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

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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

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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

carbon black **#1**

inkjet colorants **#1**

cesium formate **#1**

activated carbon **#2**

fumed metal oxides **#2**

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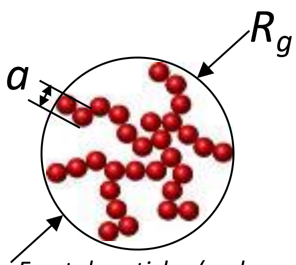
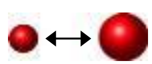
Cabot toolbox includes carbons for EDLC applications

Particle ← Attribute ← Property ← Function ← Application

Particle

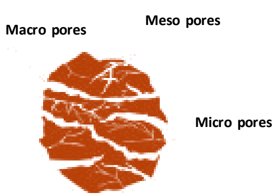


Fractal particles (carbon black, SiO2, Al2O3)



Colloidal particles (SiO2)

Graphenes



Activated Carbon

Attribute

- Particle Size
- Aggregate Size/Shape
- Purity
- Pore Structure
- Surface Chemistry

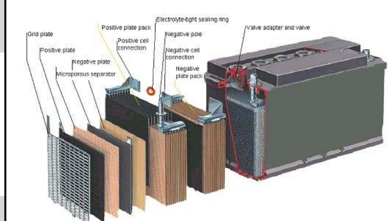
Property / Function

Property	Function
Rheological	Slurry viscosity, stability, solid loading
Mechanical	Electrode adhesion, density, porosity, stability
Electrical	Electrical conductivity, ionic conductivity
Flow	Paste viscosity, dispersion, anti-settling, solid loading
Surface reactivity	Moisture absorption, adhesion, hydrophobic, hydrophilic, stability
Thermal	Thermally insulating or conductive

Application

Li-Ion Batteries

Lead Acid Batteries



Supercapacitors

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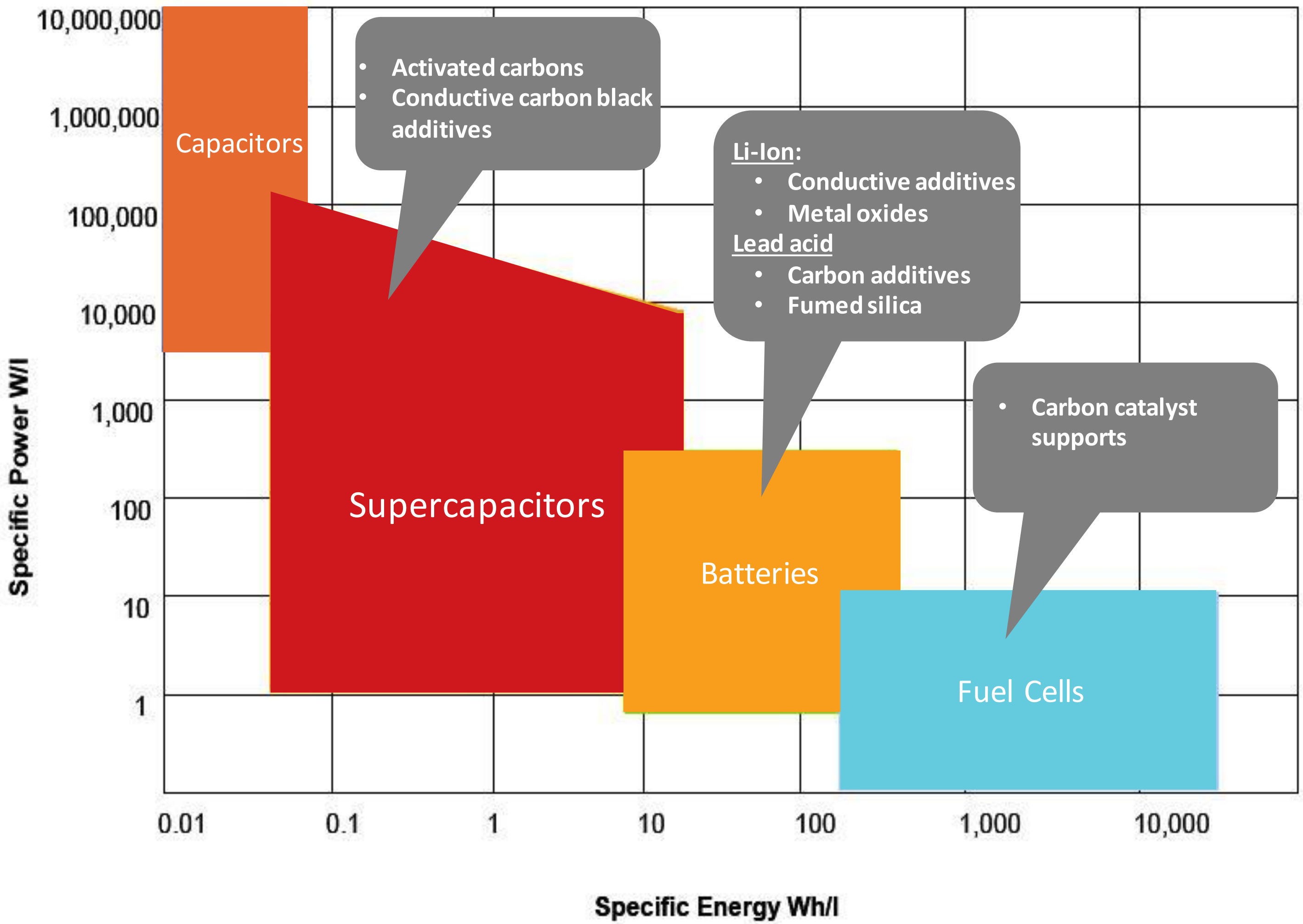
Cabot has strong presence in energy storage technologies



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EDLC’s have gained significant traction in various industries

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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)

The containerised ultracapacitor system is put into place. Image: Maxwell Technologies

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.

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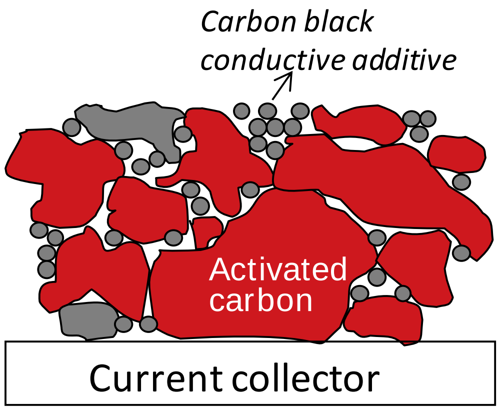
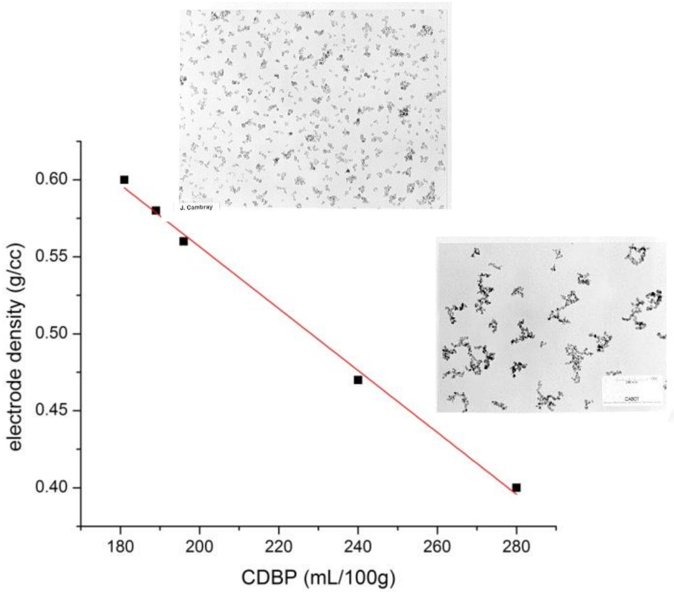
Carbon is major component of EDLC electrodes

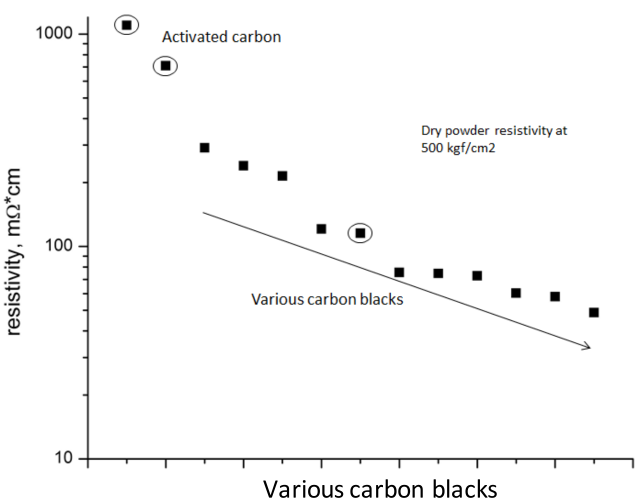
Traditional electrodes contain activated carbon and 5-10% of low surface area carbon black conductive additive

- 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

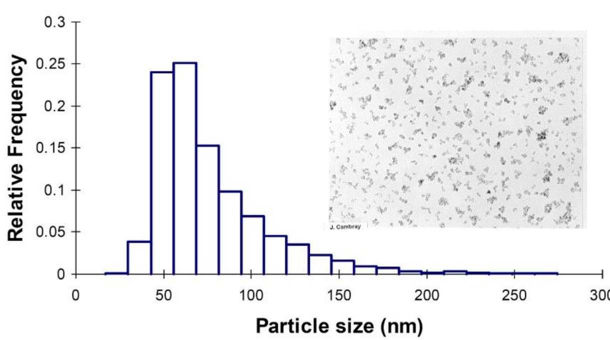


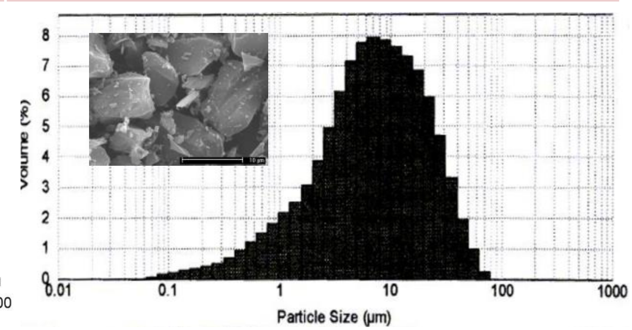
Carbon bulk conductivity and morphology can impact electrode conductivity

Cabot's carbon technology

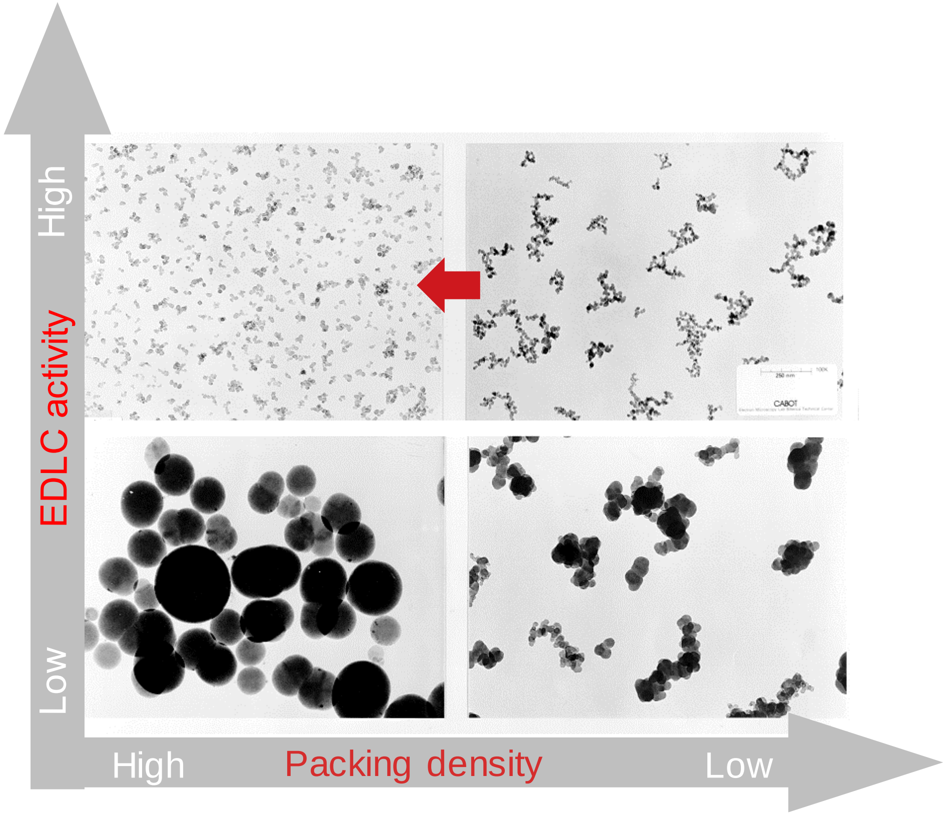
Control of key properties enables carbon black and activated carbons specifically designed for EDLC applications

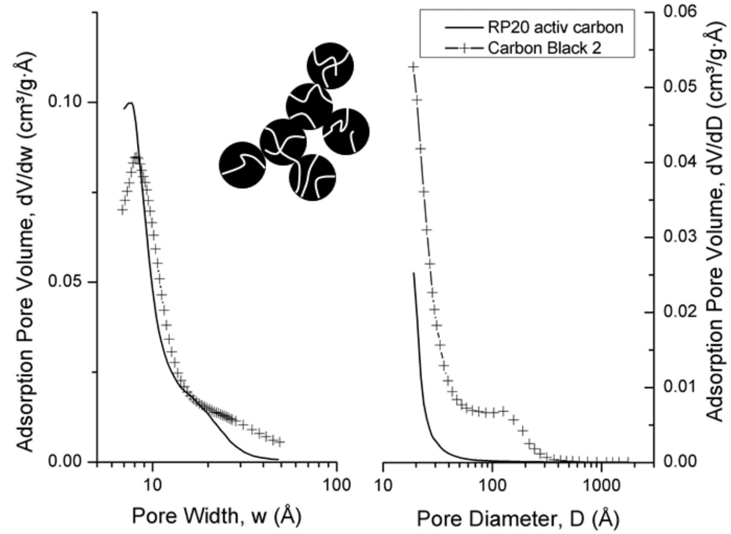
Property	Carbon Black	Activated Carbon
Surface area and porosity	Able to controllably dial-in surface area from <50m^2/g to >1000m^2/g	Large selection of starting materials and activation techniques to provide a wide range of porosity
Structure	Technologies for both low structure and high structure	Able to produce powders, granular and extrudate carbons of various shapes and dimensions
Purity	High purity	Leading technology to purify powders and granular
Crystallinity	Able to control crystallinity from amorphous to highly crystalline	Able to impregnate carbon with various chemistry for enhanced performance
Surface groups	Able to control surface properties for stability and ease of dispersion	Able to alter surface chemistry for improved adsorption performance





Cabot has developed new carbon blacks for EDLC electrodes

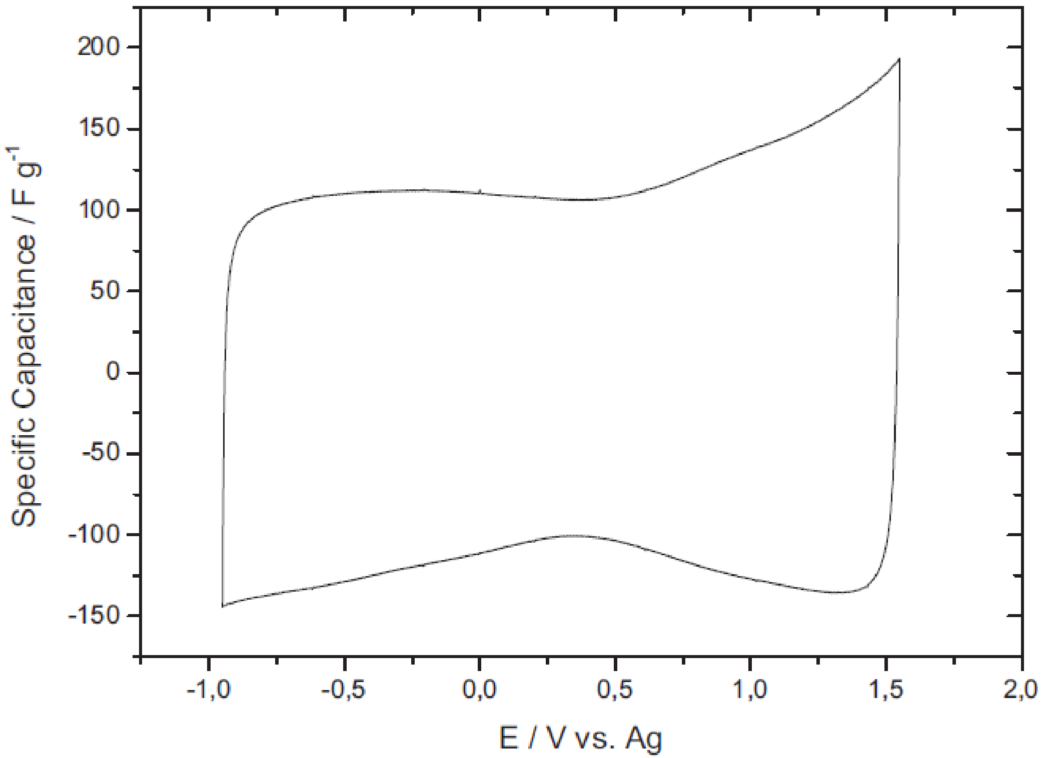


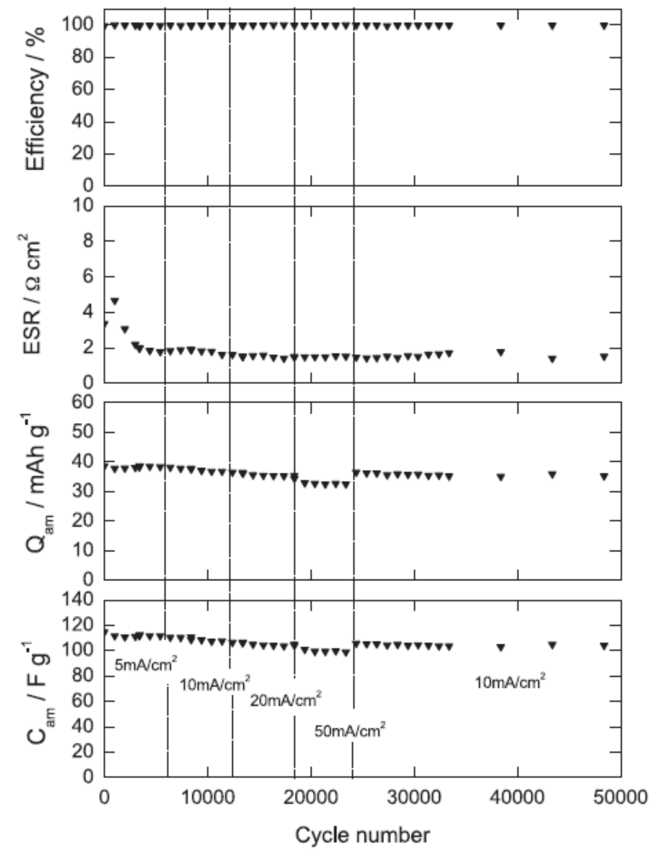


High surface area + high packing density

Controlled pore size distribution

New carbon blacks have demonstrated good performance as active materials for EDLC





A. Krause et al., *Journal of Power Sources*, **196**, 8836 (2011).

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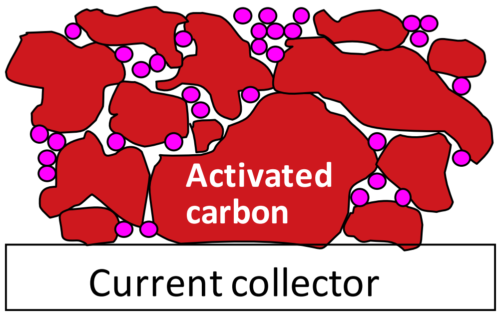
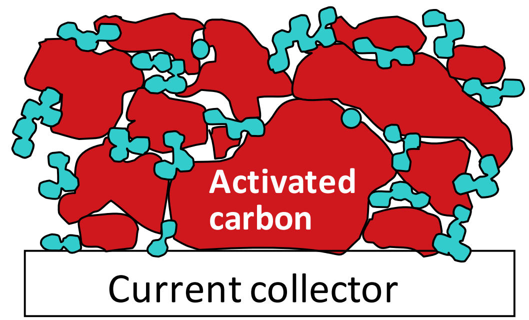
New carbon blacks can serve as both conductive additive and active material



Conductive additive: **10% standard carbon black** (70 m^2/g)

17.4 F/cc

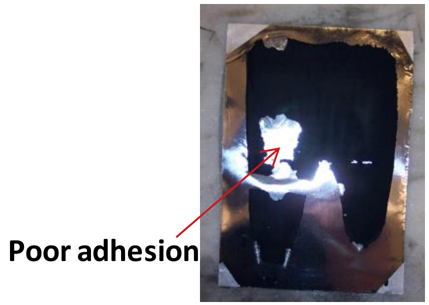


Conductive additive: **10% Cabot's SC2 carbon black** (~1400 m^2/g)

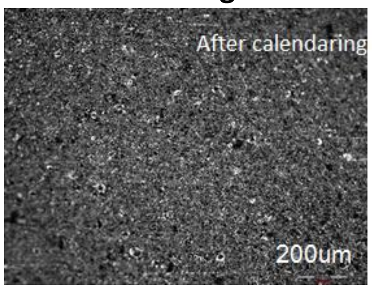
19.5 F/cc

~10% improvement in capacitance, no negative impact on ESR

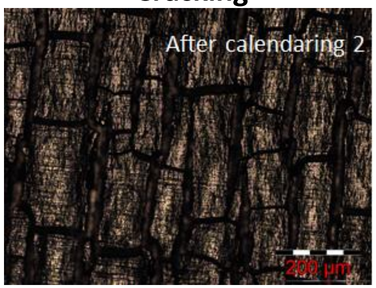
Electrode density and cycling stability are some of the remaining challenges

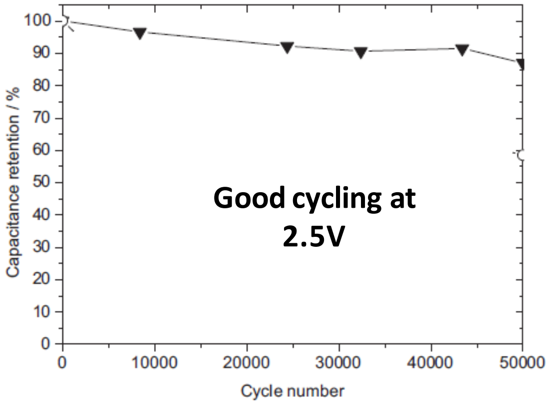


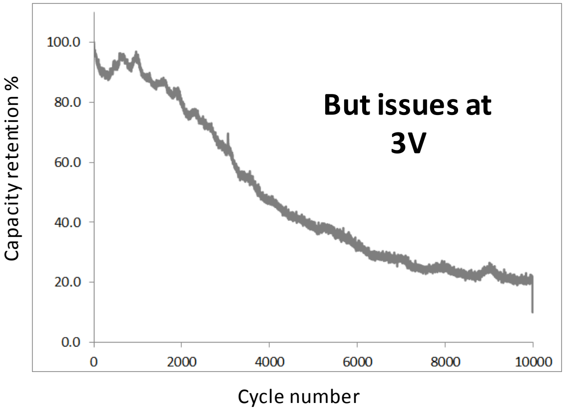
No cracking



Cracking



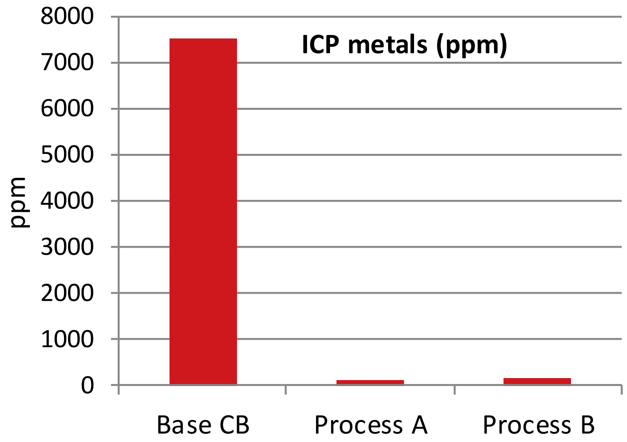


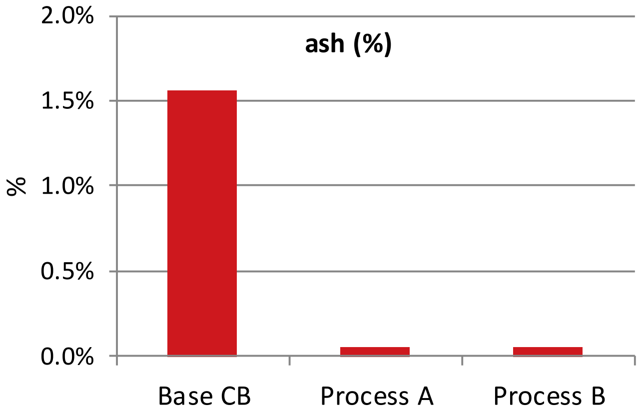


Approaches to further improve performance of EDLC carbon blacks

Improvement desired	Cabot solution
Lower internal resistance	Carbon black additive ✓
Higher capacitance	High surface area✓ and controlled pore size✓
Higher density electrodes	High powder packing density ✓ and ***optimized form***
Better cycle-life and lower gassing at high voltage	***Higher purity carbon black***

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

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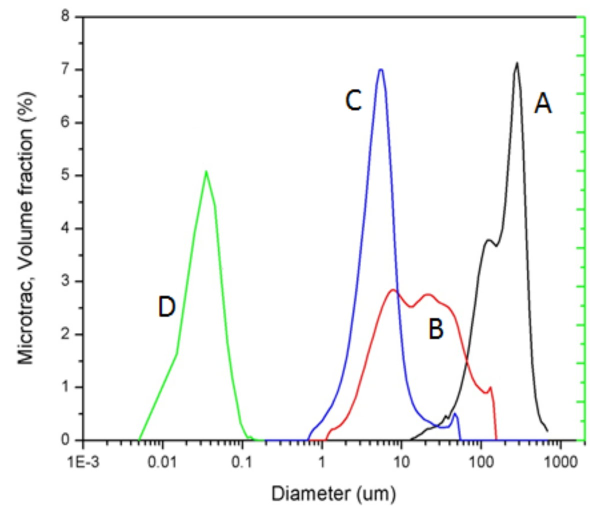
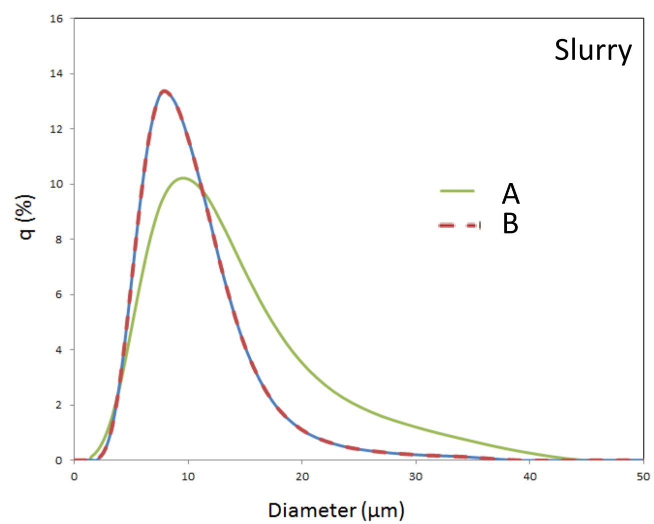
Form and particle size can be adjusted to improve processing of high surface area carbon blacks

CB form	Electrode quality	Notes
A	Poor	Limited adhesion to foil, enhanced cracking after drying, and grainy electrode
B	Good	Some drying induced cracks
C	Medium	CB does not stick to foil after drying
D	Poor	CB does not stick to foil after drying





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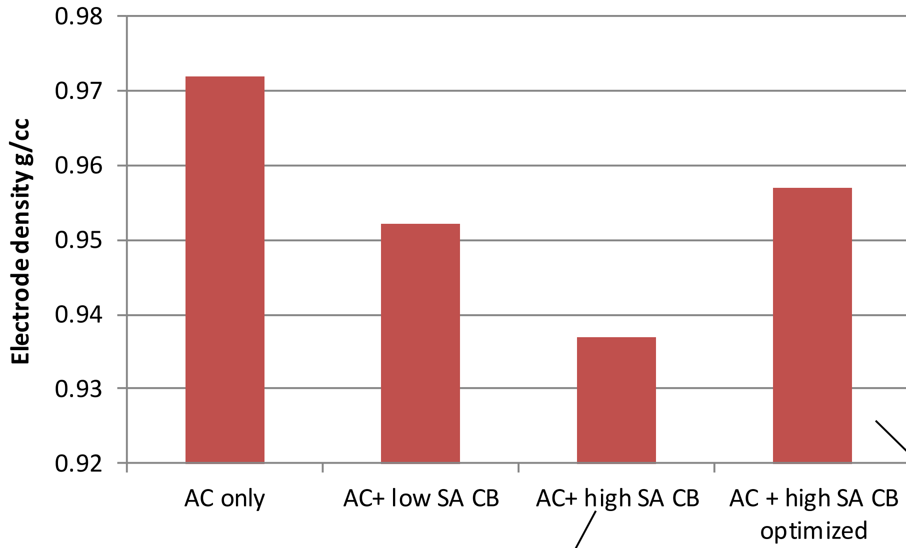
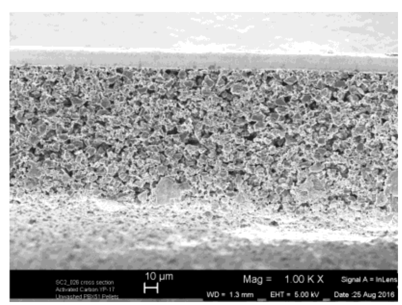
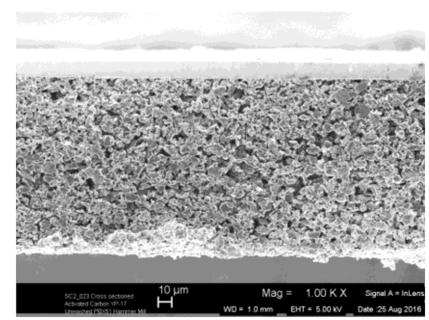
Optimization of high purity carbon black properties can improve electrode density







High purity carbon blacks were extensively tested

	Activated carbon: CB: PVDF 81:9:10
Electrode preparation	Knife casting onto current collector, followed by calendering after drying.
Electrolyte	Net4BF4 in Acetonitrile, 1.5M
Separator	Whatman glass fiber, 150 microns
Max. Voltage	3.0V

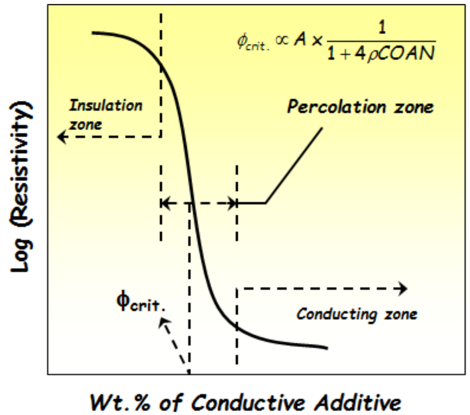
Performance testing conditions:

- ~ 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

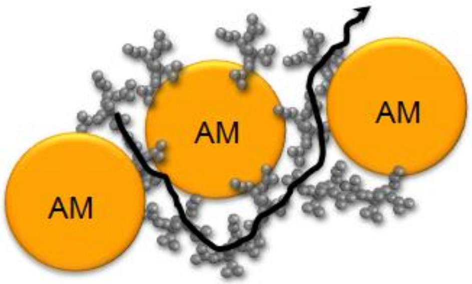
High purity carbon blacks retain their functionality as conductive additives

Volume resistance data for various electrodes

	Electrode density (g/cc)	Carbon loading (mg/cm^2)	Thru plane resistance (Ω)	Conductivity (mS/cm)
AC alone	0.8	7.59	12.5	2.52
AC + low SA CB	0.79	7.37	11.2	2.76
AC + SC2	0.79	7.88	9.5	3.26
AC + SC2-A	0.8	7.4	9.1	3.43
AC + SC2-B	0.8	7.98	8.8	3.58

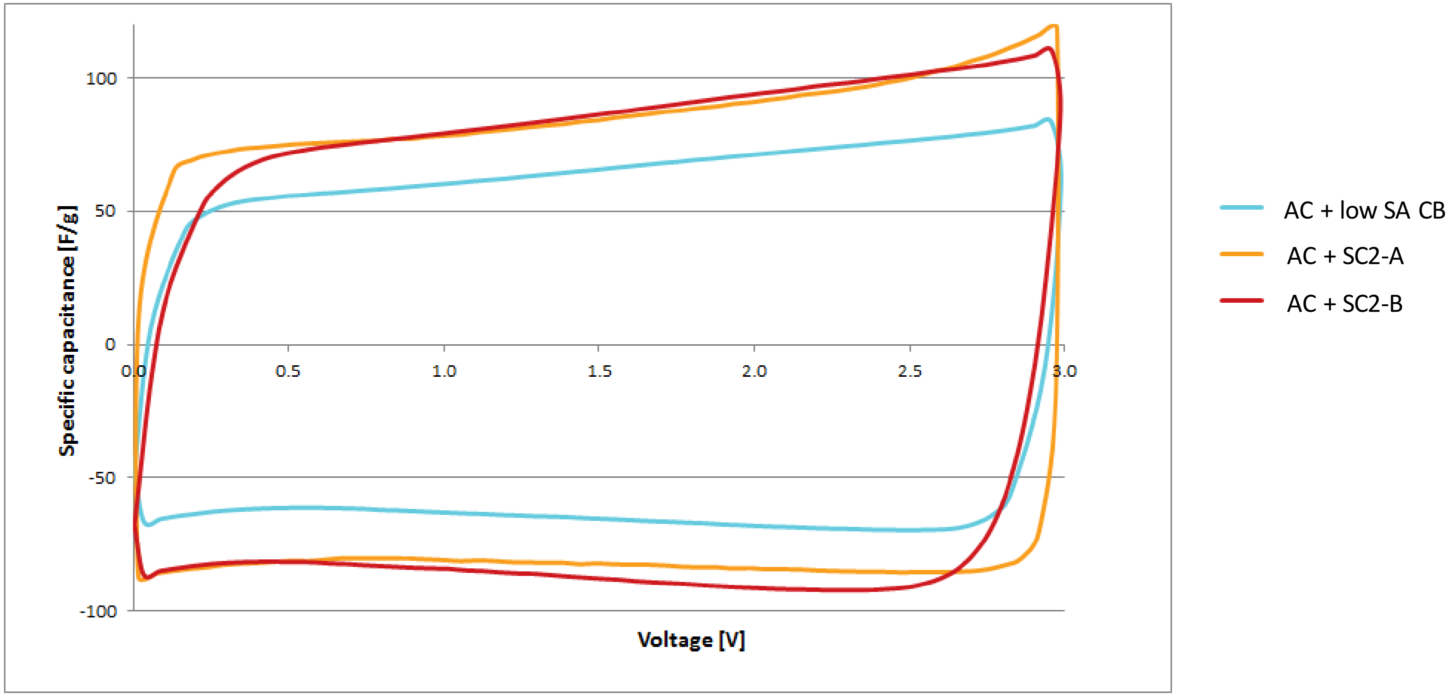


$\phi_{crit.}$ - critical volume fraction of conductive additive at percolation



High purity carbon blacks may enable higher specific capacitance

	Electrode density (g/cc)	Carbon loading (mg/cm^2)	Specific capacitance @ 1.5V (F/g)
AC + low SA CB	0.79	7.37	65.6
AC + SC2-A	0.8	7.4	82.1
AC + SC2-B	0.8	7.98	87.8



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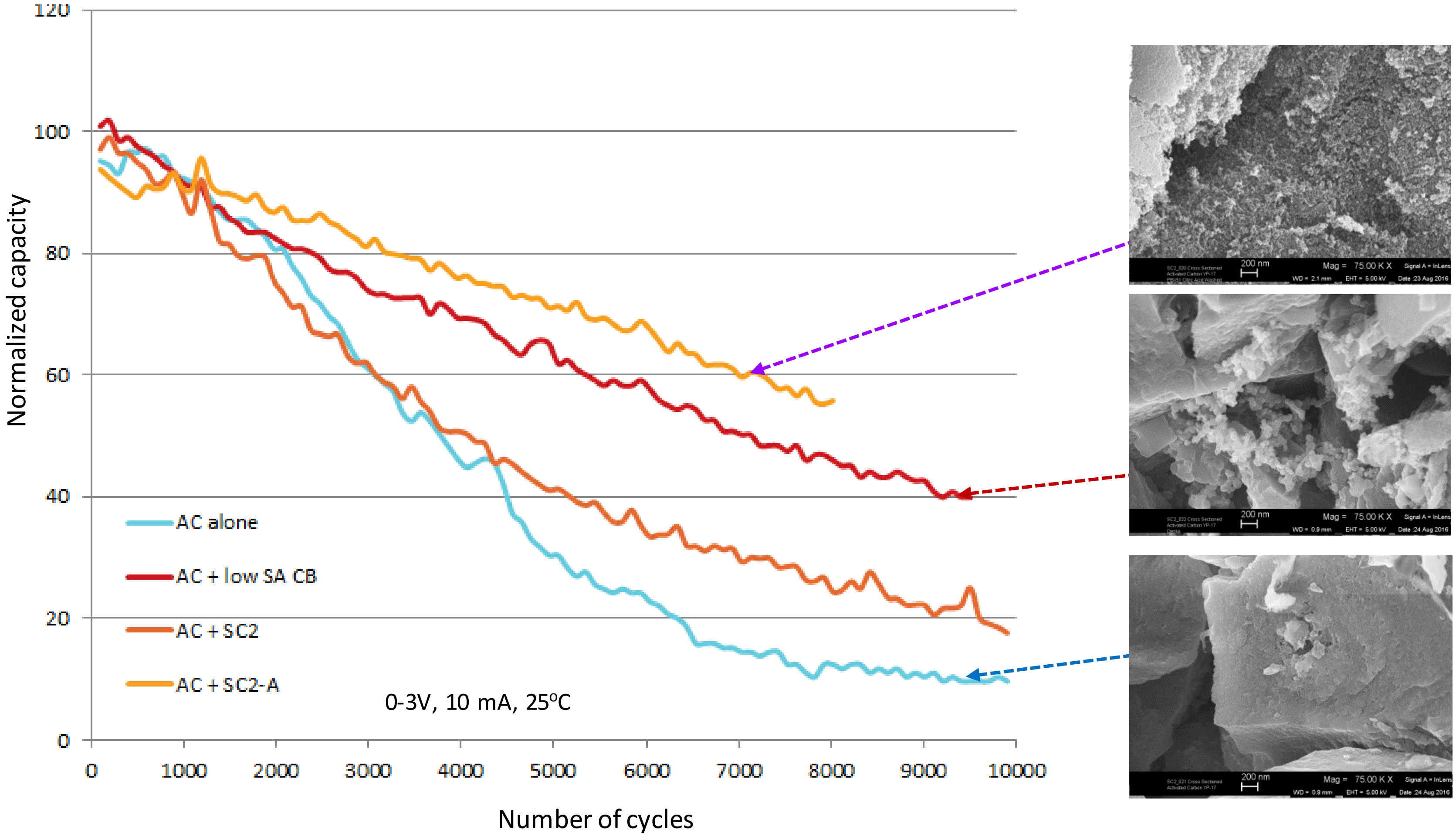
High purity carbon blacks can provide good cycle life even at higher voltages



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