Carbon Materials for Li-Ion Battery: Features and Benefits

Frühjahrstagung des Arbeitskreises Kohlenstoffe
Meitingen, 26. April 2016
Outline

- Introduction of IMERYS
- Introduction of IMERYS Graphite & Carbon
- Electrochemical Cell – Li-Ion Battery
- Carbon black and Graphite conductive additives for the positive electrode
- Specialty Graphites for the negative electrode
- Carbon-based current collector coating
IMERYS Introduction

- **Imerys, the world leader in mineral specialties for industry**
  - Created in **1999** out of the *industrial minerals* activity of **Imetal** (French group)
  - **+16,000** employees
  - **250** industrial sites in **+50** countries
  - **8** main R&D centres - **25** regional laboratories - **400** scientists and technicians
  - 2015 sales ➔ **4,087 M€**
  - **+30** minerals including bentonite, calcium carbonate, feldspar, graphite, kaolin, mica, talc and wollastonite

- **Imerys products, finding applications in everyday life**
  - Automotive, Industrial Equipments
  - Energy
  - Electronics
  - Construction
  - Decorative Materials and Fittings
  - Steelmaking and Metallurgy
  - Agri-Food
  - Paper
  - Packaging
  - Health, Beauty and Care
  - Horticulture, Protection of Flora
IMERYS Graphite & Carbon Introduction: History

- **1908** Officine del Gottardo is founded
- **1917** Synthetic Graphite manufactured for the first time
- **1924** Acquisition of Officine del Gottardo by LONZA Ltd.
- **1982** Willebroek plant (under Erachem group) starts producing Conductive Carbon Black
- **1989** Stratmin Graphite starts mining natural graphite in Canada
- **1994** LONZA G+T is acquired by IMETAL and becomes TIMCAL Ltd
- **1995** TIMCAL America is founded
- **1997** Changzhou TIMCAL Graphite Corp. is established in China
- **1999** IMETAL changes name to IMERYS; TIMCAL and Stratmin are combined into TIMCAL Group
- **2000** TIMCAL Japan KK and TIMCAL Germany are set up
- **2001** TIMCAL Fuji facility opens in Japan
- **2002** Stratmin becomes TIMCAL Canada; Terrebonne plant opens
- **2003** TIMCAL acquires the Carbon Black activities at Willebroek, Belgium
- **2005** TIMCAL representative office in the UK is launched
- **2007** TIMCAL acquires 85% of Baotou Jing Yuan Graphite Co in China
- **2008** TIMCAL celebrates 100 Years of Production in its Swiss plant Bodio
- **2010** TIMCAL representative office in Singapore is launched
- **2014** TIMCAL changes its name to Imerys Graphite & Carbon
- **2015** Imerys Graphite & Carbon opens a R&D Center in Japan
**Main Fields of Application for TIMCAL Carbon Powder-Based Solutions**

- **Alkaline Batteries**
- **Zn-C Batteries**
- **Li - Batteries**
- **Li-ion Batteries**
- **Lead Acid**
- **Fuel Cells**
- **Supercaps**
- **Can Coatings**
- **Friction Materials**
- **Powder Metallurgy & Hard Metals**
- **Carbon Brushes**
- **Foils**
- **Ceramics**
- **Pencils**
- **Catalysts**
- **Synthetic Diamonds**
- **Powders for Lubricants**
- **Conductive Plastics**
- **Conductive Rubbers**
- **Power Cable Compounds**
- **Filled PTFE**
- **Conductive Coatings & Paints**
- **Refractories**
- **Crucibles**
- **Hot Metal Toppings**
IMERYS Graphite & Carbon Introduction

- Manufacturing Plants
Introduction: Li-Ion Battery

Negative Electrode – Anode
- Graphite
- Hard Carbon
- Li$_4$Ti$_5$O$_{12}$ (LTO)
- Silicon
- Tin
- SiO$_x$
- Metal alloys
- …

Positive Electrode – Cathode
- LiCoO$_2$ (LCO, layer)
- LiNi$_x$Mn$_y$Co$_z$O$_2$ (NMC, spinel)
- LiMn$_2$O$_4$ (LMO, spinel)
- LiFePO$_4$ (LFP, olivine)
- …

Electrochemical Cell – Li-Ion Battery

- Li-Ion Battery or Li-Carbon Battery?

Cu current collector

- Electrolyte (in pores)
- Active material
  - Graphite
  - Carbon Black
- Binder

IMERYS Graphite & Carbon products are inside the positive and the negative electrode

Electrolyte (in pores)

- Active material
  - Graphite
  - Carbon Black
- Binder

Current Collector coating

- Electrolyte (in pores)
- Active material
  - Graphite
  - Carbon Black
- Binder
Carbon Conductive additives for the positive electrode

- Influence of conductive Carbon Black on the cycling stability of the positive electrode
  - Conductive Carbon Blacks improve cycling stability and efficient positive material utilisation thanks to setting up a conductive network already at low carbon additive concentration
Carbon Conductive additives for the positive electrode

- Evaluating conductive additives for positive Li-ion battery electrode
  - Carbon Black Super C65: percolation threshold at low additive amount
  - Graphite KS 6 L: compressibility and low ultimate resistivity (at high additive amounts)

\[\text{Electrical Resistivity} \left[\Omega \text{ cm}\right]\]

\[\text{Carbon Amount [wt.\%] LiCoO}_2\]

\[\text{Carbon Additive Amount [wt.\%] LiFePO}_4\]
Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - Combine the low percolation threshold of conducting Carbon Black with the good compressibility of Graphite.

Super C65 : KS6L ratios between 1:1 and 1:3 leads to **low resistivity & high density**
Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - SuperC65 : KS 6 L blend vs SuperC65 alone: same specific charge because of the similar electrical resistivity of the electrodes, but **improved charge density** when using graphite because of its greater compressibility compared to carbon black

![Charge density vs cycles](image1.png)

- Increased electrode density
  - KS 6 L acts as a compaction aid

![Specific charge vs cycles](image2.png)

- Similar electrode resistivity
Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - The adhesion decreases with increasing amount of conductive additive due to the contribution of the conductive additive to binder consumption
  - Thanks to its lower surface area compared to carbon black, graphite helps maintaining sufficient adhesion

- T-peel test (180°C)
  - Sample dimensions: 3.5 x 7.15 cm
  - PVDF binder: 5 wt.%

<table>
<thead>
<tr>
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<th>BET SSA [m²/g]</th>
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<tbody>
<tr>
<td>Super C45</td>
<td>45</td>
</tr>
<tr>
<td>Super C65</td>
<td>65</td>
</tr>
<tr>
<td>KS 6 L</td>
<td>20</td>
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Graphite and Carbon Black complementary properties in the positive electrode

- Thanks to its lower surface area compared to carbon black, graphite helps favorable rheology for electrode processing.

![Rheology measurement: cone-plate](image)

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94 wt.% LiCoO2
3 wt.% carbon black
3 wt.% PVDF
in NMP
Specialty Graphites for the Negative electrode

- Increased electrode density with Specialty Graphites Additives
  - Addition of 2 – 8% **C-NERGY™ SFG 15 L** significantly increases density of artificial graphite based negative electrodes
  - Optimal amount of SFG 15 L depends on hardness of active material and targeted electrode density

![Graph showing electrode density vs. press force](image_url)
Specialty Graphites for the Negative electrode

- Specialty Graphites Additives also work as an active material in the negative electrode
  - Very high reversible capacity: close to 372 Ah/kg, theoretical limit
  - Very high electrical conductivity

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<tr>
<td>SFG 6 L</td>
<td>17</td>
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<tr>
<td>SFG 15 L</td>
<td>9</td>
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<tr>
<td>KS 15 L</td>
<td>12</td>
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</tbody>
</table>

- Formulation: (AG + additives) : CMC : SBR = 98 :1 : 1
- Loading : 7.5±0.5 mg/cm²
- Density : 1.6 ±0.05 g/cm³
- Half coin cells vs. Li/Li⁺
- Electrolyte : EC/EMC 1:3(v/v), 1M LiPF₆
- Test condition:
  - Charge : (CC/CV) 0.1C/5mV, 0.005C cut
  - Reversible : (CC) 0.1C/1.5V
Specialty Graphites for the Negative electrode

- Specialty Graphites Additives improves Cycling Stability
  - Improved cycling stability is achieved by adding 2 – 8 % C-NERGY™ SFG 15 L to active material, independent if artificial or coated natural graphite
  - Improvement in cycling stability has to be balanced vs increase in BET surface area and binder absorption due to SFG 15 L addition

- Half cells vs. Li/Li⁺
- Electrolyte: EC/EMC 1:3 (v/v), 1 M LiPF₆
- SBR/CMC binder
- Cycling program:
  1st cycle 20 mA/g charge/discharge, then 50 mA/g charge (CCCV),
  3 C discharge (CCCV)
Carbon-based current collector coating

- Water-based Ready-to-use dispersion of very fine carbon powder
  - Allows for coating of a homogeneous carbon layer of ca. 1 µm on the current collector
  - Very little contribution to inactive volume and weight
  - Dramatically reduced impedance in positive electrodes, leading to improved high rate performance of the cell
Summary

- **C-NERGY™** conductive Carbon Blacks and Graphites have **complementary properties** for Li-ion battery **cathodes**
  - Conductive Carbon Blacks lead to lower percolation threshold enabling higher specific charge
  - Graphite additives help to improve the reversible charge density and the electrode adhesion
  - Graphite additives help to improve the manufacturing of electrode due to favorable rheology

- **C-NERGY™** L-grades **specialty graphites** are very efficient as **active additive** for Li-ion battery **anodes** thanks to
  - improved cycling stability and battery lifetime
  - increased electrode density
  - reduced volume resistivity

- **C-NERGY™** water-based ready-to-use dispersions for **current collector**
  - Dramatically reduced impedance in positive electrodes, leading to improved high rate performance of the cell
My special thanks to:

T. Hiroyuki, F. Mornaghini, P. Ulmann