Improving Battery Performance through Particle Size Analysis

Particle Analysis
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Outline

- 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”
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.
- 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.
- [Link](http://www.physics.ox.ac.uk/history.asp?page=Exhibit1)
Our buddy: Zinc Carbon

- 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?

Particles!
Raman Imaging

XploRA

- XploRA microscope
- grating
- slit
- pinhole
- Light source
- CCD
- Video camera
- sample
- XY stage

Explo the future

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Raman imaging results

Hypercube: X, Y, shifts

Spectra for each point

Image showing spatial distribution of each material
Raman imaging of Li ion electrodes

LiCoO₂ with extra oxide

carbon

LiCoO₂
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

GD Profiler
Battery Structure

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!

- 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

Alkaline battery

- Graphite particle size
  - Smaller lowers resistivity at low loadings (5%)
  - Lowers flex strength
  - D90’s from 10 to 100 microns

- MnO₂ 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

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

<table>
<thead>
<tr>
<th>Data Name</th>
<th>Graph Type</th>
<th>Median Size</th>
<th>Std.Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Powder-A</td>
<td></td>
<td>182.1 µm</td>
<td>130.8 µm</td>
</tr>
<tr>
<td>Zinc Powder-B</td>
<td></td>
<td>181.3 µm</td>
<td>132.6 µm</td>
</tr>
<tr>
<td>Zinc Powder-C</td>
<td></td>
<td>180.5 µm</td>
<td>129.3 µm</td>
</tr>
</tbody>
</table>
Measuring MnO₂

- Yes, laser diffraction works here as well.
## Size: Particle Diameter (μm)

<table>
<thead>
<tr>
<th>Sizes</th>
<th>Colloidal</th>
<th>Nano-Metric</th>
<th>Fine</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apps</td>
<td>Macromolecules</td>
<td>Suspensions and Slurries</td>
<td>Powders</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DLS – SZ-100</td>
<td>Light Obscuration</td>
<td>Disc-Centrifuge</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PSA300, Camsizer</td>
<td></td>
<td>Microscopy</td>
<td></td>
</tr>
</tbody>
</table>
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$_2$O$_4$
• Lithium iron phosphate LiFePO$_4$

Anode Materials
• Carbon C
• Lithium Li
• Lithium titanate Li$_2$TiO$_3$

LA Series Laser Diffraction
Repeatability (measure same material)

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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
<th>Run 6</th>
<th>Run 7</th>
<th>Run 8</th>
<th>Run 9</th>
<th>Run 10</th>
<th>Average</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$TiO$_3$</td>
<td>16.7</td>
<td>16.6</td>
<td>16.7</td>
<td>16.6</td>
<td>16.7</td>
<td>16.6</td>
<td>16.8</td>
<td>16.8</td>
<td>16.8</td>
<td>16.9</td>
<td>16.7</td>
<td>0.51%</td>
</tr>
</tbody>
</table>
**Instrument to Instrument Agreement**

Two different instruments

<table>
<thead>
<tr>
<th></th>
<th>LA #1</th>
<th>LA #2</th>
<th>diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>9.75</td>
<td>9.64</td>
<td>0.1</td>
</tr>
<tr>
<td>Li$_2$TiO$_3$</td>
<td>16.7</td>
<td>16.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

_D$_{50}$ values_
Lithium ion material lot to lot variation

Here, 5 different lots of lithium cobalt oxide (LiCoO$_2$) were measured. Note that there is some variation between the lots.

<table>
<thead>
<tr>
<th>Lot</th>
<th>Median Size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>11.3</td>
</tr>
<tr>
<td>No.2</td>
<td>11.8</td>
</tr>
<tr>
<td>No.3</td>
<td>12.2</td>
</tr>
<tr>
<td>No.4</td>
<td>12.5</td>
</tr>
<tr>
<td>No.5</td>
<td>11.9</td>
</tr>
</tbody>
</table>
Dispersion

Sample State

Tertiary

Secondary

Primary

Association: Electrostatic, Van der Waals, etc.

Agglomerate size

Ultrasound, mixing, dispersant.

dispersion

particle size

stability

Zeta Potential

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Large Scale Storage

- 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

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

Fused White Alumina

No ultrasonic

1 minute

3 minute

Fused White Alumina

In aqueous 0.2% hexametaphosphate

10 minute

5 minute
Dispersants: More than just water

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

- Here we use NMP.

<table>
<thead>
<tr>
<th>line</th>
<th>ultrasonic</th>
<th>mode 1 (μm)</th>
<th>mode 2 (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>none</td>
<td>12.96</td>
<td>72.69</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.23</td>
<td>7.16</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.24</td>
<td>6.08</td>
</tr>
</tbody>
</table>
Evaluating ball milling (and ultrasound)
Image Analysis: Two Approaches

Static:
particles fixed on slide,
stage moves slide

Dynamic:
particles flow past camera

0.5 – 1000 um
2000 um w/1.25 objective

1 – 3000 um
Data Evaluation

1. Raw Image
2. Binarize
3. Find Edges
4. Analyze Each Particle
5. Output Distribution
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

Metal powder by Camsizer XT

Tin and Lead Solder Powder
Particle Shape

- Image capture with PSA300
Concluding Comments

- Battery performance depends on particle size.

- Particle size can be determined by a number of techniques including laser diffraction and image analysis.

- Questions?
Questions?

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Thank you
Thank you