Carbon Black Additives for Electric Double Layer Capacitors (EDLC): Impact on Capacity and Cycle Life

Miodrag Oljaca, Aurelien DuPasquier, Paolina Atanassova, Scott Sawrey, Derek Li, Michael Wang

Cabot Energy Materials

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Presentation Outline:

- Overview of Cabot and carbon technology
- Role of carbon blacks in EDLC
- New additives to address future requirements
About Cabot Corporation

- Over 130 years in operation
  - Founded 1882
  - NYSE: CBT since 1968
- Global specialty chemicals and performance materials company
- 44 manufacturing sites in 21 countries
- Core technical competencies in fine particles and surface modification
- FY2016 sales of $2.4B
## Cabot Toolbox includes carbons for EDLC applications

<table>
<thead>
<tr>
<th>Particle</th>
<th>Attribute</th>
<th>Property</th>
<th>Function</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractal particles (carbon black, SiO₂, Al₂O₃)</td>
<td>Particle Size</td>
<td>Rheological</td>
<td>Slurry viscosity, stability, solid loading</td>
<td>Li-Ion Batteries</td>
</tr>
<tr>
<td>Colloidal particles (SiO₂)</td>
<td>Aggregate Size/Shape</td>
<td>Mechanical</td>
<td>Electrode adhesion, density, porosity, stability</td>
<td></td>
</tr>
<tr>
<td>Graphenes</td>
<td>Purity</td>
<td>Electrical</td>
<td>Electrical conductivity, ionic conductivity</td>
<td></td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>Pore Structure</td>
<td>Flow</td>
<td>Paste viscosity, dispersion, anti-settling, solid loading</td>
<td>Lead Acid Batteries</td>
</tr>
<tr>
<td></td>
<td>Surface Chemistry</td>
<td>Surface reactivity</td>
<td>Moisture absorption, adhesion, hydrophobic, hydrophilic, stability</td>
<td>Supercapacitors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermal</td>
<td>Thermally insulating or conductive</td>
<td></td>
</tr>
</tbody>
</table>

- **Li-Ion Batteries**: 
- **Lead Acid Batteries**: 
- **Supercapacitors**
Cabot has strong presence in energy storage technologies

- Activated carbons
- Conductive carbon black additives

Li-Ion:
- Conductive additives
- Metal oxides
- Lead acid
- Carbon additives
- Fumed silica

- Carbon catalyst supports

Batteries

Fuel Cells

Capacitors
EDLC’s have gained significant traction in various industries

EDLCs can address some of the weaknesses of Li-ion batteries:
- Fast charge
- Fast discharge
- High cycle life
- Low temperature performance
- Safe/robust operation

Ultracapacitor Module for Hybrid Bus Market (October 12, 2016, PRNewswire)

Ultracapacitors Deployed in Ireland Microgrid Energy Storage System (Feb. 18, 2015 /PRNewswire)

A large-scale system combining advanced batteries and ultracapacitor energy storage to provide grid services (Jun 10, 2016, Energy Storage News)

Ultracapacitors Vital To 48 Volt Mild Hybrid Systems (January 21st, 2016, GAS2)
New trends in EDLC industry have implications on carbon additive requirements

Macro trends/Barriers
- Reduce cost
- Increase energy density
- Safety/Toxicology

Directions/Approaches
- Denser electrodes
- Higher voltages
- New electrolytes
- New carbons

Issues
- Cycling stability at higher voltages
- Electrode porosity
- Morphology optimization
- Safety/purity
- Swelling/depercolation
- Solids/drying
- Uniformity/homogeneity
- Adhesion/cohesion
- Gassing

Material needs/Implications
- Stable conductive network
- High purity
- Dispersion quality
- Inertness at high voltage
- High packing density
- Good wettability

There is a need to design improved carbon additives that can help remove some of the trade-offs.
Carbon is major component of EDLC electrodes

Traditional electrodes contain activated carbon and 5-10% of low surface area carbon black conductive additive

- Activated carbon provides most of the active surface area
- Carbon black properties can also impact EDLC performance

Carbon black morphology and form can impact electrode density

Carbon bulk conductivity and morphology can impact electrode conductivity
### Cabot’s carbon technology

Control of key properties enables carbon black and activated carbons specifically designed for EDLC applications

<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon Black</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface area and porosity</strong></td>
<td>Able to controllably dial-in surface area from $&lt;50\text{m}^2/\text{g}$ to $&gt;1000\text{m}^2/\text{g}$</td>
<td>Large selection of starting materials and activation techniques to provide a wide range of porosity</td>
</tr>
<tr>
<td><strong>Structure</strong></td>
<td>Technologies for both low structure and high structure</td>
<td>Able to produce powders, granular and extrude carbons of various shapes and dimensions</td>
</tr>
<tr>
<td><strong>Purity</strong></td>
<td>High purity</td>
<td>Leading technology to purify powders and granular</td>
</tr>
<tr>
<td><strong>Crystallinity</strong></td>
<td>Able to control crystallinity from amorphous to highly crystalline</td>
<td>Able to impregnate carbon with various chemistry for enhanced performance</td>
</tr>
<tr>
<td><strong>Surface groups</strong></td>
<td>Able to control surface properties for stability and ease of dispersion</td>
<td>Able to alter surface chemistry for improved adsorption performance</td>
</tr>
</tbody>
</table>
Cabot has developed new carbon blacks for EDLC electrodes

High surface area + high packing density

Controlled pore size distribution
New carbon blacks have demonstrated good performance as active materials for EDLC

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New carbon blacks can serve as both conductive additive and active material.

- **Activated carbon**
  - Current collector
  - Conductive additive: **10% standard carbon black** (70 m²/g)
  - Capacitance: 17.4 F/cc

- **Activated carbon**
  - Current collector
  - Conductive additive: **10% Cabot’s SC2 carbon black** (∼1400 m²/g)
  - Capacitance: 19.5 F/cc

~10% improvement in capacitance, no negative impact on ESR.
Electrode density and cycling stability are some of the remaining challenges.
# Approaches to further improve performance of EDLC carbon blacks

<table>
<thead>
<tr>
<th>Improvement desired</th>
<th>Cabot solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower internal resistance</td>
<td>Carbon black additive ✓</td>
</tr>
<tr>
<td>Higher capacitance</td>
<td>High surface area ✓ and controlled pore size ✓</td>
</tr>
<tr>
<td>Higher density electrodes</td>
<td>High powder packing density ✓ and <strong>optimized form</strong></td>
</tr>
<tr>
<td>Better cycle-life and lower gassing at high voltage</td>
<td><strong>Higher purity carbon black</strong></td>
</tr>
</tbody>
</table>
Acid wash to improve purity of carbon black

- Cabot utilizes a commercial scale acid extraction/wash process to purify the base carbon black and reduce metals and ash content in order to improve cycling stability and reduce gassing
- Morphology and surface area is preserved through acid wash process
Form and particle size can be adjusted to improve processing of high surface area carbon blacks

<table>
<thead>
<tr>
<th>CB form</th>
<th>Electrode quality</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Poor</td>
<td>Limited adhesion to foil, enhanced cracking after drying, and grainy electrode</td>
</tr>
<tr>
<td>B</td>
<td>Good</td>
<td>Some drying induced cracks</td>
</tr>
<tr>
<td>C</td>
<td>Medium</td>
<td>CB does not stick to foil after drying</td>
</tr>
<tr>
<td>D</td>
<td>Poor</td>
<td>CB does not stick to foil after drying</td>
</tr>
</tbody>
</table>

![Graph showing distribution of particle sizes]
Optimization of high purity carbon black properties can improve electrode density

![Bar chart showing electrode density g/cc for different samples: AC only, AC+ low SA CB, AC+ high SA CB, AC + high SA CB optimized.](chart.png)
High purity carbon blacks were extensively tested

<table>
<thead>
<tr>
<th></th>
<th>Activated carbon: CB: PVDF 81:9:10</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrode preparation</strong></td>
<td>Knife casting onto current collector, followed by calendering after drying.</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>Net4BF4 in Acetonitrile, 1.5M</td>
</tr>
<tr>
<td><strong>Separator</strong></td>
<td>Whatman glass fiber, 150 microns</td>
</tr>
<tr>
<td><strong>Max. Voltage</strong></td>
<td>3.0V</td>
</tr>
</tbody>
</table>

**Performance testing conditions:**

- ~ 100 µm thick electrodes, 15 mm diameter.
- 6 x 2032 coin cells per sample
- CV cycling: 0-3 V, 10 mV/s, 25°C, 90th cycle shown
- Constant current cycling: 10 mA, 0-3V, 25°C, 10k cycles
High purity carbon blacks retain their functionality as conductive additives

Volume resistance data for various electrodes

<table>
<thead>
<tr>
<th></th>
<th>Electrode density (g/cc)</th>
<th>Carbon loading (mg/cm²)</th>
<th>Thru plane resistance (Ω)</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC alone</td>
<td>0.8</td>
<td>7.59</td>
<td>12.5</td>
<td>2.52</td>
</tr>
<tr>
<td>AC + low SA CB</td>
<td>0.79</td>
<td>7.37</td>
<td>11.2</td>
<td>2.76</td>
</tr>
<tr>
<td>AC + SC2</td>
<td>0.79</td>
<td>7.88</td>
<td>9.5</td>
<td>3.26</td>
</tr>
<tr>
<td>AC + SC2-A</td>
<td>0.8</td>
<td>7.4</td>
<td>9.1</td>
<td>3.43</td>
</tr>
<tr>
<td>AC + SC2-B</td>
<td>0.8</td>
<td>7.98</td>
<td>8.8</td>
<td>3.58</td>
</tr>
</tbody>
</table>

![Graph showing percolation and resistivity](image)
High purity carbon blacks may enable higher specific capacitance

<table>
<thead>
<tr>
<th></th>
<th>Electrode density (g/cc)</th>
<th>Carbon loading (mg/cm²)</th>
<th>Specific capacitance @ 1.5V (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC + low SA CB</td>
<td>0.79</td>
<td>7.37</td>
<td>65.6</td>
</tr>
<tr>
<td>AC + SC2-A</td>
<td>0.8</td>
<td>7.4</td>
<td>82.1</td>
</tr>
<tr>
<td>AC + SC2-B</td>
<td>0.8</td>
<td>7.98</td>
<td>87.8</td>
</tr>
</tbody>
</table>
High purity carbon blacks can provide good cycle life even at higher voltages.
Summary

• There is ongoing need to increase capacity, operating voltage and cycle life and reduce cost of EDLC
• Cabot has developed high surface area carbon blacks that can serve as both conductive additive and active material for EDLC
• We have recently improved purity and form of these new carbon blacks
• Results suggest that high purity SC2 carbon blacks can improve cycle life of EDLC’s operating at higher voltage

For more information on high purity carbon black for EDLC applications contact Miki Oljaca at miki.oljaca@cabotcorp.com