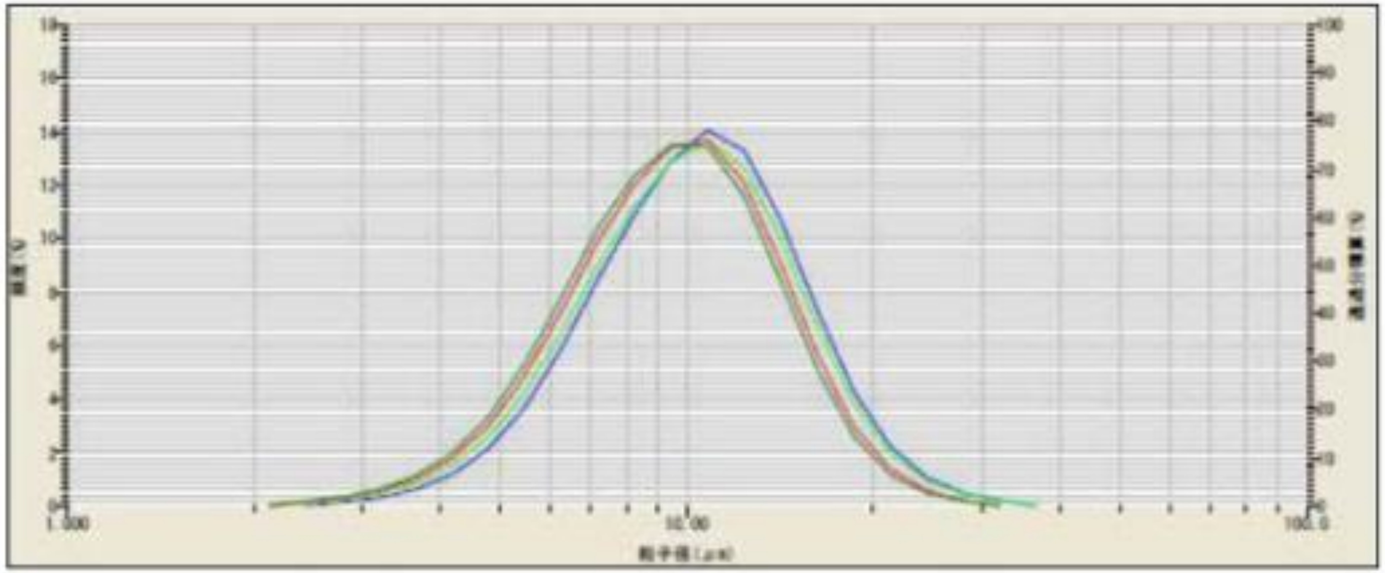


Lot	Median (m)
No. 1	11.3
No. 2	11.8
No. 3	12.2
No. 4	12.5
No. 5	11.9

Figure 1 and Table 1: Five lots of $LiCoO_2$ powder

Lithium Manganese Oxide

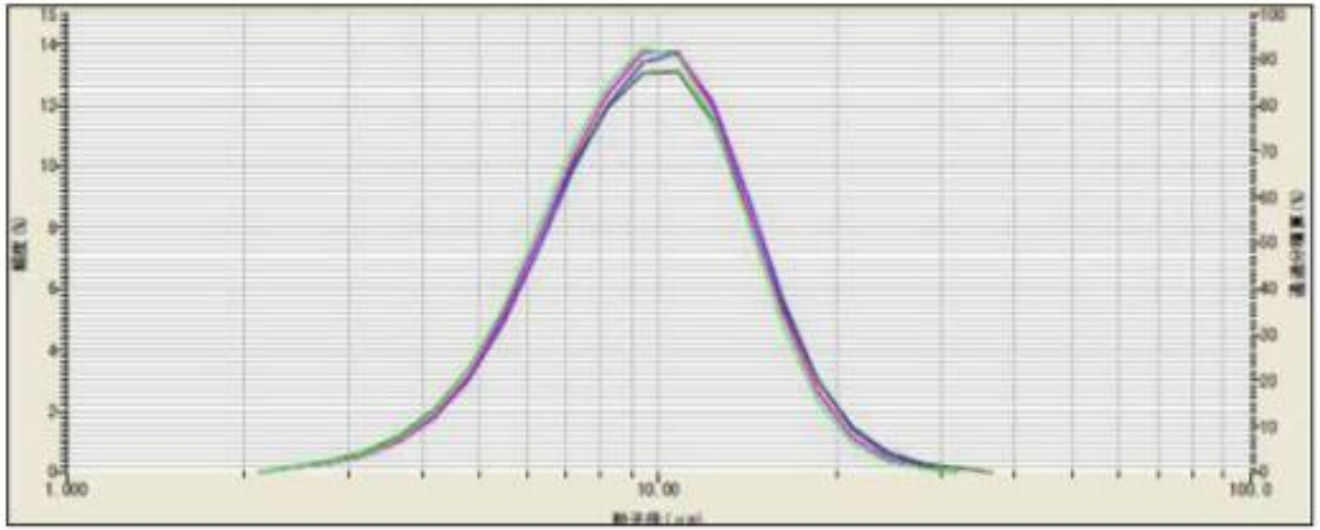
This is an example of using ultrasound to break up loose agglomerates of particle.



Ultrasound	Median (m)	Color
None	10.46	blue
1 min	10.14	light green
3 min	9.67	red
5 min	9.42	dark green

Figure 2 and Table 2: The effect of ultrasound on $LiMn_2O_4$

Repeats (different days)



	Median (m)
Day 1	9.75
Day 2	9.52
Day 3	9.18
Day 4	9.49
Day 5	9.5
Mean	9.49
COV	1.90%

Figure 3 and Table 3: Method validation testing on multiple days of $LiMn_2O_4$

1.90% CoV!

Great repeatability with the LA-960

Repeated runs with 0.5% CoV

Great tool to track changes in your process.

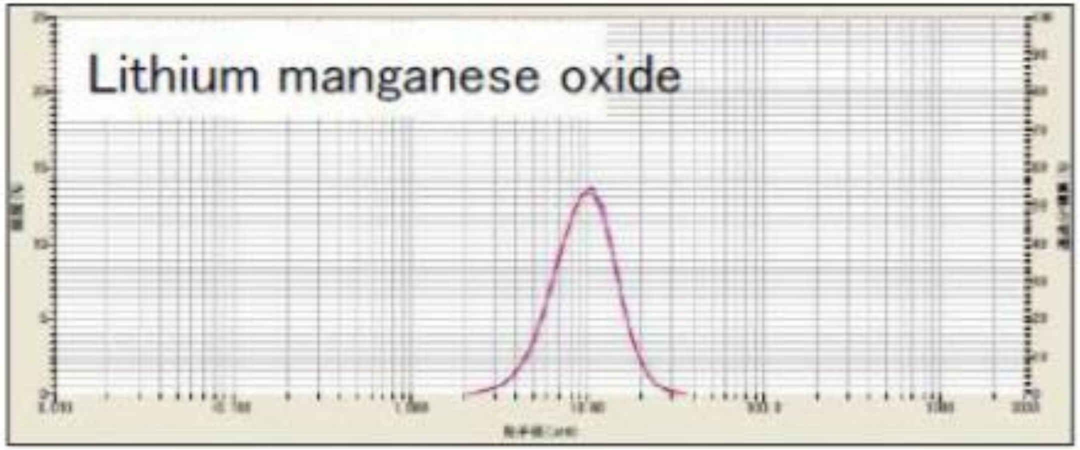
Sample	$LiMn_2O_4$	Li_2TiO_3
R1	9.75	16.70
R2	9.93	16.6
R3	9.75	16.7
R4	9.66	16.6
R5	9.83	16.7
R6	9.78	16.6
R7	9.76	16.8
R8	9.75	16.8
R9	9.79	16.8
R10	9.6	16.9
Ave	9.76	16.7
COV	0.90%	0.51%

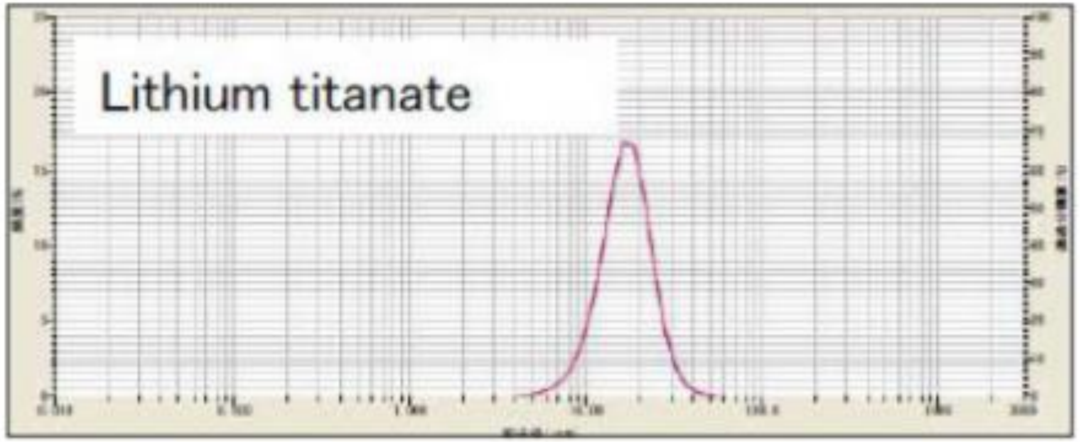
Figure 6: Reproducibility over 10 results for $LiMn_2O_4$ and Li_2TiO_3

Two different analyzers!

	950 1	950 2	Δ
LiMnO	9.75	9.64	0.1
LiTi	16.7	16.9	0.2

Figure 7: Instrument to instrument agreement for $LiMn_2O_4$ and Li_2TiO_3 on two different LA-960 systems

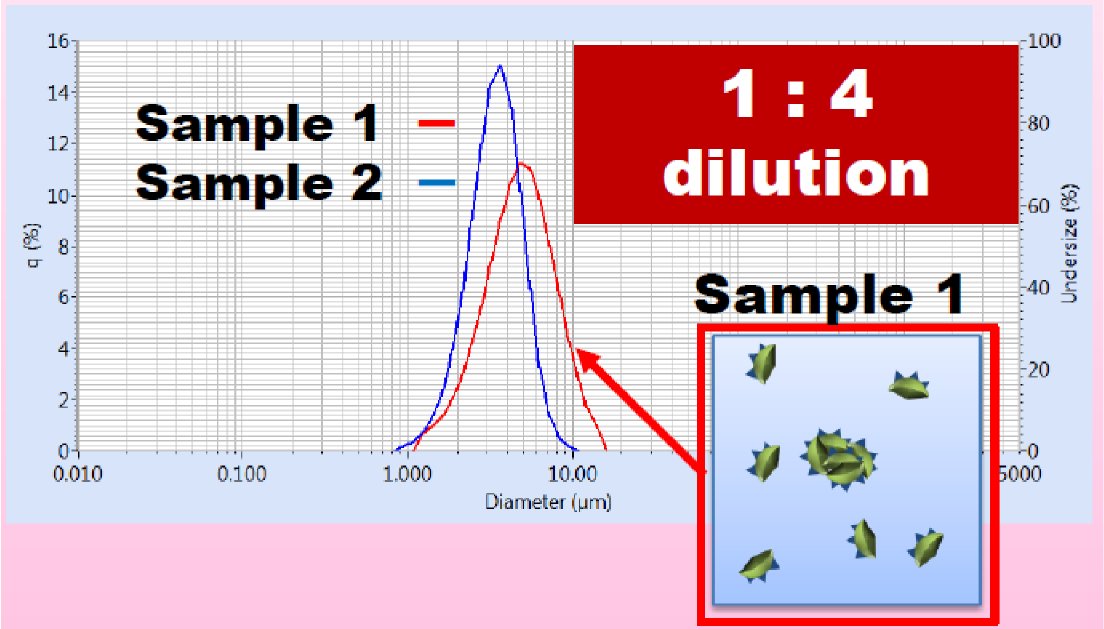


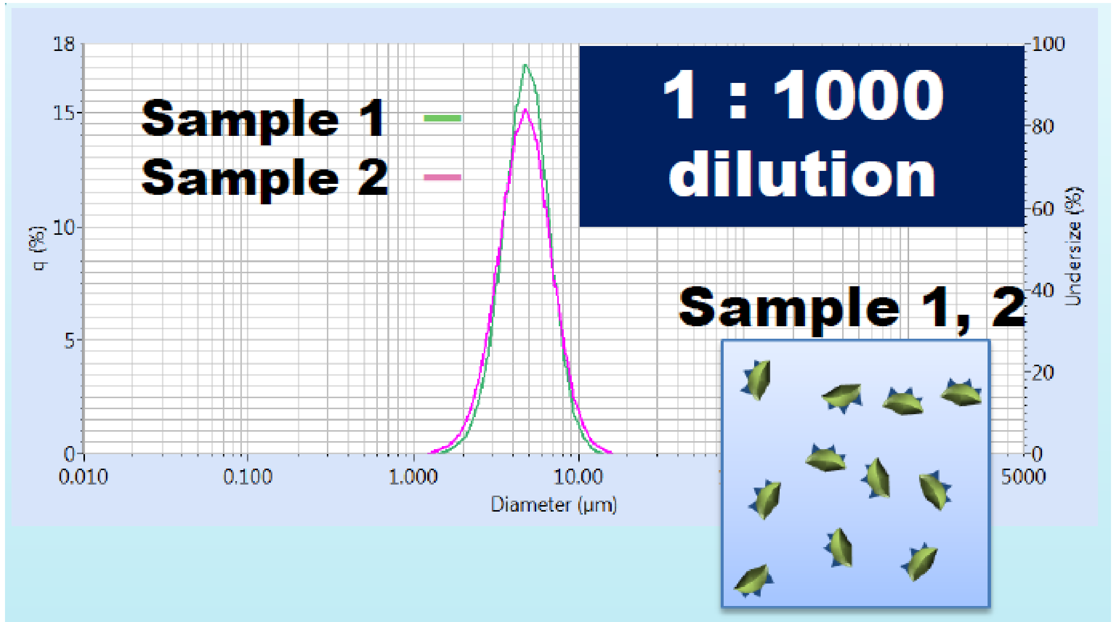


This is important when manufacturing or using the powders at multiple sites.

Less dilution?

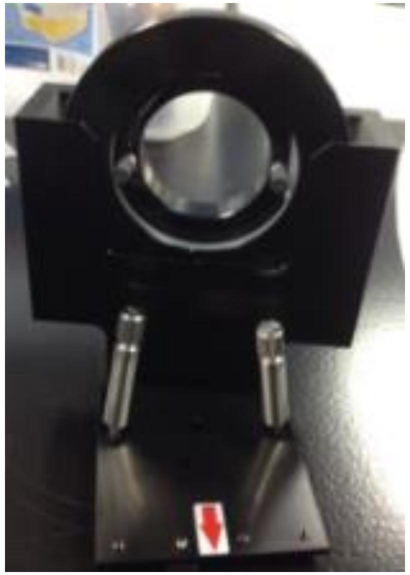
Battery Electrode: Sample 1 and 2 had different performance.





High dilution can suppress the interesting aggregation.

High Concentration Cells



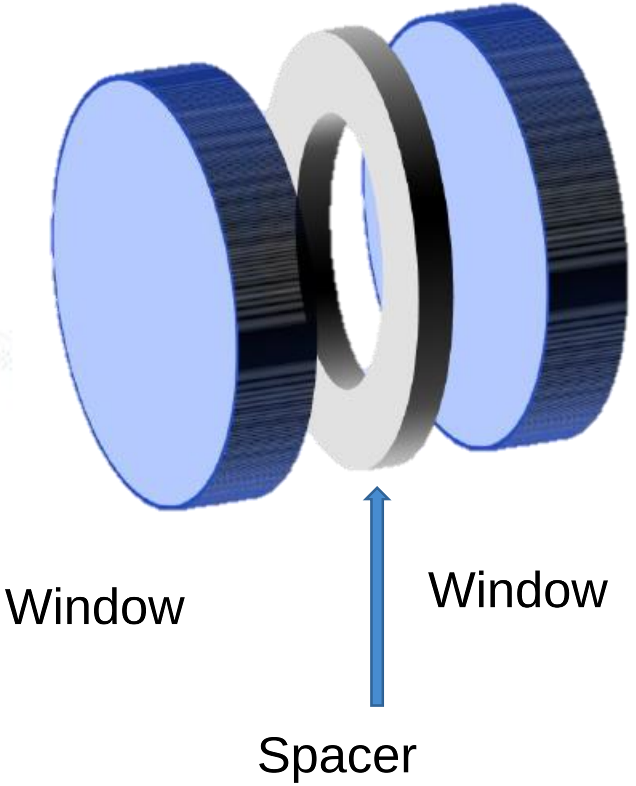
HL Cell

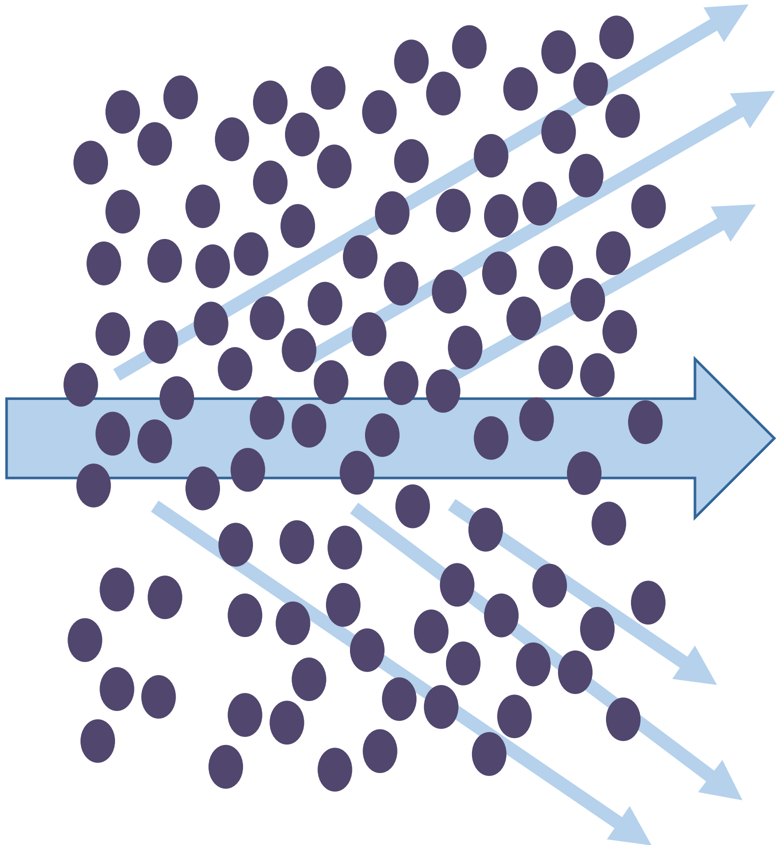
Volume (mL)	0.5 – 2 mL
Ranger (µm)	0.01 – 500

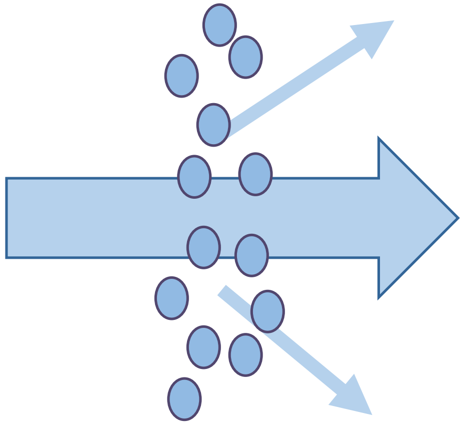
Paste Cell

Volume (mL)	~0.3
Ranger (µm)	0.01 - 100

How?







Narrow spacer means short optical path length.

The future?: Nanoparticles

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ACS APPLIED MATERIALS & INTERFACES

Cobalt Nanoparticles Chemically Bonded to Porous Carbon Nanosheets: A Stable High-Capacity Anode for Fast-Charging Lithium-Ion Batteries

Vinodkumar Etacheri[*†‡], Chulgi Nathan Hong[†§], Jialiang Tang[†], and Vilas G. Pol[*†]

Since surface area is important…nanoparticles are exciting.

Nanoparticles

Everything below 1 micron (always)?
Just need size?
Want zeta potential (yes, charge is important in slurries!)

SZ-100

Fast, repeatable

Nanoparticles

Need distribution details?
Need concentration?

ViewSizer 3000

Omoshiro-okashiku
Joy and Fun
おもしろおかしく
நன்றி
Terima kasih
Gracias
谢谢
Danke
Tack ska du ha
Σας ευχαριστώ πάρα πολύ
धन्यवाद
Grazie
THANK YOU
شكرًا
ขอบคุณครับ
Obrigado
Большое спасибо
ありがとうございました
Cảm ơn
Merci
감사합니다
Dziękuję