Tailor Made
Carbon and Graphite Based Anode Materials
for Lithium Ion Batteries

Heribert Walter, Battery+Storage 2013
Agenda

- SGL Group at a Glance
- Anode Materials Overview
- Material Synthesis and Modification
- New Generation Anodes: Carbon/Graphite composites
- Summary
Company Profile

• 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

• 47 production sites worldwide

• Service network covering more than 100 countries

• Sales of ~€ 1.7 bn in 2012

• Head office in Wiesbaden/Germany

• Approx. 6,700 employees worldwide

• Listed on MDAX
Light Weight & Energy Systems – SGL’s Contribution to E-Mobility

Light Weight with Carbon Fiber Composites

C-Fiber  CF-Fabric  Source: BMW

Plus

Energy Systems – Li-Ion Batteries & Fuel Cells

C-coating  graphite  Anode graphite

10 µm

Gas Diffusion Layer

Electro-Mobility
Joint Forces for Best Solutions

More than 10 Years Cooperation

World Largest Anode Production & Leading Edge Technology Know How
Anode Material Requirements
Success of Carbon Based Anodes

Technical Requirements of a good anode material:
- Large reversible capacity
- Small irreversible capacity
- High rate capability
- Safety
- Compatibility with electrolyte and binders

Reason of commercial success of C-based anode:
- Low cost material
- Good cycling stability (SEI, excellent reversible capacity theoretical 372 mAh/g)
- Lightweight
- Electrochemical potential close to metallic Li

LIB anode material world market size
- Carbon based
- LTO
- Artificial graphite
- Natural graphite

Yano Research Institute, 2012
Carbon and Graphite Based Anode Materials
Overview

Graphite
- Natural
  - Spheroidized graphite
- Artificial
  - Mesophase
  - Carbon coated graphite

Amorphous Carbon
- Hard Carbon
- Soft Carbon
  - Si/Sn- carbon composites

Other carbon-based materials like carbon fibers, expanded graphite, graphene, graphite foils
Typical Production Processes

Raw Material

- Raw material
- Heat treatment
- Milling and rounding
- Carbon coating

Order and disorder

XRD: turbostratic disorder, amount of rhombohedral graphite, stacking faults, crystallite dimension

Raman: $R = \frac{I_D}{I_G}$

C-rate, cycling stability, capacity
Graphitization degree is determined via raw material and process temperature.
Lithium Storage in Amorphous Carbons
Disordered Structure

**Amorphous Carbon Structure**
- 'Intercalation' or 'adsorption' of Li$^+$ Ions
- ‘Intercalation’ type
- Adsorption type

**Carbonization temperature <2500°C**
- Only intercalation type used for real applications, typical capacities < 300 mAh/g

**Soft carbon**
- Amorphous phase
- Crystalline phase

**Hard carbon**
Lithium Intercalation into Graphite
Ordered Structure

Crystal hexagonal graphite structure

Li⁺ ‘intercalation’ into the graphite planes

Graphitization temperature
>2500°C

Theoretical capacity 372 mAh/g
Typical capacity 330-360 mAh/g
Typical Production Process
Milling and Rounding

- **Raw material**
- **Heat treatment**
- **Milling and rounding**
- **Carbon coating**

- Graphite with medium particle size
  - Medium D$_{50}$ value (i.e. 20 µm)
  - very small D$_{50}$ value (i.e. 10 µm)

- Graphite with very small particle size
  - d$_{50}$ between 10 and 30 µm
  - d$_{90}$ < 70 µm
  - avoid large amount of fine particle fraction

Graphite with medium particle size

Graphite with very small particle size

Particle size distribution and shape

- Specific Capacity in mAh/g
- Log (Dis.-)/Charging Time

- Consumer
- EV
- HEV

BROAD BASE. BEST SOLUTIONS.
Typical Production Process
Carbon Coating

- Raw material
- Heat treatment
- Milling and rounding
- Carbon coating

Surface Area
BET specific surface area and active surface area

Irreversible capacity, rate capability

Source: Hitachi Chemicals
From Process to Properties
Process Overview

Materials and Tools

Raw materials
• Coke base

Pre-treatment
• Grinding and crushing

Graphitisation process
• Procedure / Furnace
• 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
## Anode Material for Automotive Application
### Comparison of Different Material

<table>
<thead>
<tr>
<th>Material</th>
<th>Item</th>
<th>Energy</th>
<th>Life</th>
<th>Power</th>
<th>Safety</th>
<th>Cost</th>
<th>BPEV</th>
<th>HEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial graphite (MAG)</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>😊</td>
<td>🌻</td>
</tr>
<tr>
<td>Artificial Graphite (Low Cost)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>😊</td>
<td>😊</td>
</tr>
<tr>
<td>Natural Graphite (w/ coating)</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>😊</td>
<td>😊</td>
</tr>
<tr>
<td>Meso carbon</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>😊</td>
<td>😊</td>
</tr>
<tr>
<td>Hard Carbon (Amorphous)</td>
<td>- -</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>😊</td>
<td>😊</td>
</tr>
<tr>
<td>Soft Carbon (Amorphous)</td>
<td>- -</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>😊</td>
<td>😊</td>
</tr>
</tbody>
</table>

Source Hitachi
Carbon-Silicon Composites

Need for high capacity anodes to improve the overall cell capacity

Silicon-Carbon Composites are promising next generation anode materials

Highest benefit to cell capacity is for anode material up to 1000 mAh/g with the actual cathodes → higher than 80% carbon

Extreme volume expansion during lithiation/delithiation of about 300% (graphite 6-10%) leads to cracking of Si particles and electrode, resulting in Poor Cycling stability.

Advantage of Carbon-Silicon Composite Anodes:

C/Si-Composites: Silicon nanoparticles within a carbon matrix

• Compensate the volume expansions of silicon
• Good electronic and ionic conductivity
• Protect the silicon from contact with the electrolyte
Graphite anode accounts for over 95% of current anode market (Yano report)

Carbon and Graphite properties can be tailored to meet battery requirements by adapting the raw materials and production processes

Next generation anodes are most likely C-Si based. The carbonaceous material (80C / 20 Si) to guarantee overall electrode performances

To get optimum cell capacity the target anode capacity is <1000 mAh/g. Thus amorphous carbon will be the dominant element in composites

Take away:
Carbon and graphite are the anodes of today, tomorrow and the day after tomorrow!
Thank You for your Attention!

www.sglcarbon.com
heribert.walter@sglcarbon.de