Artificial Graphite for Lithium Ion Batteries

Dr. Roland Müller

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Agenda

- SGL Group at a Glance
- Graphite Properties
- Production of Artificial Graphite
- Anode Materials in Lithium Ion Batteries
- Natural Graphite in Battery Application & Outlook
SGL Group is one of the world’s largest manufacturers of carbon-based products.

- Comprehensive portfolio ranging from carbon and graphite products to carbon fibers and composites
- 45 production sites worldwide
- Service network covering more than 100 countries

- Sales of ~€ 1,4 bn in 2010
- Head office in Wiesbaden/Germany
- Approx. 6,300 employees worldwide
- Listed on MDAX
Best Solutions: Best in class products, services and ideas to satisfy current and future needs of our customers

Our markets

- Iron and steel
- Aluminium
- Semiconductor
- High temperature technology
- Mechanical engineering
- Automotive
- Chemicals
- Energy and environmental technology
  - LIB Anode materials
- Aerospace
- High performance sports
Our carbon based products offer sustainable solutions towards less CO₂

2010 Sales (in €m)

1,382

approx. 65% of Group Sales

10%
10%
80%

Light weight
Alternative energies

Energy efficiency

Aerospace
Automotive
Wind
Solar
Scrap recycling
Batteries
Automotive
Cooling systems

~ 900

approx. 65% of Group Sales

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Greek: Graphein = to write

Lattice of graphite

Pencils

Diamonds
### Graphite Monocrystal

<table>
<thead>
<tr>
<th>properties</th>
<th>parallel to atomic layer</th>
<th>perpendicular to atomic layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>density [g/cm³]</td>
<td>2.27</td>
<td>2.27</td>
</tr>
<tr>
<td>E Modulus [GPa]</td>
<td>10</td>
<td>0.35</td>
</tr>
<tr>
<td>spec. electr. resistance [µΩ m]</td>
<td>0.5</td>
<td>10,000</td>
</tr>
<tr>
<td>therm. expansion [10E-6/K]</td>
<td>-1.5</td>
<td>28.6</td>
</tr>
<tr>
<td>therm. conductivity [W/mK]</td>
<td>&gt; 400</td>
<td>&lt; 8</td>
</tr>
<tr>
<td>layer line distance [nm]</td>
<td>0.142</td>
<td>0.335</td>
</tr>
</tbody>
</table>
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Artificial Graphite: Manufacturing Process

- Raw material storage: Coke, graphite, anthracite
- Crushing
- Grinding
- Screening, Sieving
- Storages for classified fractions
- Weighting
- Mixing
- Extrusion
- Vibro-moulding
- Isostatic pressing
- Baking (~ 1000°C)
- Impregnation
- Rebaking
- Graphitization (3000°C)
Production of Artificial Graphite

Raw materials:
- coke, pitch
- Coal tar pitch coke, isotropic
- Coal tar pitch coke, needle
- Petrol coke, regular
- Natural graphite

Steps:
1. Milling
2. Mixing
3. Molding
4. Baking
5. Graphitizing
6. Milling
Production of Artificial Graphite

Raw materials: coke, pitch

Milling
Mixing
Molding
Baking
Graphitizing
Milling

Mill

Mixer
Production of Artificial Graphite

Raw materials: coke, pitch

Milling

Mixing

Molding

Baking

Graphitizing

Milling

Extrusion

Die-molding

Vibrating

Isostatic pressing
Production of Artificial Graphite

Raw materials: coke, pitch

Milling → Mixing → Molding → Baking → Graphitizing

Ringfurnace

or alternatives:
- Tunnel Furnace
- Belt Furnace
- Car Bottom Kiln
- Cover Furnace
Production of Artificial Graphite

Raw materials: coke, pitch

Milling

Mixing

Molding

Baking

Graphitizing

Acheson Graphitisation

Long Process Times

Various Formats

Castner Lengthwise Graphitisation

Shorter Process Times

Same cross section
Graphitization

Development of Crystallite Alignment

Graphite lattice formation

800°C Calcination
1200°C S&N release
1400°C Puffing
2200°C Graphitization
>2400°C Hexagonal Graphite (abab)

$\frac{c}{2} \approx 3.44 - 3.354 \text{ Å}$

$L_c \approx 400 - 600 \text{ Å}$

$L_a \approx 800 - 1100 \text{ Å}$

Source: Marsh, 1991
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**Li-Ion Batteries**

**Operation Principle**

- **Negative electrode / Anode:** Graphite
  \[ \text{LiC}_6 \leftrightarrow C_6 + \text{Li}^+ + e^- \]

- **Positive electrode / Cathode:** LiCoO$_2$
  \[ 2\text{Li}_{0.5}\text{CoO}_2 + \text{Li}^+ + e^- \leftrightarrow 2\text{LiCoO}_2 \]

**Cell reaction:**
\[ \text{LiC}_6 + 2\text{Li}_{0.5}\text{CoO}_2 \leftrightarrow C_6 + 2\text{LiCoO}_2 \]
Carbon & Graphite in LIB

Characterisation of Graphites for Li-Ion Batteries
Crystallite Size

Determination by X-ray diffraction (XRD) and Raman spectroscopy

\[ L_c > \text{ca. 50 nm} \]
\[ L_a < \text{ca. 100 nm} \]
\[ d_{(002)} \leq \text{ca. 3.38 Å} \]

Smaller \( L_c \)
Larger \( L_a \)
Larger \( d_{(002)} \)

Rapid charge / discharge
Good cycling stability
Capacity tends to decrease
Synthetic Graphite for Li-Ion Batteries
First Cycle

Irreversible capacity (= charge capacity - discharge capacity) = Coulomb Efficiency

Staging compounds:

IV \( \text{LiC}_{36-50} \)
III \( \text{LiC}_{25-30} \)
II L \( \text{LiC}_{18} \)
II \( \text{LiC}_{12} \)
I \( \text{LiC}_6 \)

Intercalation

[Graph showing potential vs. capacity with stages and chemical species labeled]
Comparison Hard Carbon, Soft Carbon & Synthetic Graphite Rate Capability

Hard Carbon

Soft Carbon

Graphite

Synthesis Temperature: 800 - 1500°C
Significant properties changes with temperature

Synthesis Temperature: 2800 - 3000°C
Rate Capability of Different Carbon Types for LIB & Their Raw Materials

<table>
<thead>
<tr>
<th>Type</th>
<th>Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial Graphite</td>
<td></td>
</tr>
<tr>
<td>Synthetic Graphite</td>
<td></td>
</tr>
<tr>
<td>Natural Graphite</td>
<td></td>
</tr>
<tr>
<td>Soft Carbon</td>
<td></td>
</tr>
<tr>
<td>Hard Carbon</td>
<td></td>
</tr>
</tbody>
</table>

Measurement: CC; potential window: 1.5 - 0.02V vs. Li metal
## Comparison of Carbon / Graphite

<table>
<thead>
<tr>
<th>Item</th>
<th>Hard Carbon</th>
<th>Soft Carbon</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strength</td>
<td>High Stability versus electrolyte = Long Life</td>
<td>High Coulomb Efficiency &gt; 90 - 95%</td>
<td></td>
</tr>
</tbody>
</table>
<pre><code>                      | High power density | High electrode density |
</code></pre>
<p>| Weakness   | Low Coulomb Efficiency 75 – 80 % | CE 80 – 85% | Low Stability versus electrolyte = Short Life |
| Low electrode density | Low Coulomb Efficiency = Short Life |
|            |             |             | Poor power density |</p>

**Coexistence**

**Improvement**
Characterisation of Graphite for Li-Ion Batteries
Particle Shape and Orientation in the Composite Electrode

Particle shape and its orientation and particle size distribution determine the
- electrode density (packing density)
- electrical resistivity (contact points between particles)

(and thus energy density and power density) and electrode kinetics (rate capability and power)

Example of composite electrode:
Flake-type graphite: ~ 0.5 - 1.0 g/cm³
Spherical graphite: up to 1.7 g/cm³
Graphites for Li-Ion Batteries
From Materials to Performance

Materials and Tools
- Raw materials
  - Coke base
- Pre-treatment
  - Grinding and crushing
- Graphitisation process
  - Procedure / Oven
  - Temp. and duration
- Post-treatment
  - Grinding and crushing
  - Morphology tailoring
  - Chemical modification
  - Coating

Materials Properties
- Structure
  - 2H/3R ratio
  - Turbostratic disorder
  - Lattice defects
- Morphology
  - Particle shape
  - Particle size
  - Particle size distribution
  - BET surface area
  - Porosity
- Chemistry
  - Surface chemistry
  - Lattice doping

Electrochemical Performance
- Reversible capacity
- Irreversible capacity
- Cycling stability
- Rate capability
- PC tolerance
- Ageing behaviour
- Self-Discharge
- Electrode Processability
- Safety
### Comparison of Anode Materials for Automotive Batteries

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy</th>
<th>Life</th>
<th>Power</th>
<th>Safety</th>
<th>Cost</th>
<th>EV</th>
<th>HEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial Graphite</td>
<td>++</td>
<td>+</td>
<td>o</td>
<td>+</td>
<td>o</td>
<td>++</td>
<td>o</td>
</tr>
<tr>
<td>Natural Graphite *</td>
<td>++</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>++</td>
<td>+</td>
<td>o</td>
</tr>
<tr>
<td>Hard Carbon</td>
<td>o</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>o</td>
<td>o</td>
<td>++</td>
</tr>
<tr>
<td>Soft Carbon</td>
<td>o</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>o</td>
<td>++</td>
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* with Coating
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Substantial Growth for Automotive Applications from 2015

Anode Materials for LIB
Spherical Natural Graphite Demand

mt/a

Source: SGL/IIT
Production concentration of critical raw minerals materials
74% of world NG production out of China

Flake & Amorphous Graphite, (1) incl. DPR Corea

Industrial Minerals
Flake Graphite has to be rounded for LIB applications

Rounding is a difficult mechanical process carried out in an array of mills.

Currently it has a low yield of 30 - 40% only

Figure 1 SEM images of various graphites. (upper) natural graphite; (below) sample after sphereic-treatment.
Outlook: Graphite for LIB

- Spherical Natural Graphite plays an important role due to good cost / performance ratio

- Volume scenarios for 2020 require a significant increase in Natural Graphite mining & processing Capacity (yield for SNG)

- Supply risk assessments will play a more important role in reliable supply chains with focus on local EV productions

- Artificial Graphite is the choice for high performance LIB

- Raw material availability for Artificial Graphite is NOT restricted or highly concentrated.

- Capacity can be ramped up according to demand

- Artificial Graphite has potential for further cost / performance improvements regarding EV / PHEV / HEV
Summary

SGL Group is the leading Artificial Graphite Anode Material Producer based on

- more than 100 years experience in Carbon / Graphite business
- more than 10 years in manufacturing anode material
- plus innovative materials for energy storage
  - thermal management (ECOPHIT)
  - conductive additive (Conductograph)
  - EDLC supercaps
  - Carbon felts for Redox Flow Batteries (SIGRACELL)
  - Bipolar plates for Redox Flow Batteries (SIGRACET)
Thank You for Your kind Attention

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