Carbonaceous Anode Materials and Conductive Additives as Key To Higher Performance Lithium-ion Batteries

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Imerys Graphite & Carbon in Lithium-Ion Battery Applications

500+ employees including 30+ in R&D

6 industrial sites

1000+ customers

2 R&D laboratories

- Headquarters
- Sales Offices
- R&D Laboratories
- Industrial Sites
Carbon in Electrochemical Lithium-Ion Cells

- electrolyte (in electrode pores)
- carbon active material
- conductive graphite
- conductive carbon black
- binder

IMERYS carbon products are inside the positive and the negative electrode

- electrolyte (in electrode pores)
- active material
- conductive graphite
- conductive carbon black
- binder

negative electrode (anode)

- Li⁺

positive electrode (cathode)

current collector coating
aluminum current collector

copper current collector
Carbonaceous Anode Materials and Conductive Additives as Key To higher Performance Lithium-ion Batteries

Carbon conductive additives for the positive electrode
Carbon conductive additives for the negative electrode
Electrochemically active carbon materials
Carbon/silicon composites
Carbon Black and Graphite Additives in the Positive Electrode

**Graphite and Carbon Additives**

- **Graphite** and **carbon black** are used as conductive additives in positive electrodes.

**Electrical Resistivity**

- The resistivity of different graphite and carbon black additives is plotted against carbon content.
- **KS6L**, **SFG6L**, **Super C45**, and **Super C65** are compared.

**Scanning Electron Microscopy (SEM)**

- **SEM** images show the morphology of graphite and carbon black additives.
- **1 μm** scale bar on the SEM image of **Super P Li**.
- **200 nm** scale bar on the SEM image of **Super C65**.

**Transmission Electron Microscopy (TEM)**

- **TEM** images provide a closer view of the microstructure of graphite and carbon black additives.
- **Super P Li** and **Super C65** are shown with their respective scale bars.

**Notes**

- The resistivity of **C in LiCoO₂** and **C in LiFePO₄** is plotted against carbon content.
- **Super C65**, **KS6L**, **Super C45**, and **SFG6L** are compared for their conductive properties.

**References**

- IMERYS Graphite & Carbon
- AABC2017

**Implications**

- Optimizing the ratio of additives can improve battery performance.
- Graphite and carbon black enhance conductivity and stability.

**Keywords**

- Conductive additives
- Electrical resistivity
- Scanning electron microscopy
- Transmission electron microscopy
Conductive Carbon Black and Graphite Additives in NMC Electrodes

C-NERGY™ KS 6L graphite and Super C65 conductive carbon black at different carbon black : graphite ratios and a total of 2 wt.% of conductive carbon mass in NMC.

Mixtures of graphite and conductive carbon black combine
- sufficient electrical conductivity with
- increased compressibility at low carbon volume fractions.
Graphite as Compaction Aid in the Conductive Electrode Mass

Similar electrode resistivity leads to a similar specific charge of the electrode*

The graphite additive improves the electrode compressibility and charge density*

*NMC electrodes with 4 wt.% carbon conductive mass/5 wt.% PVDF binder material 1C/1D, 1 M LiPF₆ in EC/EMC 1:3 (w/w)
Mixed conductive graphite/carbon black masses show better adhesion of the electrode on the current collector foil than pure conductive carbon black.
Graphite Additives in the Negative Electrode

Density of C-NERGY™ ACTILION 1 electrodes containing C-NERGY™ SFG 15L

Influence of C-NERGY™ SFG 15L on the cycling stability of C-NERGY™ ACTILION 1 electrodes

Electrode density: 1.7 g cm⁻³
Binder material: 1.5 wt.% SBR/1.5 wt.% CMC
Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w/w)

Lithium half-cells, 1C/3D (CCCV)
Binder material: 1.5 wt.% SBR/1.5 wt.% CMC
Graphite Additives in the Negative Electrode

Influence of C-NERGY™ SFG 15L graphite on the resistance and specific charge of C-NERGY™ ACTILION 1 electrodes

Influence of C-NERGY™ SFG 15L graphite on the specific charge retention of C-NERGY™ ACTILION 1 electrodes at 2 C cell discharge rate*

*Symmetric coin cell, **Lithium metal coin half-cell
Binder: 1.5 wt.% SBR/1.5 wt.% CMC
Electrode density: 1.7 g cm⁻³
Electrolyte: EC/EMC 1:3 (w/w), 1 M LiPF₆
Carbon in the Lithium-ion Battery Negative Electrode


- **Soft carbon**: Neat stacking, but short-range order
- **Hard carbon**: Long-range order stacking of carbon layers
- **Graphite**: Neat stacking, no isotropic microporosity

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**Graphite & Carbon**
Natural and Synthetic Graphite Active Materials

Flake graphite (hindered Li$^+$ diffusion)

Li$^+$ Li$^+$

20 μm

Isometric graphite (easy Li$^+$ diffusion)

Li$^+$ Li$^+$

20 μm

Spherical natural graphite


Isotropic synthetic graphite

Current collector/electrode cross-sections
Swelling of Graphite Negative Electrode

Isotropic graphite

![Graphite electrode image]

![Graphite electrode graph]

25 um
Anisotropic graphite
Graphite Anode Materials for FEV Lithium-Ion Batteries

Development objectives at cell level

- Durability
- Safety
- Energy
- Power
- Chargeability

Development objectives at material (electrode) level

- High crystallinity synthetic or natural graphite (min. 340 Ah kg\(^{-1}\), min. 500 Ah L\(^{-1}\))
- Low surface area (min. 90 % coulombic efficiency in the 1st cycle)
- Low crystalline surface morphology (stable SEI, low cell gassing)
- Isotropic texture, low swelling (min. 3000 cycles/80 % capacity retention)
- Isotropic texture and particle shape (3C discharge/80 % capacity retention)
- Consistent batch-to-batch quality, surface properties (easy processing in aqueous electrode manufacturing)
- Sustainable large scale manufacturing processes (Low CO\(_2\) footprint, environmentally benign, high yield)
- Cost efficient
ACTILION B: Surface Properties created by Surface Treatment

- **Porosity**

- **Raman Spectroscopy**

Graphitization degree
### ACTILION B: Specific Charge and Coulombic Efficiency

<table>
<thead>
<tr>
<th>C-NERGY™ graphite material</th>
<th>Reversible specific charge (mAh g⁻¹)</th>
<th>Irreversible specific charge (mAh g⁻¹)</th>
<th>Coulombic efficiency ¹ˢᵗ cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical NG</td>
<td>364</td>
<td>30</td>
<td>92</td>
</tr>
<tr>
<td>ACTILION B-001</td>
<td>357</td>
<td>28</td>
<td>93</td>
</tr>
<tr>
<td>ACTILION B-002</td>
<td>351</td>
<td>37</td>
<td>91</td>
</tr>
<tr>
<td>ACTILION B-003</td>
<td>341</td>
<td>38</td>
<td>90</td>
</tr>
</tbody>
</table>

Lithium half-cell (coin cell)
Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w:w)
Binder: 1.5 wt.% SBR/1.5 % wt. CMC
Current: 50 mA/g (CCCV)

![SEM Spherical NG](image1)
![SEM ACTILION B-002](image2)
ACTILION B: Cycling Stability and Electrode Impedance

- Cycling stability at 2C/1D*

- Impedance spectroscopy**

* Lithium-ion coin cell with NMC positive electrode
  Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w:w), 1 wt.% VC
  Binder: 1.5 wt.% SBR/1.5 % wt. CMC
  Charge : 2C to 4.2V (CCCV at 0.1C)
  Discharge : 1C to 2.8V

** Symmetric coin cell, 50 % SOC
  Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w:w)
  Binder: 1.5 wt.% SBR/1.5 % wt. CMC
### ACTILION B: Electrode Resistance and High Current Rate Discharge

#### Direct current resistance of electrodes*

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>DCR (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical NG</td>
<td>19.5</td>
</tr>
<tr>
<td>ACTILION B-001</td>
<td>25.5</td>
</tr>
<tr>
<td>ACTILION B-002</td>
<td>22.7</td>
</tr>
<tr>
<td>ACTILION B-003</td>
<td>24.1</td>
</tr>
</tbody>
</table>

*Symmetric coin cell, 50 % SOC, 1C pulse (20 s)
Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w:w)
Binder: 1.5 wt.% SBR/1.5 % wt. CMC

#### High current rate continuous discharge**

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>2C/0.2C (%)</th>
<th>3C/0.2C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical NG</td>
<td>96.0</td>
<td>72.0</td>
</tr>
<tr>
<td>ACTILION B-001</td>
<td>97.5</td>
<td>74.2</td>
</tr>
<tr>
<td>ACTILION B-002</td>
<td>92.2</td>
<td>66.7</td>
</tr>
<tr>
<td>ACTILION B-003</td>
<td>98.5</td>
<td>78.9</td>
</tr>
</tbody>
</table>

**Lithium coin half-cell
Electrolyte: 1 M LiPF₆ in EC/EMC 1:3 (w:w)
Binder: 1.5 wt.% SBR/1.5 % wt. CMC
CO₂ Footprint of the C-NERGY™ ACTILION B Negative Electrode Materials

Electric Vehicles

From 250 000 units produced in 2015 to 2 000 000 units produced in 2025 using a CAGR of 23,11%

Simulation based on a 25kWh battery pack model

Study by: tallis consulting (2016)

Up to 1988 ktons of CO₂e SAVED
Technology Evolution of the Negative Electrode Material

- **C/Si composites**

- Evolution of the lithium-ion battery negative electrode technology for PHEV and FEV*

*Source: Boston Consulting Group, 2016
Nano-Silicon/Graphite Composite Electrodes

- Capacity increase of graphite electrode by addition of particulate nano-silicon

![Graph showing specific charge vs cycle number with three lines representing 8%, 14%, and 0% silicon.](image)

**Lithium-half cell (coin cell)**

**Electrolyte:** 1 M LiPF$_6$ in EC/DEC 3:7 (v,v), 2 wt.% FEC

**Binder:** 6 wt.% CMC/PAA (1:1)

50 mA g$^{-1}$ CCCV

**Scanning electron microscopy**
### Influence of Carbon Additives on Silicon/Carbon Composite Electrode Performance

<table>
<thead>
<tr>
<th>Negative electrode composition</th>
<th>Electrochemical results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon [wt.%]</td>
<td>ACTILION 1 [wt.%]</td>
</tr>
<tr>
<td>Nano-Silicon</td>
<td>Graphite</td>
</tr>
<tr>
<td>14</td>
<td>80.0</td>
</tr>
<tr>
<td>14</td>
<td>68.8</td>
</tr>
<tr>
<td>14</td>
<td>72.0</td>
</tr>
<tr>
<td>14</td>
<td>72.0</td>
</tr>
</tbody>
</table>
Carbon in Electrochemical Lithium-Ion Cells

negative electrode (anode)  
- 

separator  

Li⁺  
e⁻  

positive electrode (cathode)  

IMERYS carbon products are inside the positive and the negative electrode

· electrolyte (in electrode pores)
· carbon active material
· conductive graphite
· conductive carbon black
· binder

· electrolyte (in electrode pores)
· active material
· conductive graphite
· conductive carbon black
· binder

current collector coating  
aluminum current collector  
copper current collector
The support of the IMERYS R&D team is gratefully acknowledged.

Thank you for your attention.