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Explore the future

Improving Battery Performance through Particle Size Analysis

Particle Analysis
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Date: 02/26/2014

Outline

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Scientific

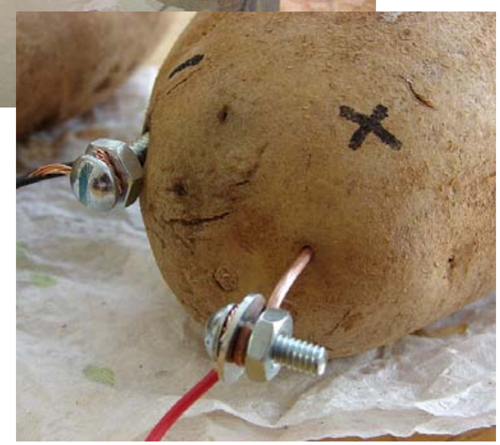
- Battery history
- Particles in batteries
- Measurements of particle size

History

- March, 1749, Benjamin Franklin uses term "battery to describe a group of linked capacitors.
- 2013 National Geographic Article: Supercapacitors Amp Up as an Alternative to Batteries"
  http://news.nationalgeographic.com/news/energy/2013/08/130821-supercapacitors/

History

- March, 1800 Volta describes producing current with a stack of zinc and copper with brine soaked cloth in between.
- Now we have copper/zinc potato batteries.
- ~200 years later Amos Latteier builds a 5000 pound potato battery (http://latteier.com/potato/)



Oxford Bell

- Battery operated bell at Oxford bell starts ringing in ~1840.
- 2001 discussed in Annals of Improbable Research (Volume 7, Issue 3).
- 2014, bell still ringing, we still don't know how these batteries were made. The key seems to be that the bell requires very little energy so the batteries last a long time.
- http://www.physics.ox.ac.uk/history.asp?page=Exhibit1

Our buddy: Zinc Carbon

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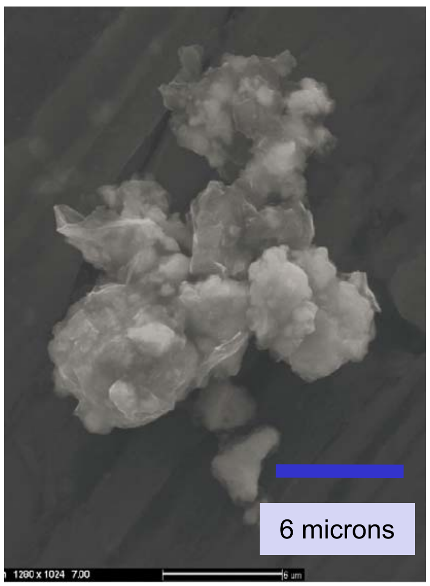
- 1896 from National Carbon Company
- Positive terminal is graphite rod surrounded by Mn(IV) oxide/carbon powder. Carbon powder is to increase conductivity.

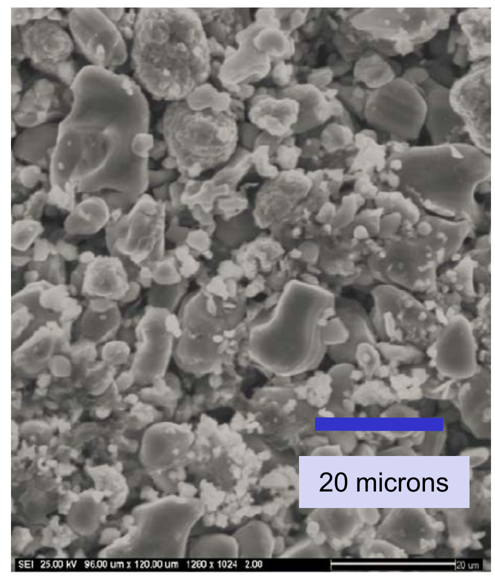
But my battery is solid!

- A battery is usually solid and quite durable.
- But what if we look inside a Li-ion battery?

Anode



Cathode



Particles!

Raman Imaging

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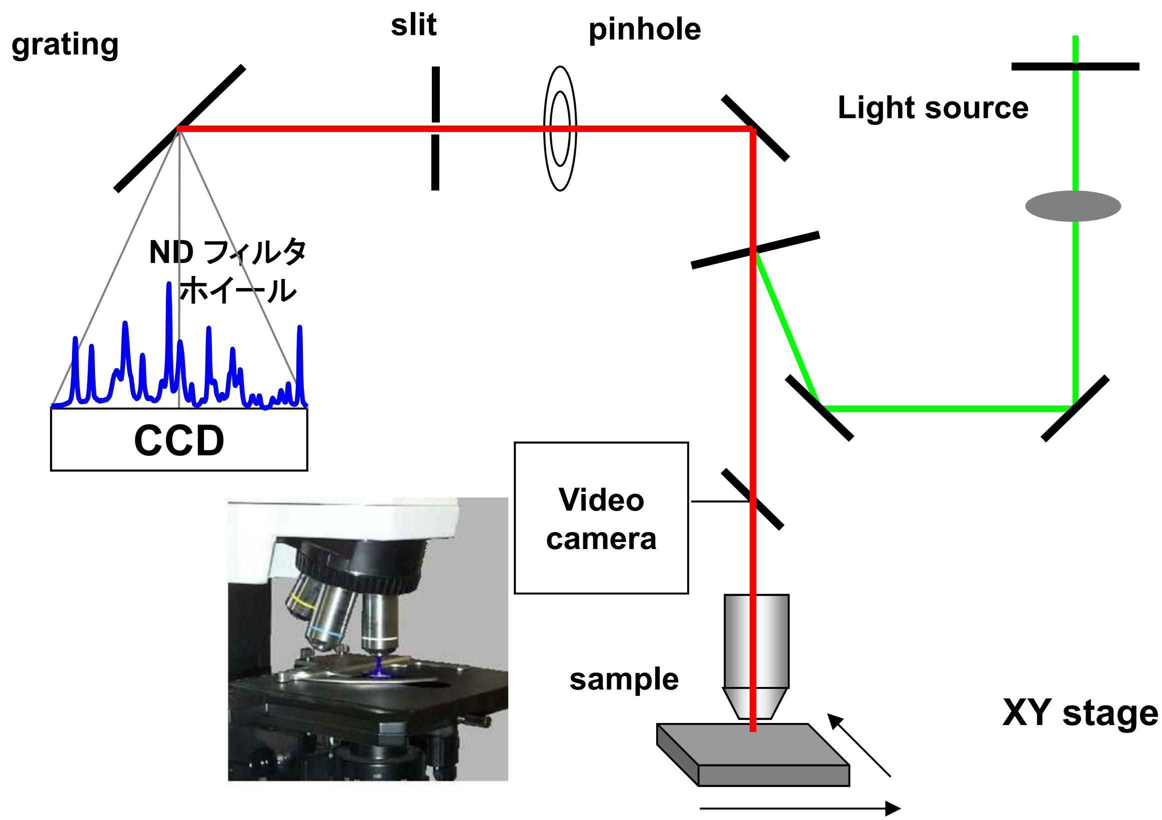
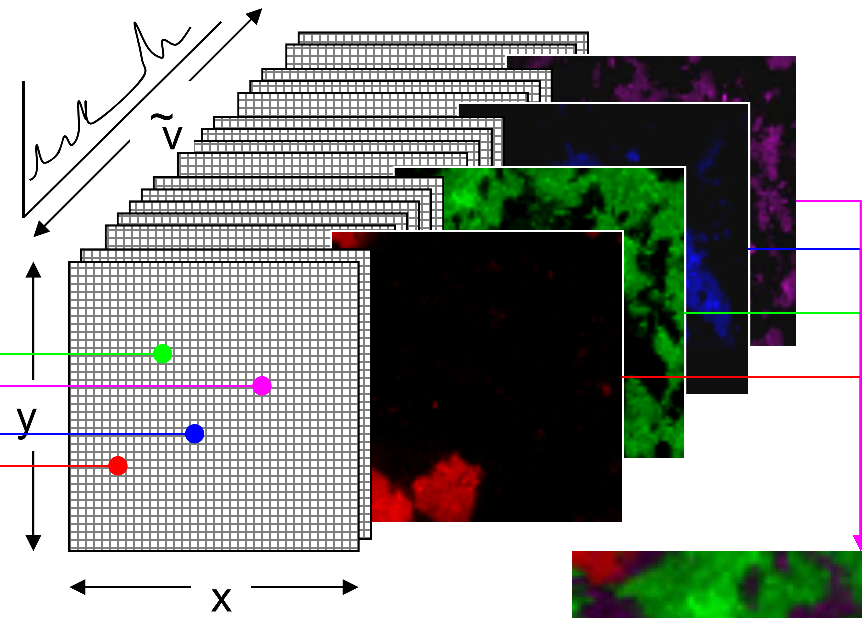
XploRA

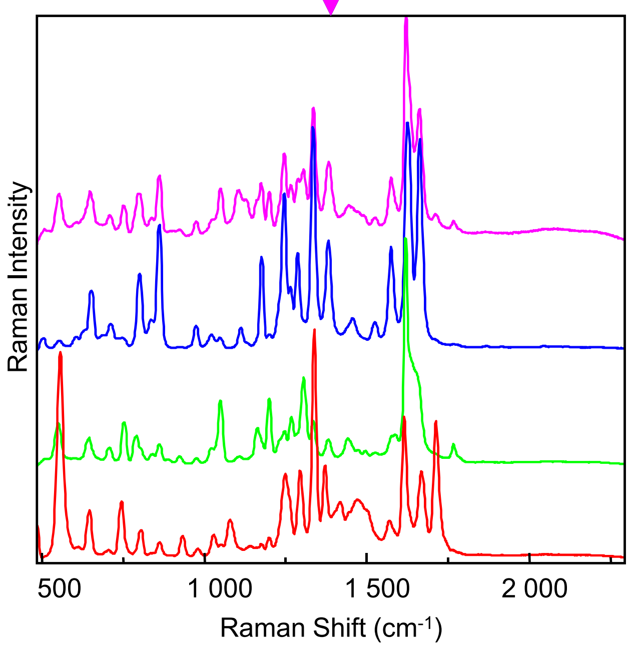


Raman imaging results

Hypercube:

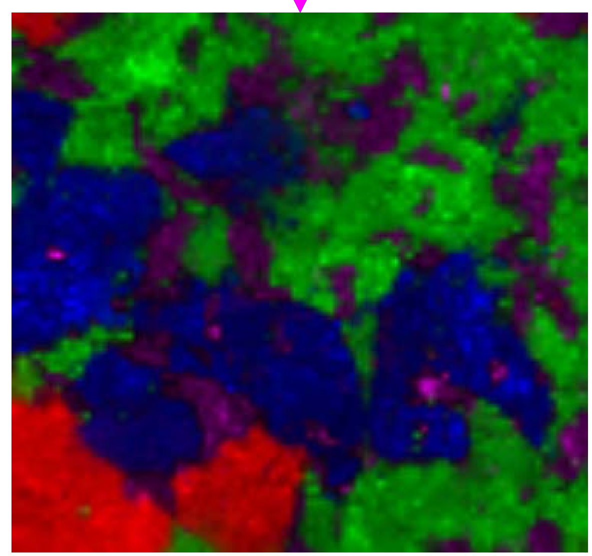
X, Y, shifts



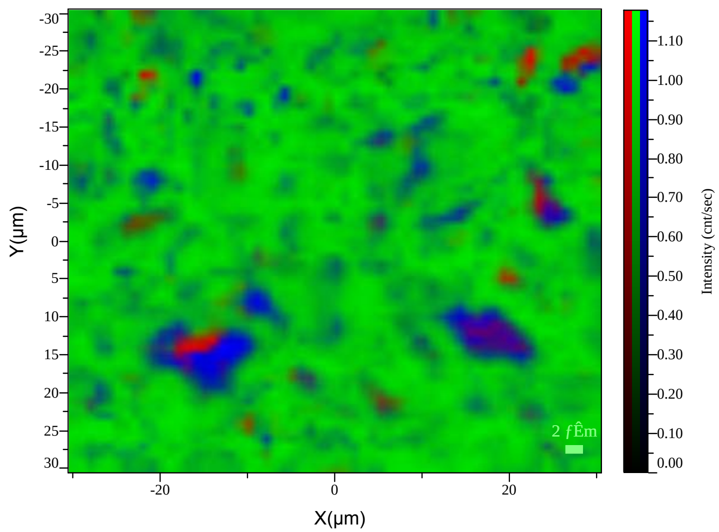


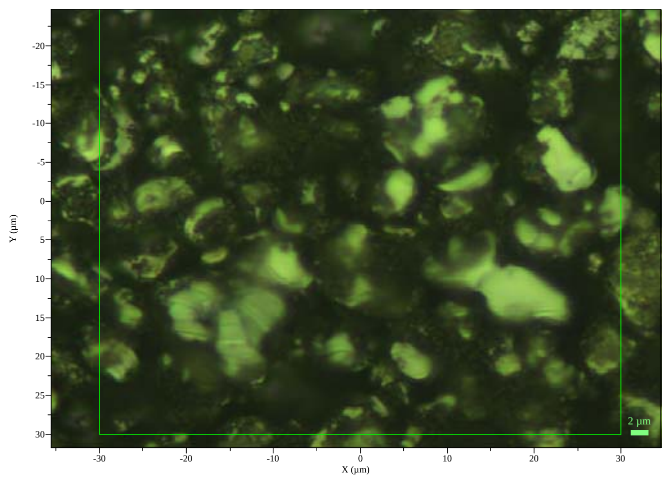
Spectra for each point

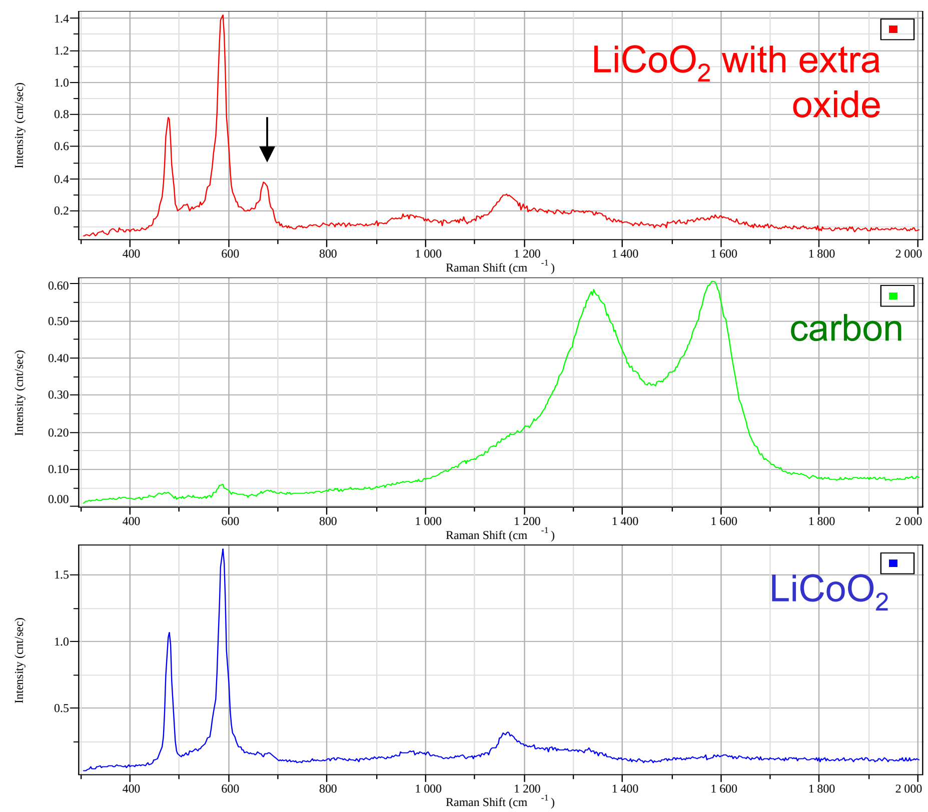
Image showing spatial distribution of each material



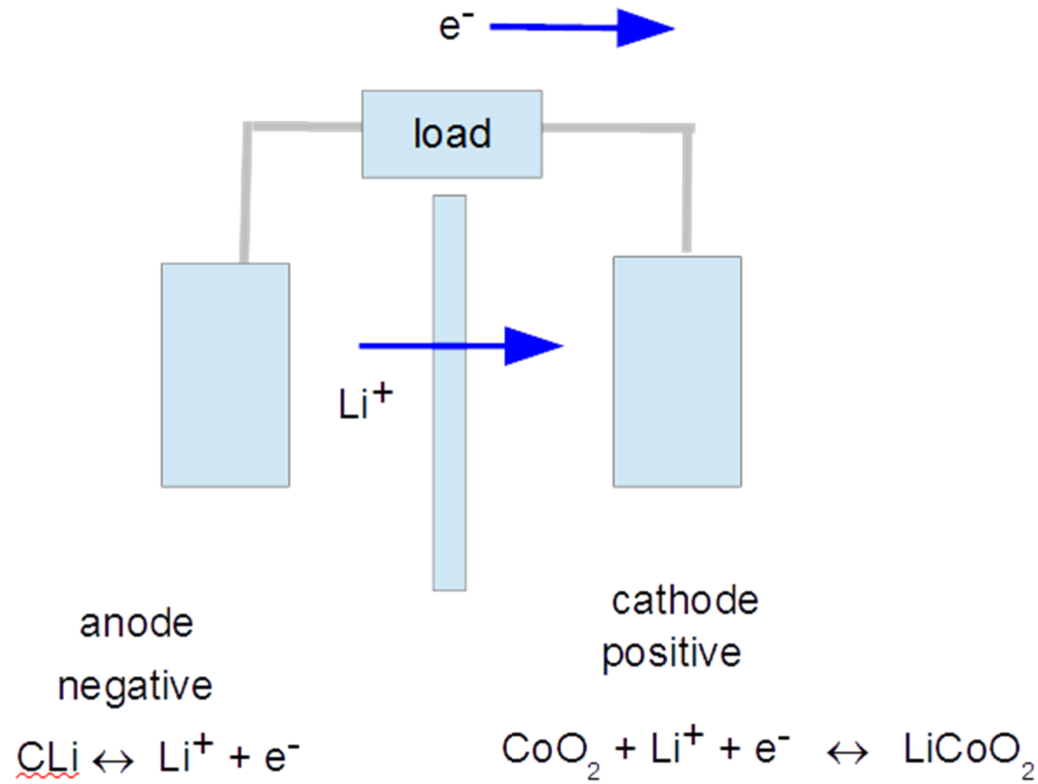
Raman imaging of Li ion electrodes







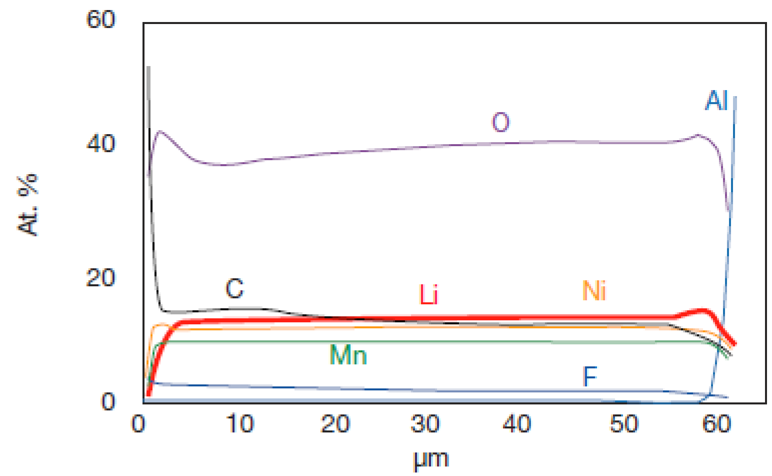
Battery Basics



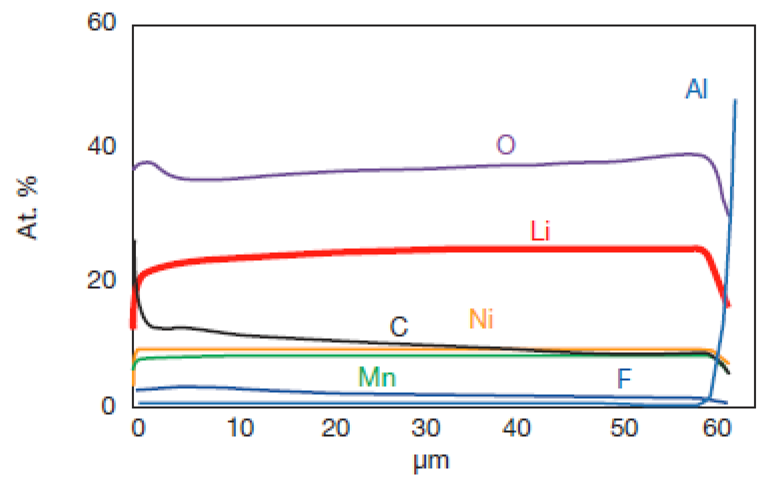
Chemistry sets potential (voltage)…
But the voltage drops due to resistance (electrical and ionic).

Moving Li

- Glow discharge
- Look at Li level
- Pulsed RF GD OES Depth Profile Analysis of the positive electrode



State Of Charge 100 %



State Of Charge 0 %

GD Profiler

Battery Structure

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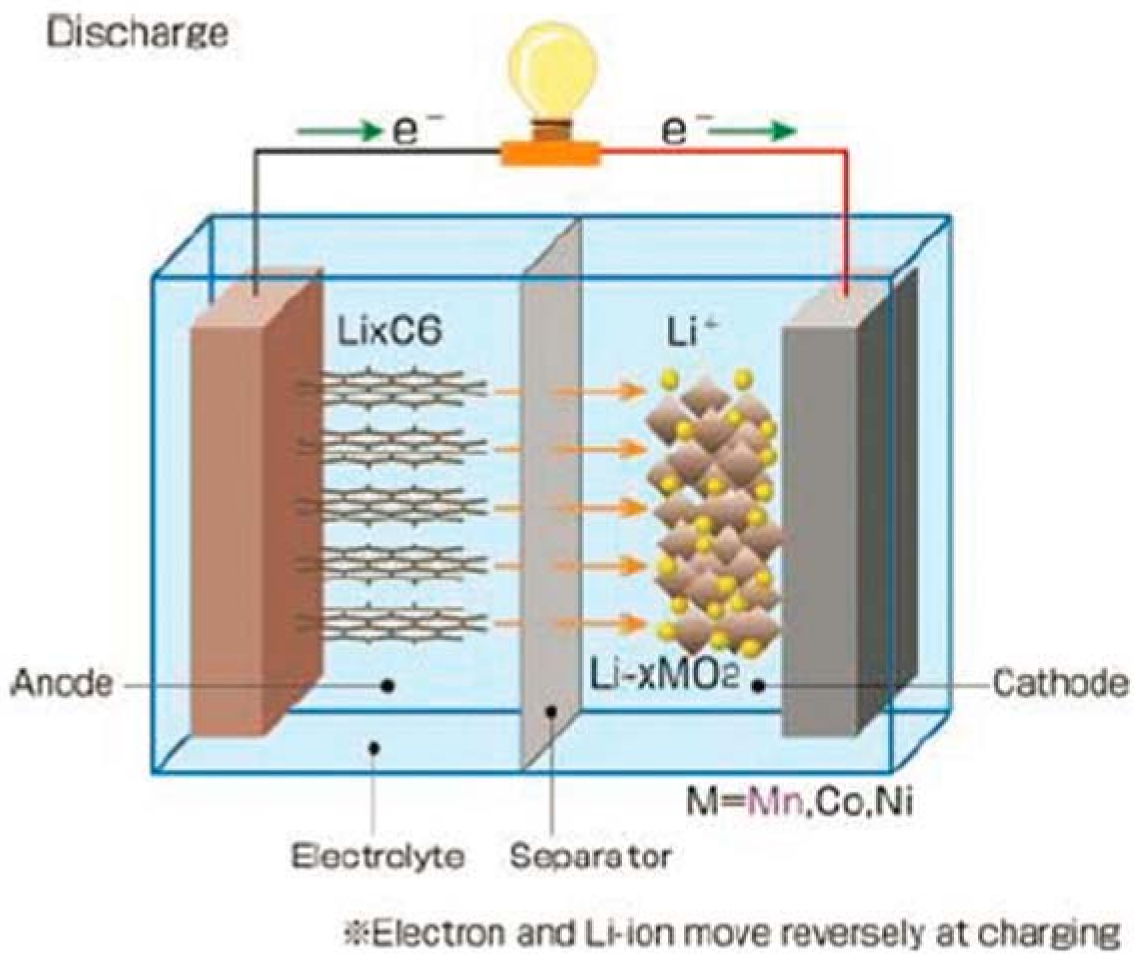
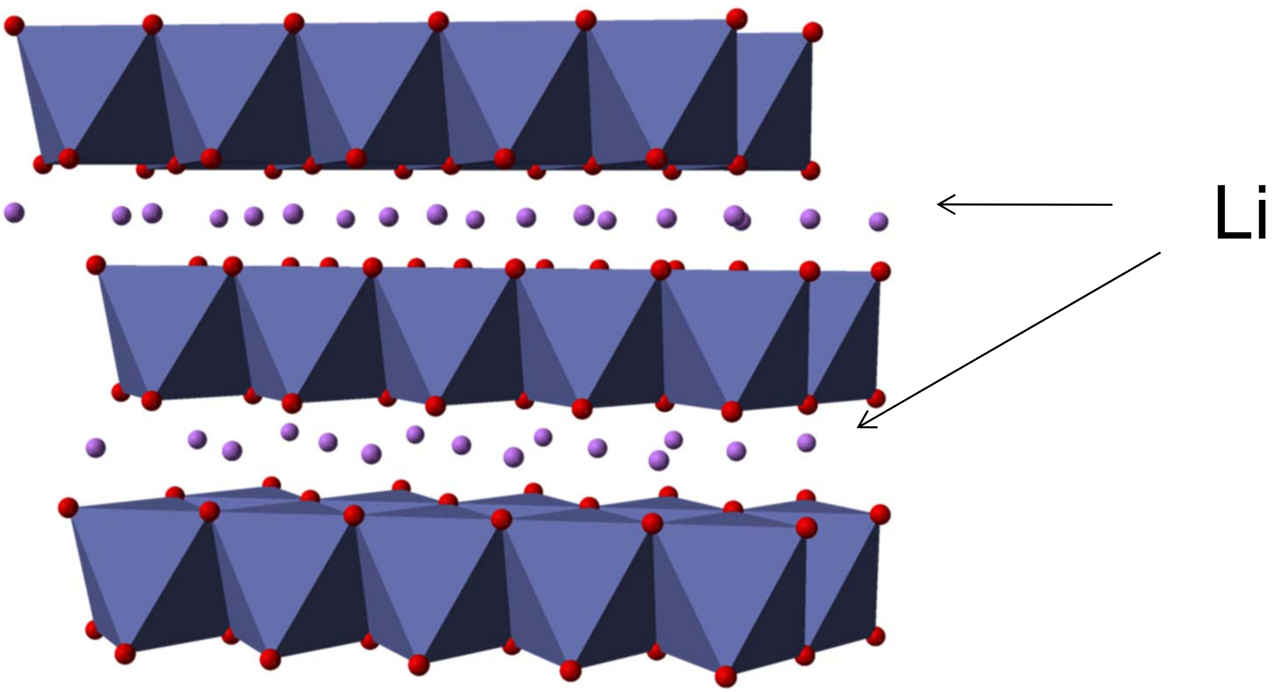
■ How do I get electrons and ions to move?



Microscopic View

- $LiCoO_2$
- Li moves into CoO_2 octahedra slabs
- How fast can the LI get in there?



Particle Size!

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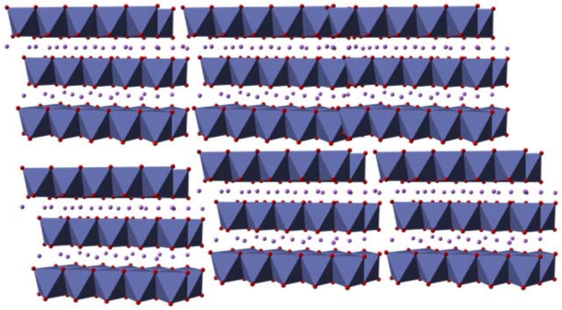
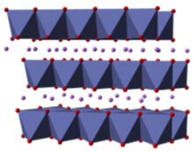
- Need to consider diffusion of Li+ into CoO_2 when considering charge/discharge rate (or power, not energy)!
- As particles get smaller, area for diffusion increases
- Also area for undesirable side reactions increases

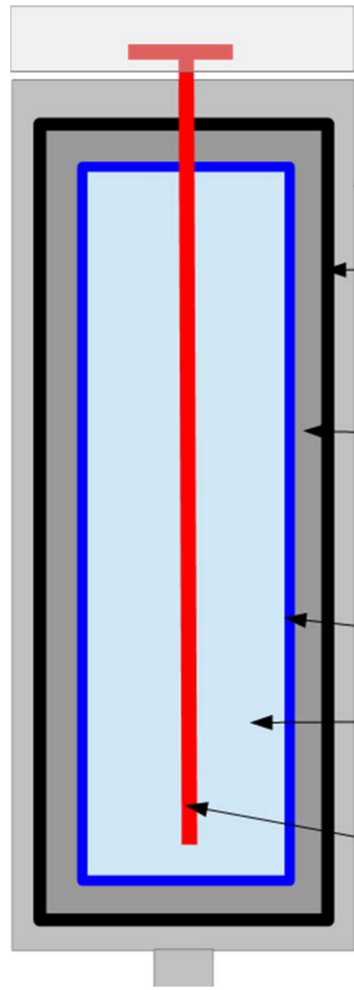




See M. Park, et al., J. Power Sources (2010), doi:10.1016/j.jpowsour.2010.06.060

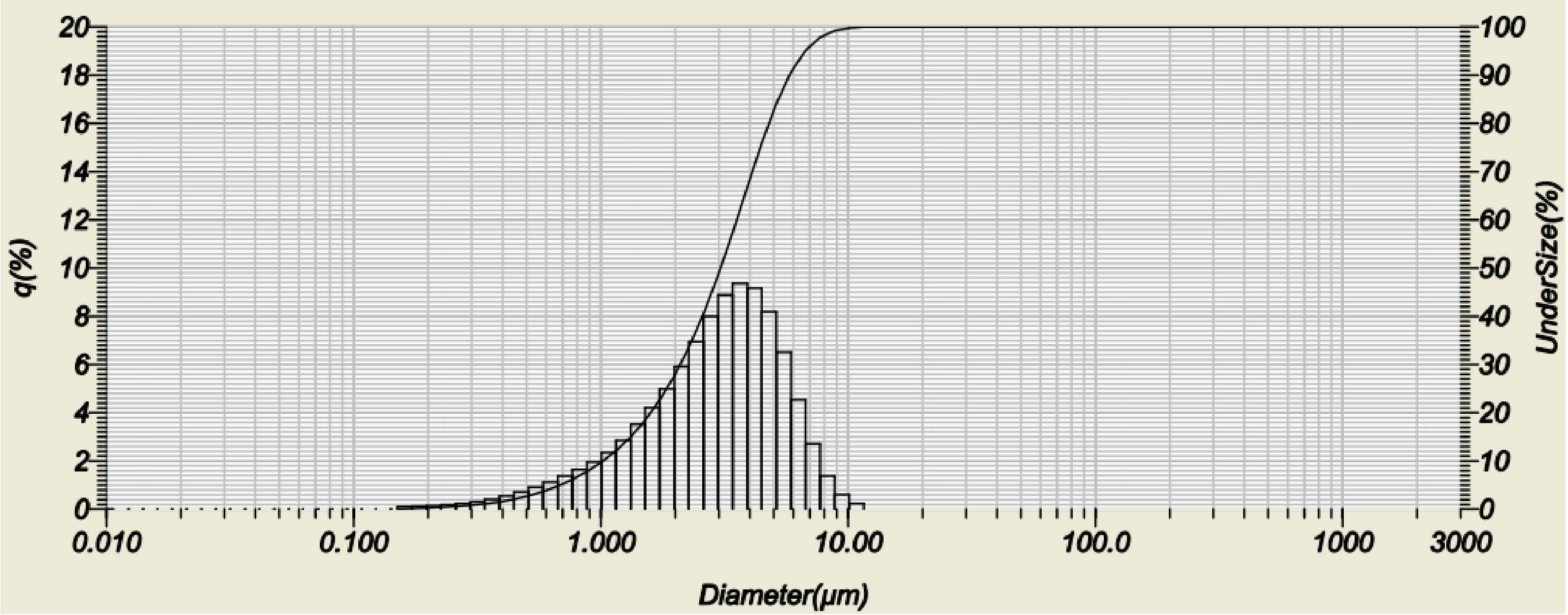
Alkaline battery

- Graphite particle size
  - Smaller lowers 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



Measuring Zinc Powder

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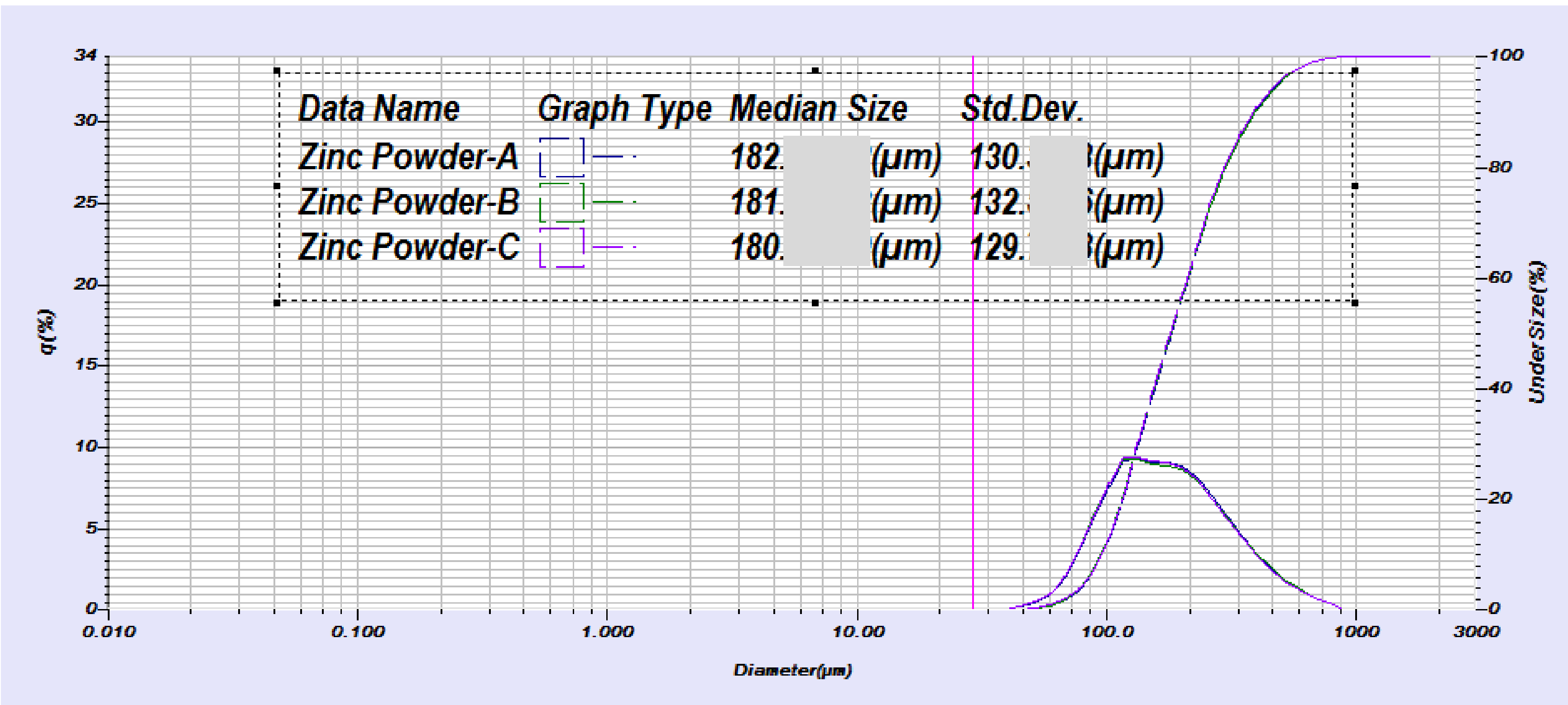
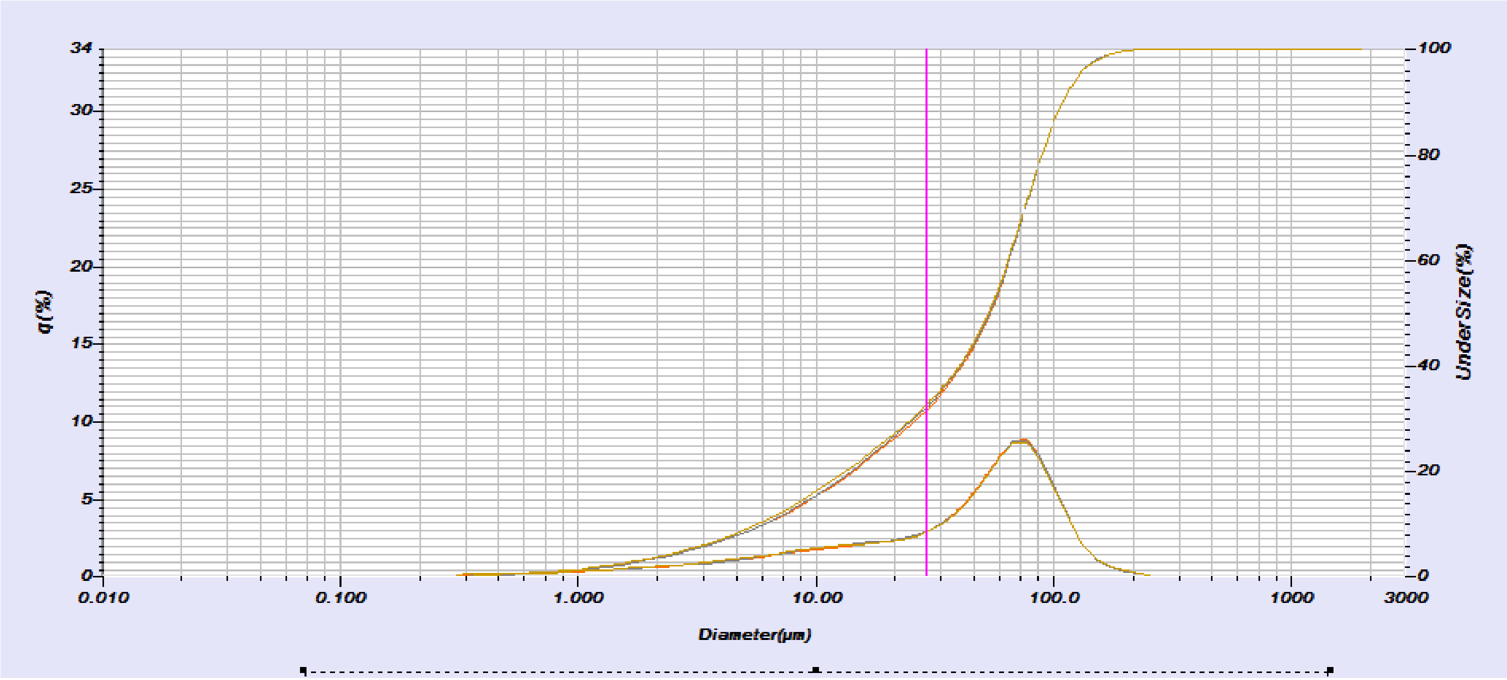
This sample was measured dry by laser diffraction･･･there is no need to disperse it in liquid.

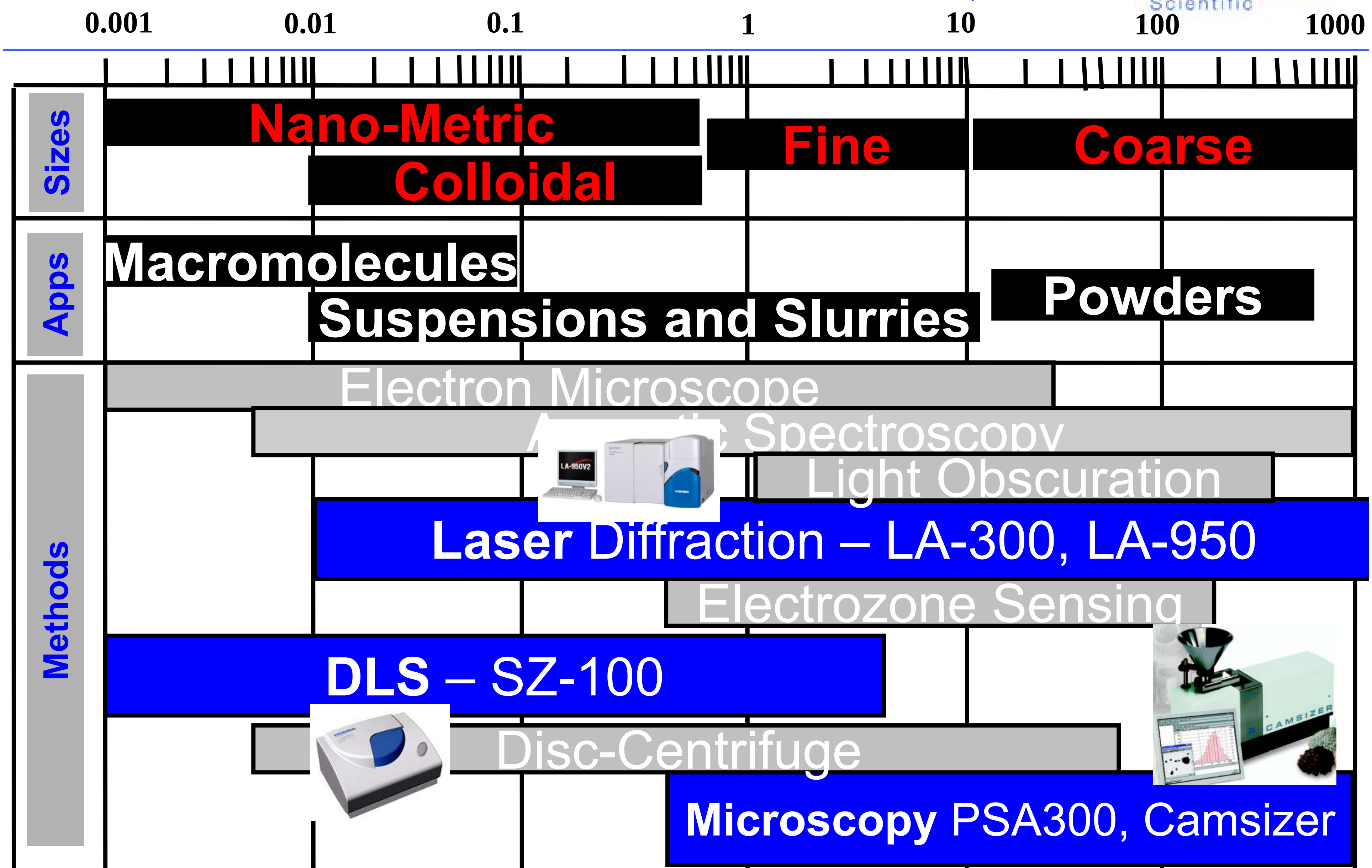


Measuring MnO2

- Yes, laser diffraction works here as well.

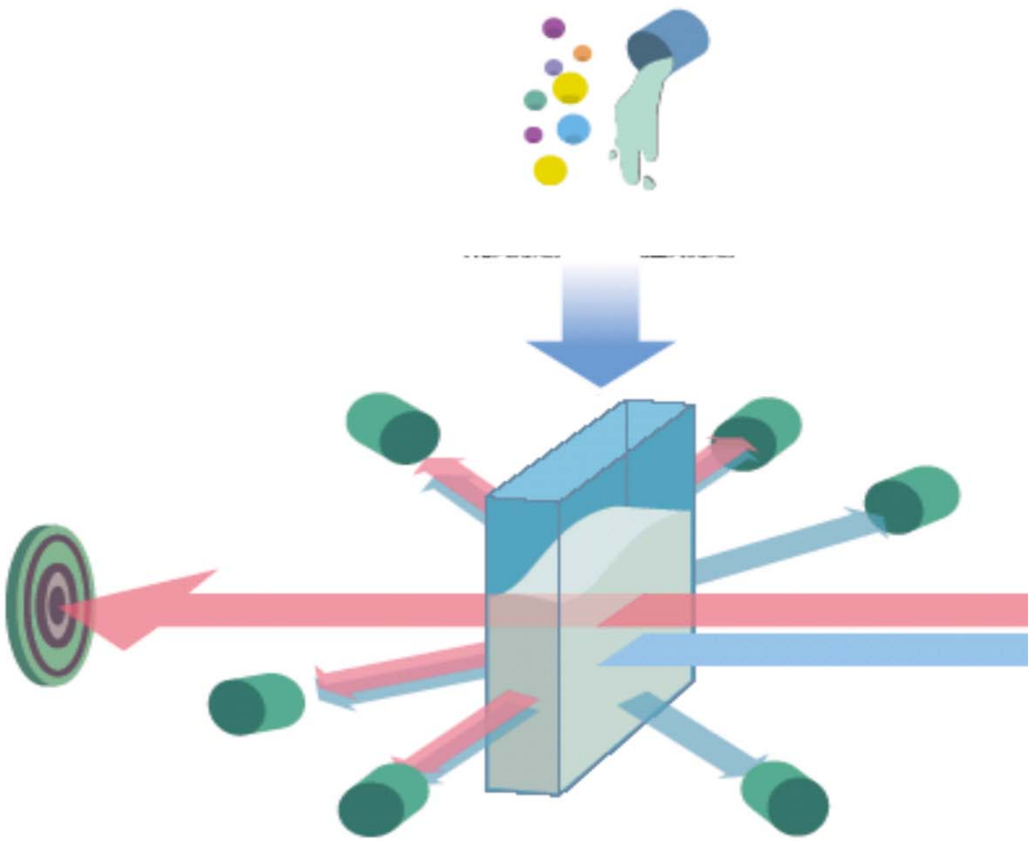


Size: Particle Diameter (μm)

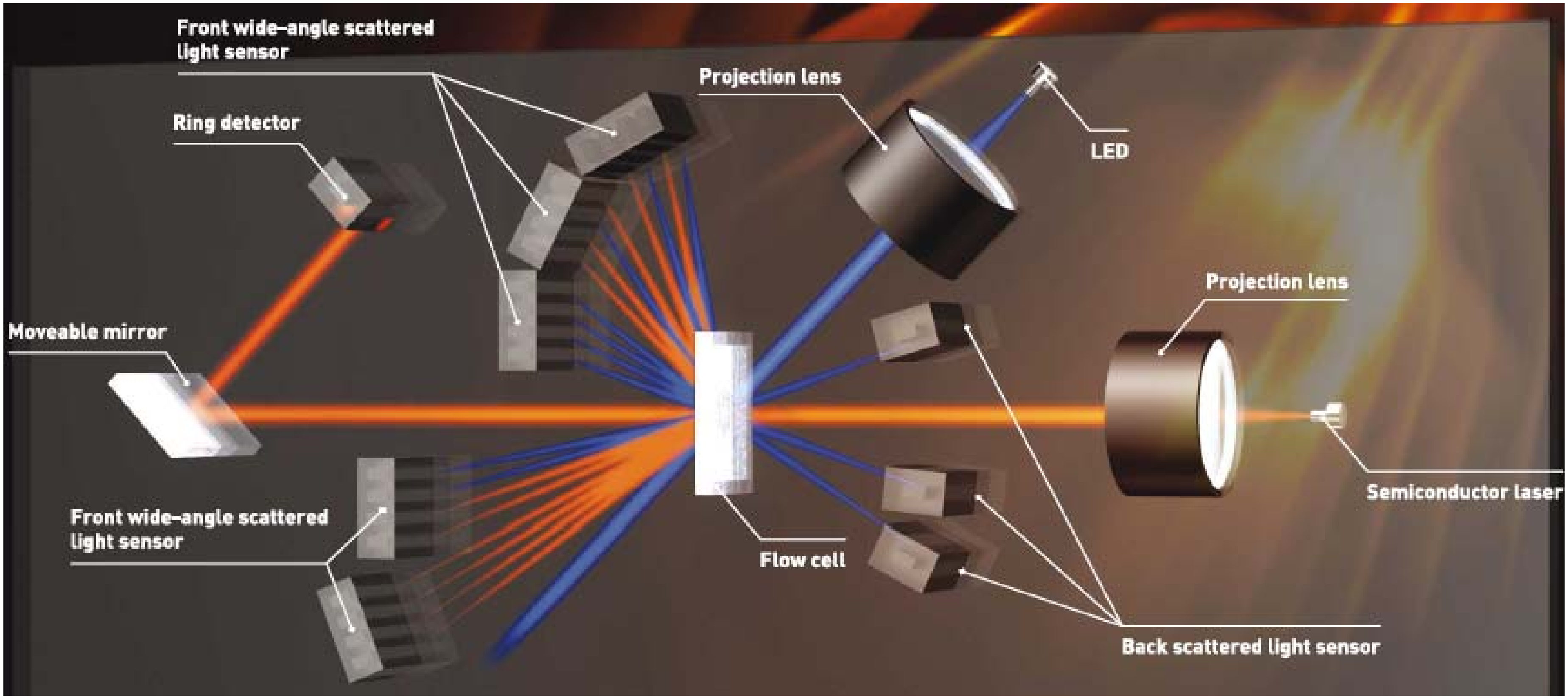


Laser Diffraction

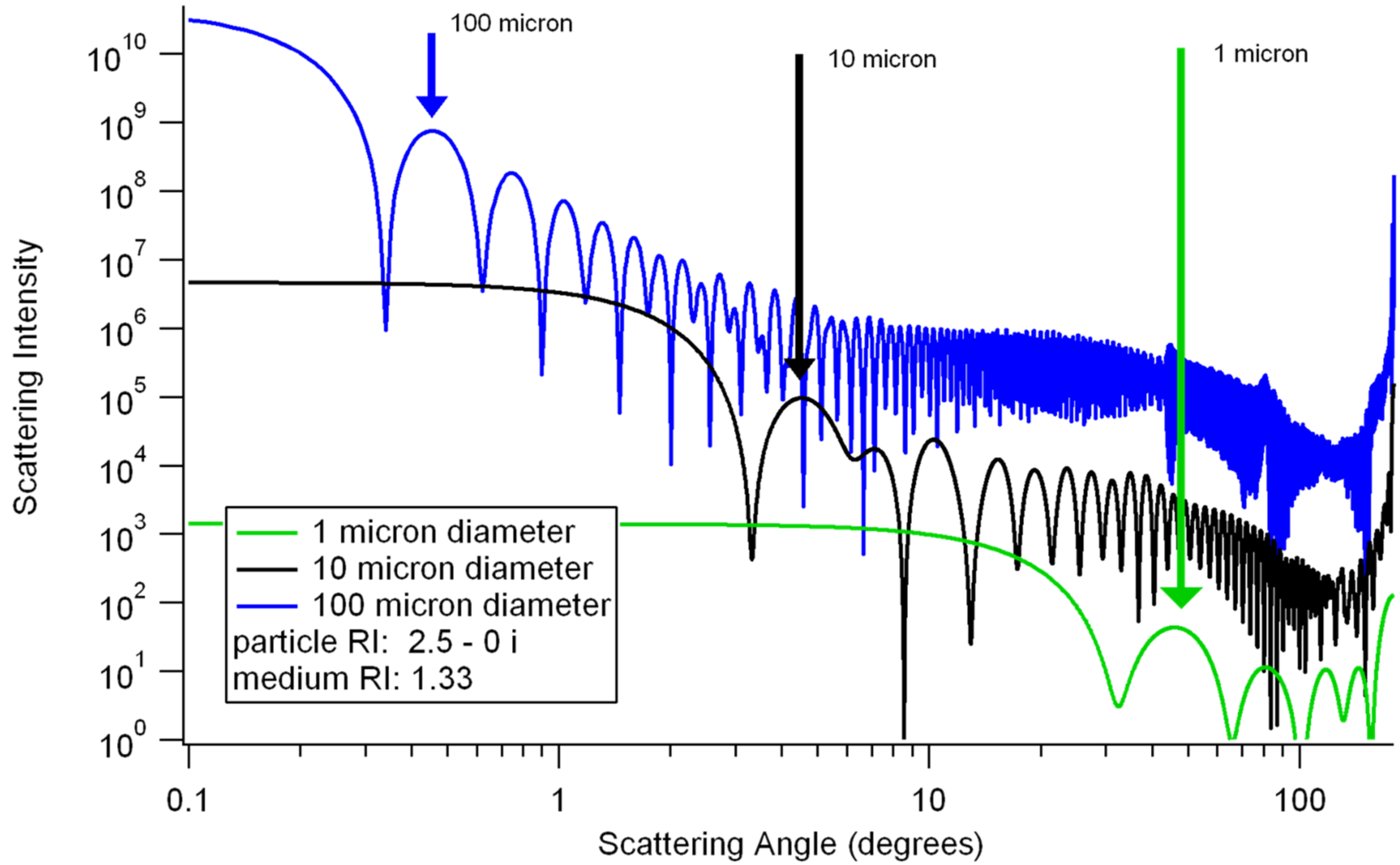
Measure the variation in scattered intensity with angle to find particle size.



LA-950 Optics



Scattered Intensity and Size



As diameter increases, intensity (per particle) increases and location of first peak shifts to smaller angle.

Li Battery Materials

Cathode Materials:
•Lithium cobalt oxide $LiCoO_2$
•Lithium nickel oxide $LiNiO_2$
•Lithium manganese oxide $LiMn_2O_4$
•Lithium iron phosphate $LiFePO_4$
Anode Materials
•Carbon C
•Lithium Li
•Lithium titanate Li_2TiO_3

LA Series Laser Diffraction

Repeatability (measure same material)

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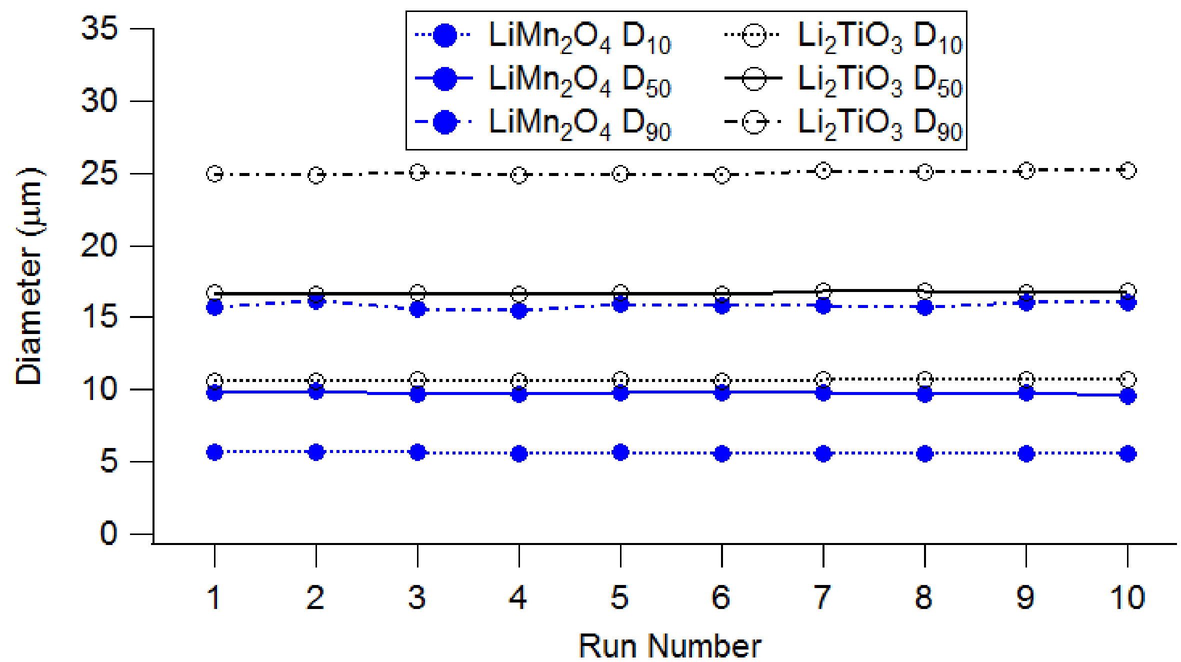
Below are results from measuring to different lithium compounds. Each compound was measured ten times and the relative standard deviation was found.

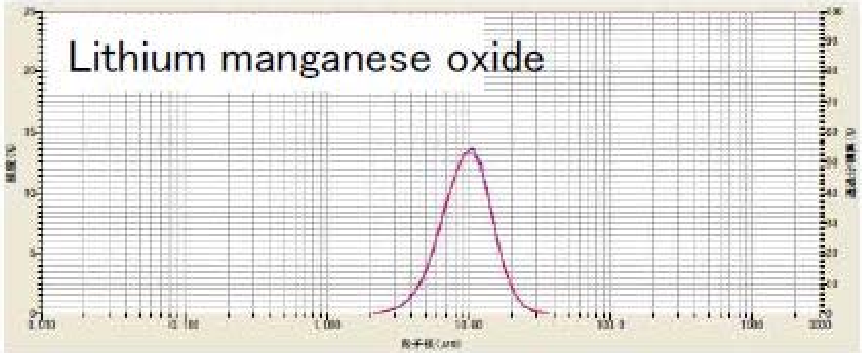
Samples were measured in aqueous suspension. The mixing level and circulation level were both set to 3 during measurement.

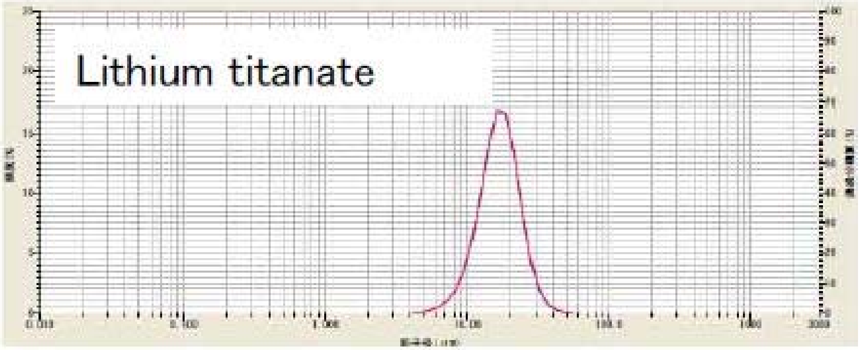


Sample	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Average	RSD
$LiMn_2O_4$	9.75	9.93	9.75	9.66	9.83	9.78	9.76	9.75	9.79	9.60	9.76	0.90%
Li_2TiO_3	16.7	16.6	16.7	16.6	16.7	16.6	16.8	16.8	16.8	16.9	16.7	0.51%

Instrument to Instrument Agreement

Two different instruments





D_{50} values

	LA #1	LA #2	diff
$LiMn_2O_4$	9.75	9.64	0.1
Li_2TiO_3	16.7	16.9	0.2

Lithium ion material lot to lot variation

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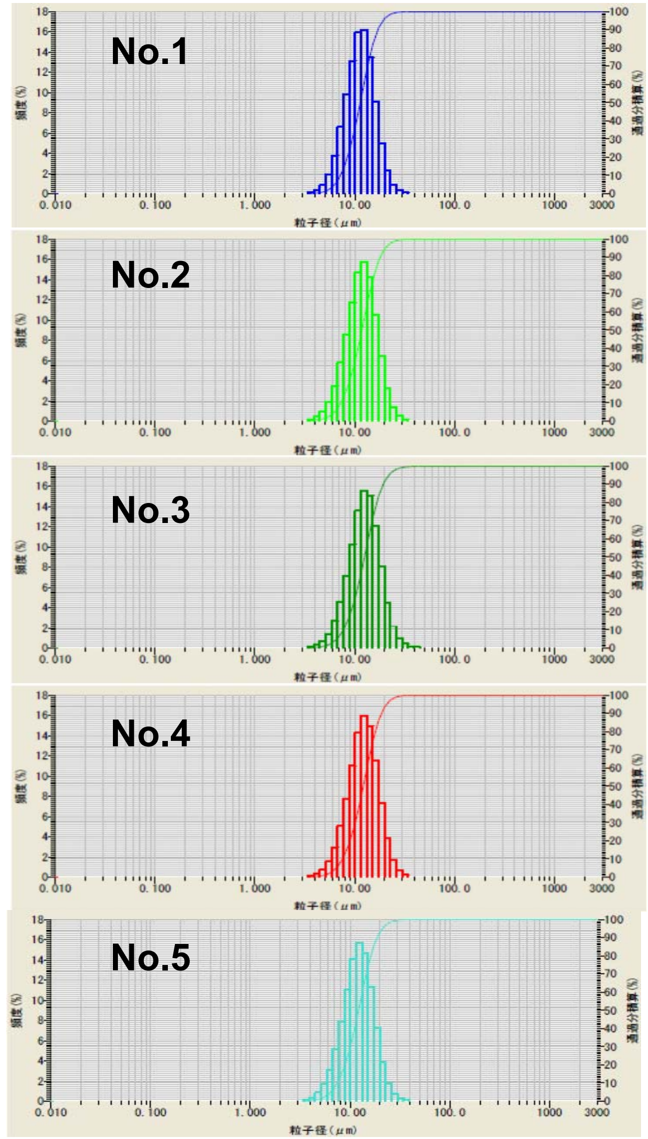
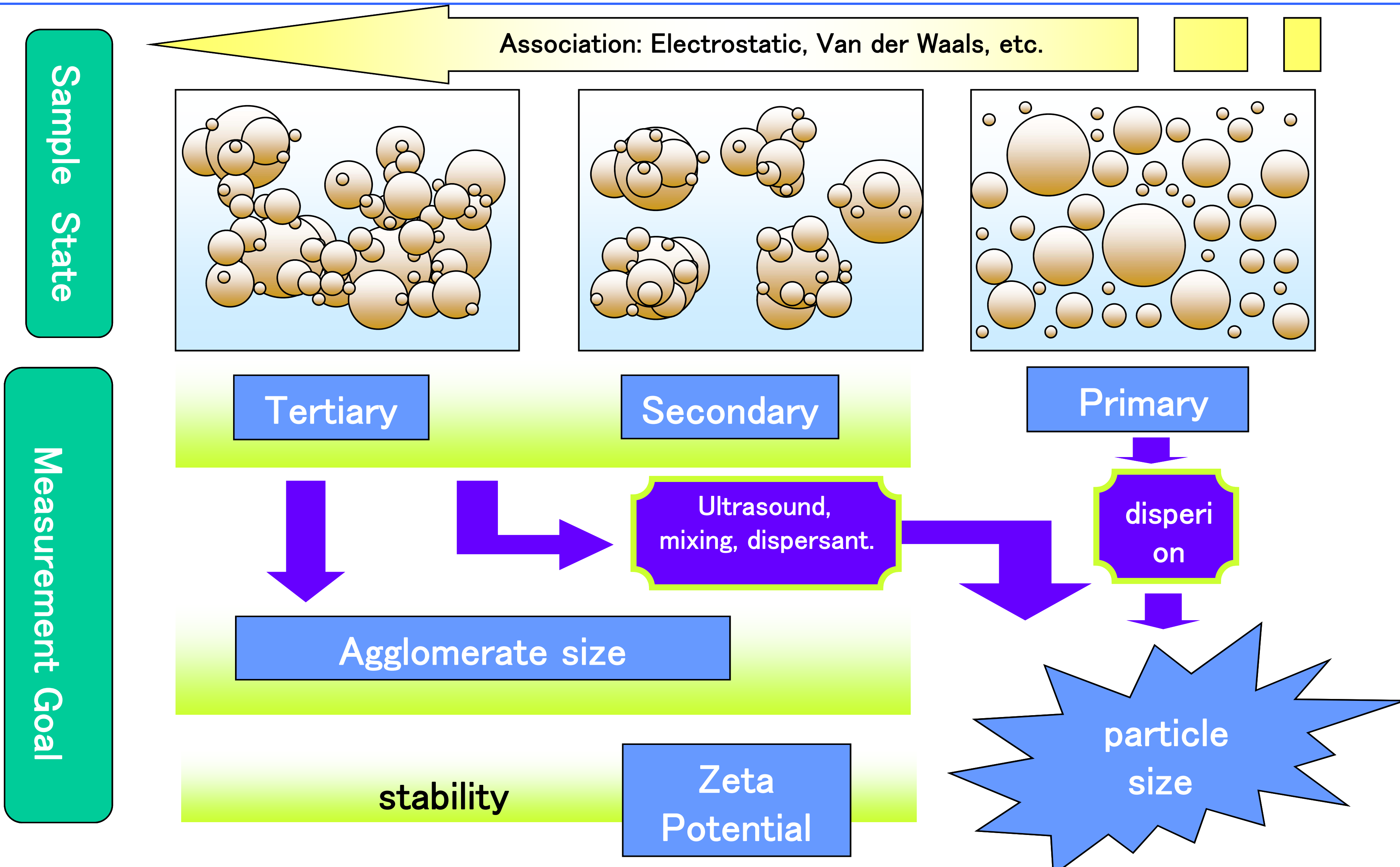
Here, 5 different lots of lithium cobalt oxide ($LiCoO_2$) were measured. Note that there is some variation between the lots.

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



Dispersion



Association: Electrostatic, Van der Waals, etc.
Sample State
Measurement Goal
Tertiary
Secondary
Primary
Ultrasound, mixing, dispersant.
disperi on
Agglomerate size
particle size
stability
Zeta Potential

Large Scale Storage

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- Sodium sulfur battery
- Molten sodium and sulfur at 300 C.
- Load leveling (store wind/solar power) for the grid
- BASE – Beta alumina solid electrolyte
- Alumina lid (to keep out moisture among other things
- Both require alumina. And particle size is important.

Effect of ultrasound

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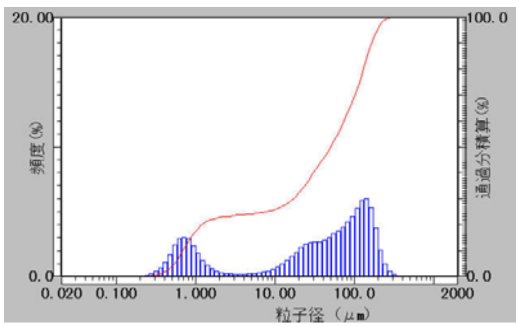
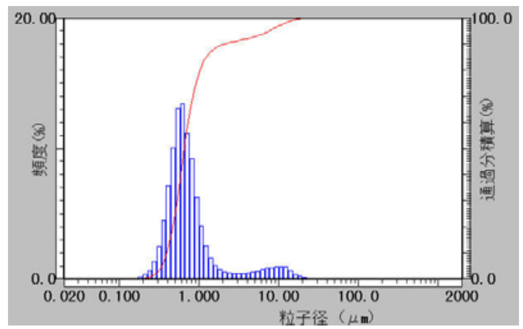
Fused White Alumina

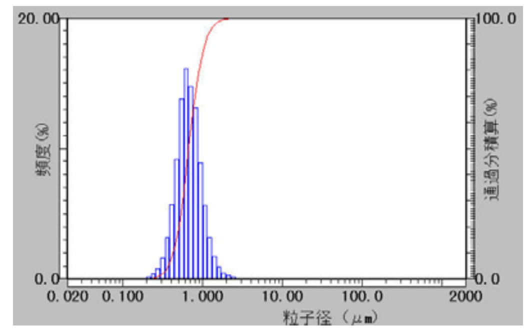
To measure alumina accurately we need to use the built in ultrasonic probe to break up loose aggregates.



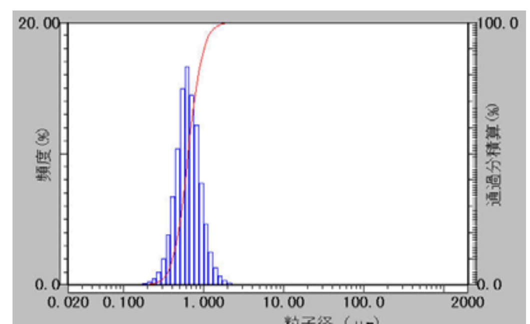
No ultrasonic



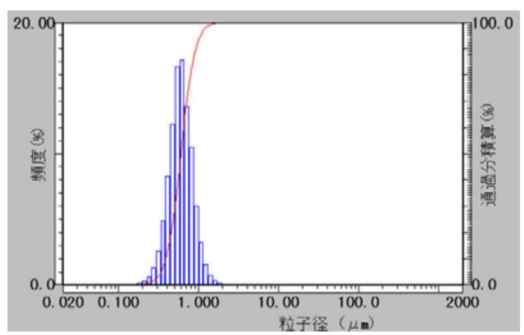
1 minute



3 minute



5 minute



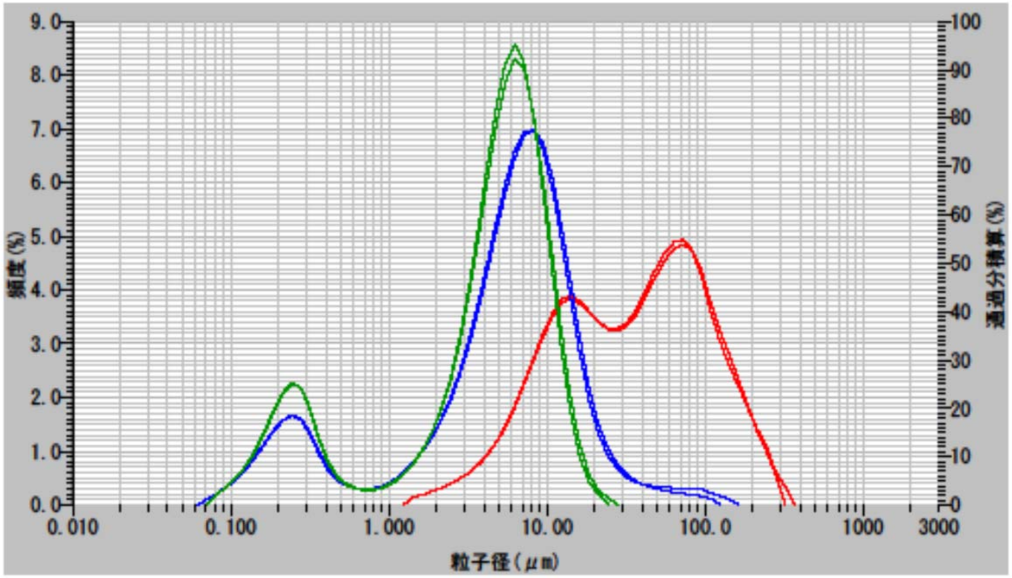
10 minute

Fused White Alumina

In aqueous 0.2% hexametaphosphate

Dispersants: More than just water

- Some materials are not readily dispersed in water and should be measured in another dispersant.
- Here we use NMP.



line	ultrasonic	mode1（μm）	mode 2（μm）
red	none	12.96	72.69
blue	5	0.23	7.16
green	10	0.24	6.08

Evaluating ball milling (and ultrasound)

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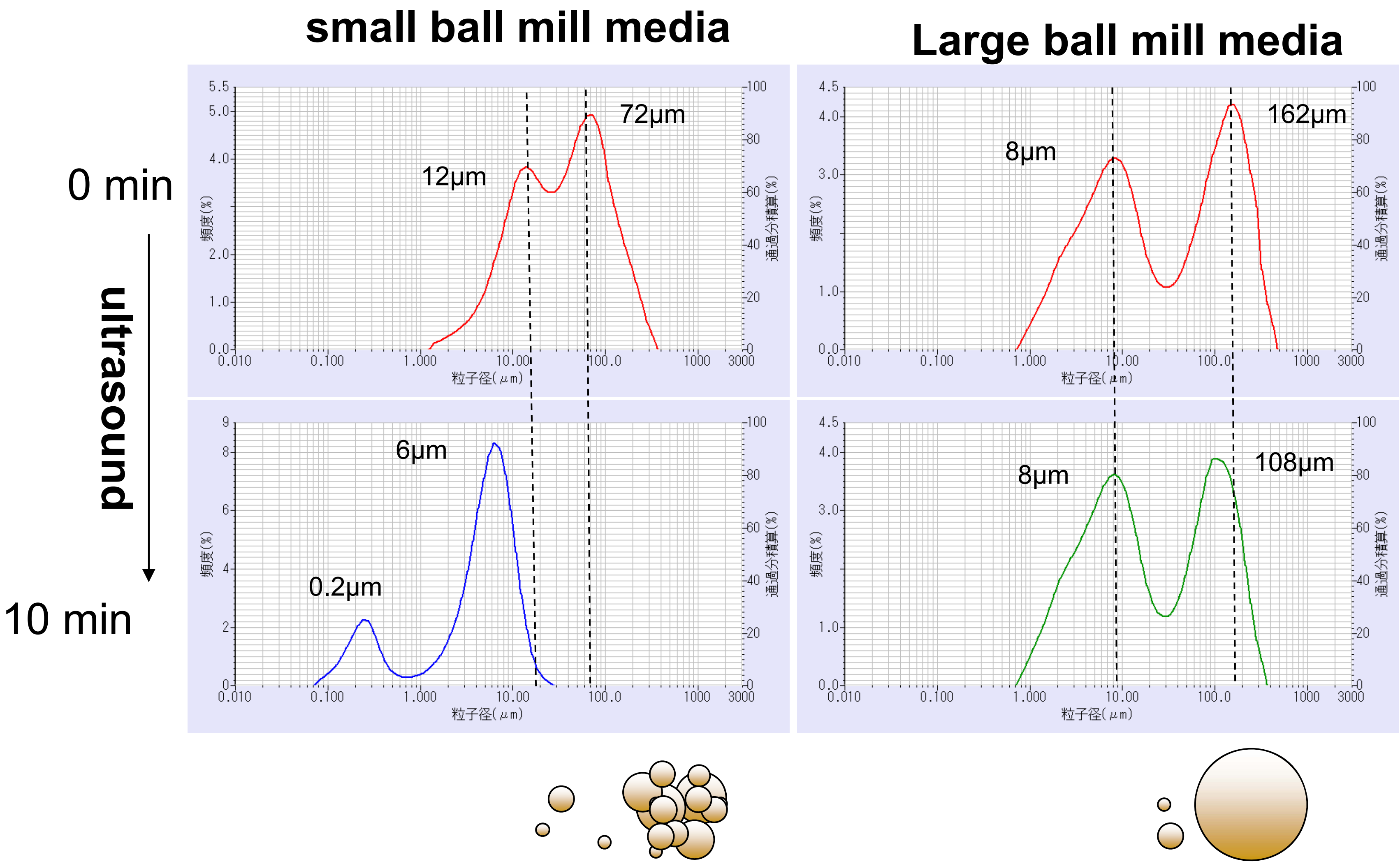

Image Analysis: Two Approaches

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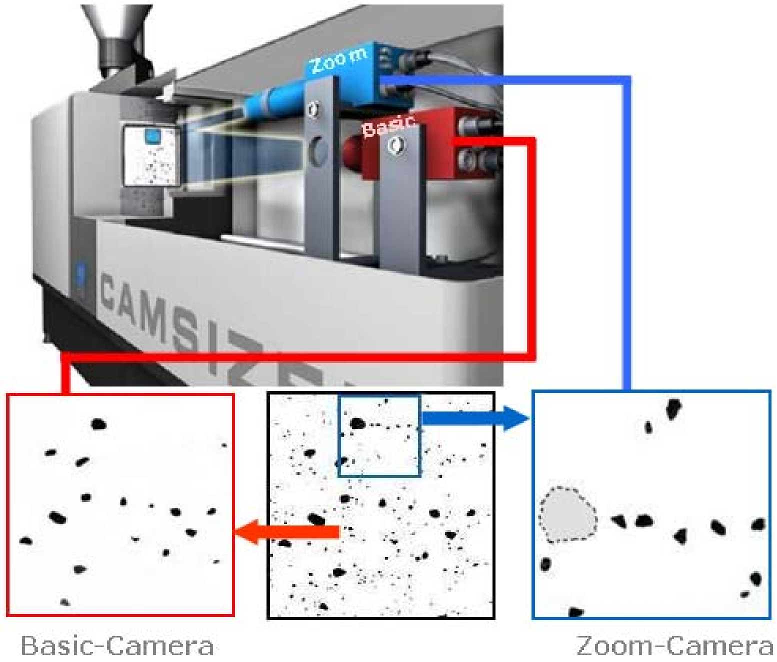
Static:
particles fixed on slide,
stage moves slide

0.5 – 1000 um
2000 um w/1.25 objective

Dynamic:
particles flow past camera



1 – 3000 um

Data Evaluation

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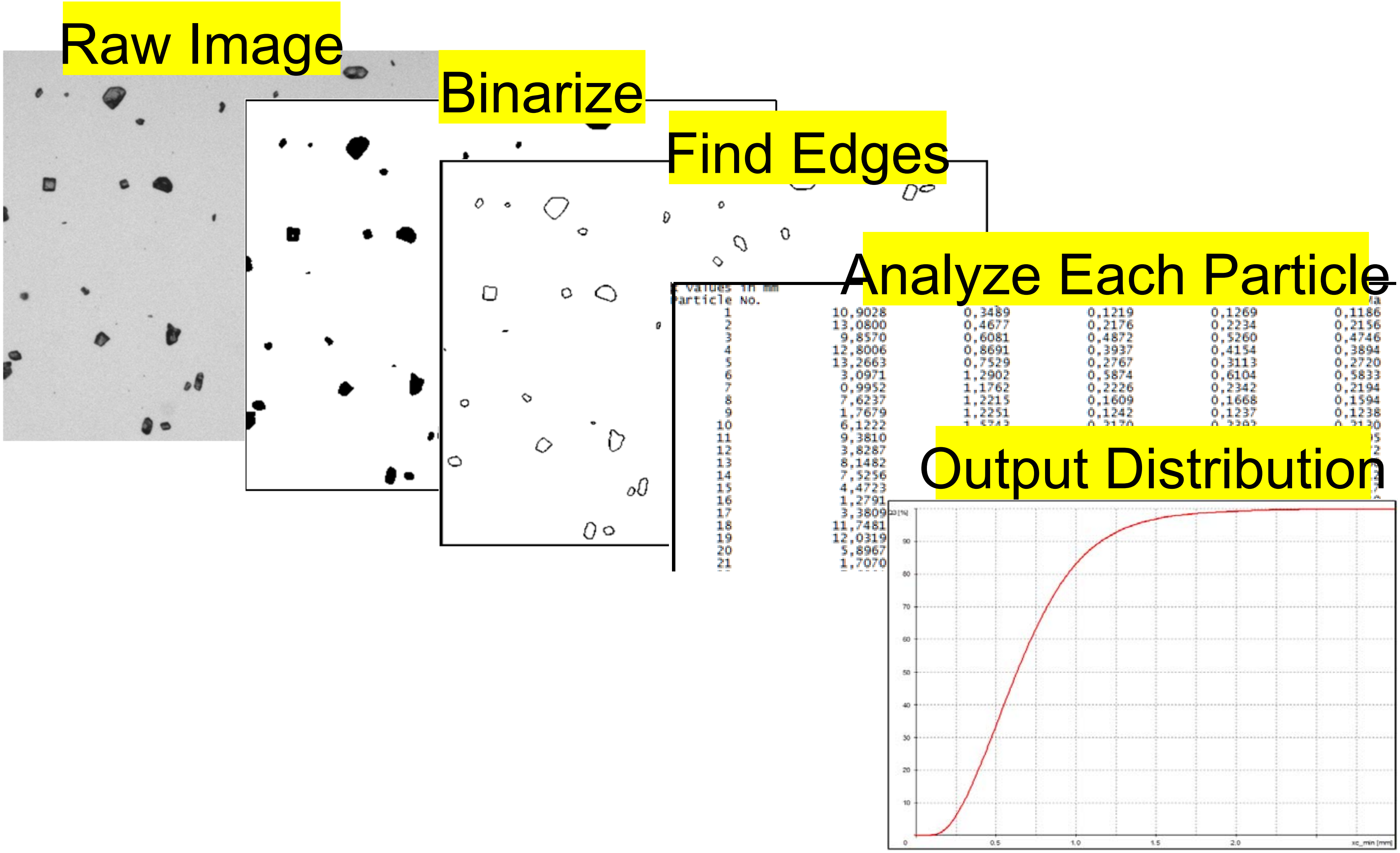

Dynamic Image Analysis: Moving Particles

Use gravity, or, better, vacuum (from a compressed air supply and venturi) in order to draw particles through instrument. Vacuum helps keep the windows clean.

Reproducibility

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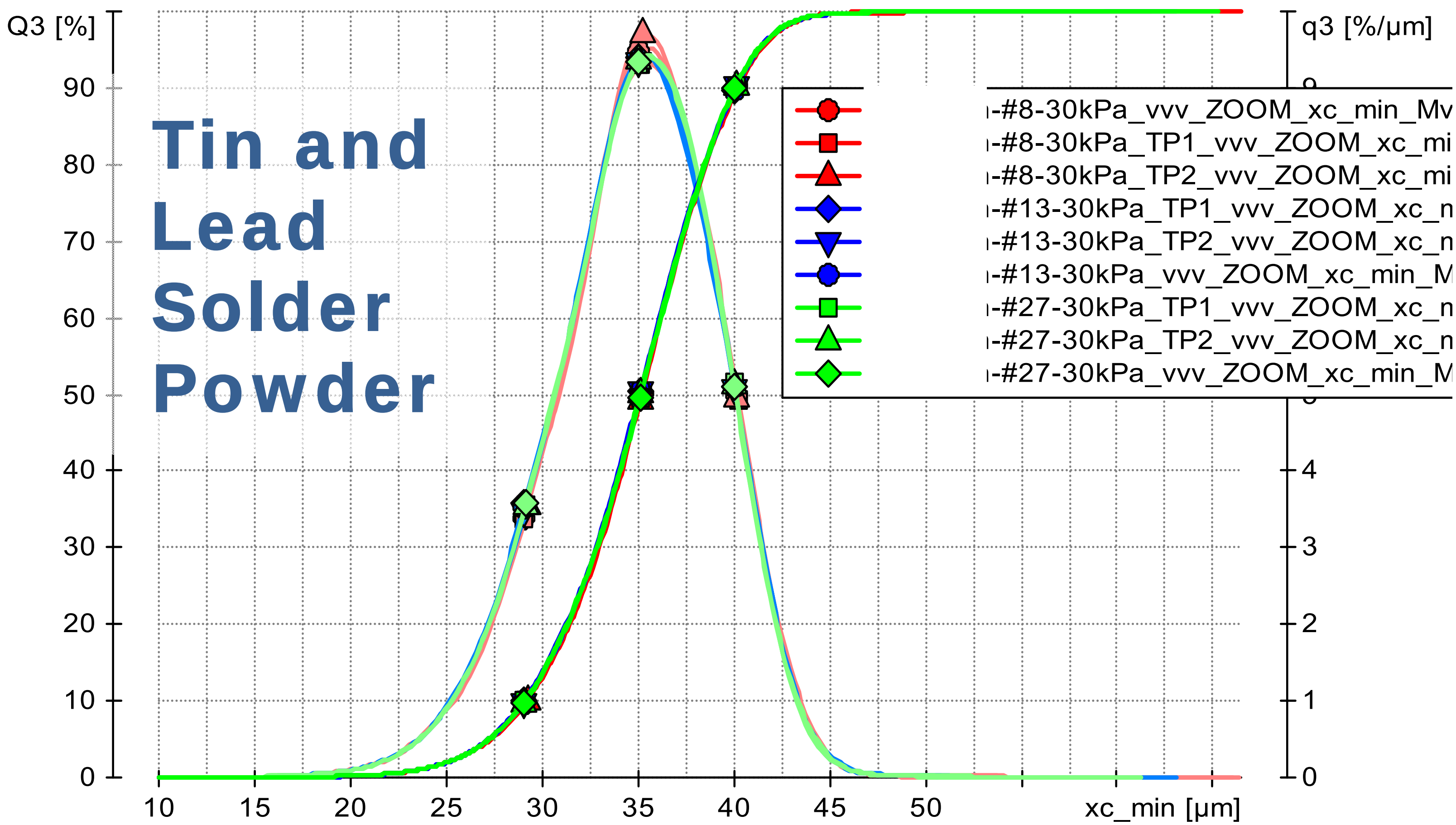
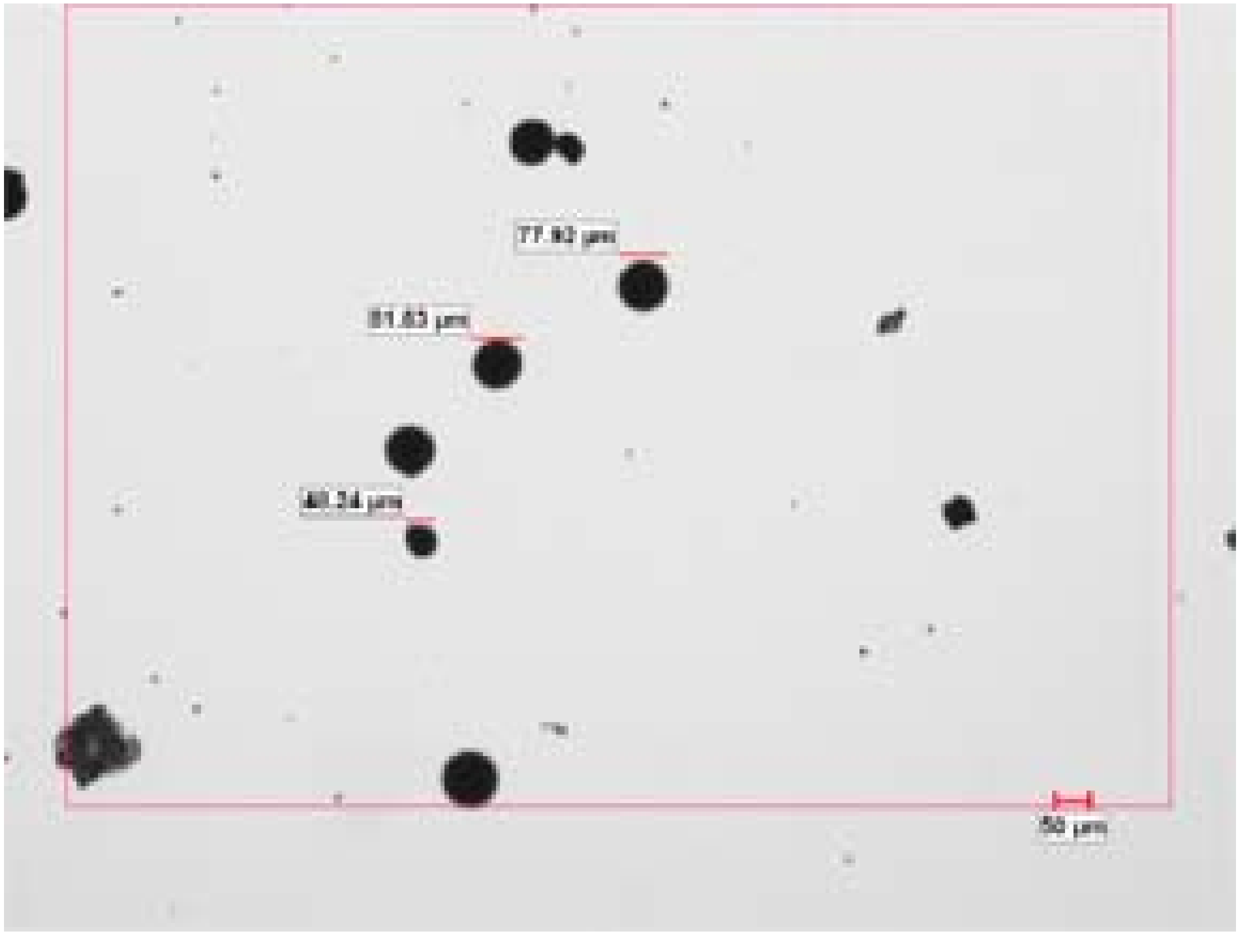
Metal powder by Camsizer XT



Particle Shape

- Image capture with PSA300



Concluding Comments

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- Battery performance depends on particle size.
- Particle size can be determined by a number of techniques including laser diffraction and image analysis.
- Questions?

Questions?

www.horiba.com/us/particle

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Thank you

Thank you

ありがとうございました

Cảm ơn

ขอบคุณครับ

谢谢

اشْكُر

Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

Tacka dig

நன்றி

Danke

Merci

Obrigado

감사합니다

Большое спасибо