Technical Information B-TI 2

Additives for Electrical Energy Storage & Conversion
Additives for Electrical Energy Storage & Conversion

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BYK Products for Electrical Energy Storage & Conversion

Improving the Production Process and Product Performance
Our additives provide innovative solutions to influence the behavior of materials at the interface. Some of the key steps during the production of Li-ion batteries, supercapacitors and fuel cells are relying on the dispersion of particles, the control over interfaces, as well as the accurate coating of substrates. Therefore, BYK additives can create value for our customers in the area of electrical energy storage and conversion. In the field of electrochemical energy storage & conversion we provide solutions for the following components/systems:

BYK Additives for Components and Systems in Electrochemical Energy Storage & Conversion

- **Li-Ion Batteries**
  - Additives for Electrodes
  - Additives for Separator Coating

- **Supercapacitors**
  - Additives for Electrodes

- **Fuel Cells**
  - Additives for PEMFC
  - Additives for SOFC
Technical Service – Close to our Customers

The focus of our activities in electrochemical energy storage & conversion is lying on Li-ion batteries. In order to be close to our customers in Asia we have opened our electrochemical laboratory in Amagasaki, Japan. The laboratory serves as BYK’s technology development and support center for additives used in electrochemical energy storage & conversion systems.

Significant investment has been made to be outfitted with state-of-the-art equipment for:

- Electrode slurry preparation
- Characterization of electrode slurries and coatings
- Coating of electrodes or separators
- Li-ion cell tests

BYK Laboratories in Asia

![Map showing BYK laboratories in Asia](figure 2)
BYK delivers additives for the manufacturing of **electrodes** and **ceramic coated separators** of Li-ion cells. Although our substances are only added in small quantities, they strongly contribute to lowering the production costs as well as improving the product properties and safety of the cells.

### Where to Find BYK Additives in Li-Ion Batteries?

- **BYK additives for electrodes**
  - Wetting & dispersing additives
  - LAPONITE-RD

- **BYK additives for ceramic-coated separators**
  - Surface additives
  - Defoamers
  - Wetting & dispersing additives
Additives for Electrodes – Wetting & Dispersing Additives

Dispersion of Conductive Carbon Structures
In battery electrodes, conductive carbon structures (e.g. carbon black, carbon nanotubes, or graphene) are added to form a composite structure with the active material and binder in order to assure a high electronic conductivity. Carbon black forms agglomerates in its powder form (figure 4) and during the electrode slurry preparation it needs to be dispersed into smaller aggregates as otherwise the volume resistivity of an electrode coating including active material and binder is high (state I, figure 5). The resistivity is reaching a minimum when the carbon black agglomerates are dispersed into aggregates which are homogeneously distributed in the electrode and form an interconnected network (state II, figure 5). Further grinding into separated aggregates, however, will result in an increasing electrode resistivity, due to the loss of long-range conductive pathways in the electrode (state III, figure 5).

Scheme Representing Correlation Between Volume Resistivity of Electrode Coatings and Aggregate Size of Carbon Blacks

![Diagram showing the correlation between carbon black aggregate size and volume resistivity of electrode coatings.](figure 4)

![Diagram showing the scheme representing the correlation between volume resistivity of electrode coatings and aggregate size of carbon blacks.](figure 5)
Polymeric Wetting & Dispersing Additives

Wetting & dispersing additives combine two functionalities in one polymeric structure (figure 6). Surface-affinic functional groups of the polymers adsorb on the particle surface whereas solvent affinic parts are interacting with the solvent and binder. Thereby they accelerate the incorporation of solid particles into a liquid media and stabilize dispersed particles from re-agglomeration. The proper spacing between the particles is maintained by electrostatic repulsion and/or steric hindrance in order to assure storage stability of slurries (figure 7).

Stabilization Mechanisms of Wetting & Dispersing Additives
Additives for Electrodes – Wetting & Dispersing Additives

Wetting & Dispersing Additives for Pastes of Conductive Carbon Particles

Why Use Dispersing Additives in Electrodes?
Wetting & dispersing additives reduce the viscosity of dispersions significantly. As an example, figure 8 depicts a 9% dispersion of a Ketjen Black in N-Methyl-2-pyrrolidone (NMP) without and with additive. The sample without is a sticky paste, whereas the sample including 10% of additive on the Ketjen Black is a low viscous fluid which shows excellent storage stability. Wetting & dispersing additives are therefore used to prepare concentrates of conductive carbon structures. In electrode slurries including active material and binder they also effectively reduce the viscosity so that higher solid contents are accessible. Furthermore, due to their stabilizing effect the addition of wetting & dispersing additives drastically shorten the grinding time (figure 9).

Figure 10 depicts the cross-sectional SEM-images of LiFePO₄ (LFP) cathodes prepared without and with additive. In case of the sample including additive, the targeted carbon black aggregate size is already reached when the sample without additive still shows carbon black agglomerates and poor conductivity.

The combination of higher solid contents of electrode slurries and reduced grinding time lowers energy and labour cost during electrode production. BYK offers wetting & dispersing additives for water- and solvent-borne processes.

9% Ketjen Black in NMP

Without wetting & dispersing additive

With wetting & dispersing additive

Scheme Representing the Influence of Wetting & Dispersing Additives on Grinding Time

Targeted aggregate size

Shortened grinding time

Without wetting & dispersing additive

With wetting & dispersing additive

Grinding time
**Electrochemical Performance**

The additives can be used in electrodes without any negative effect on cycle-life or C-rate performance. Figure 11 shows the cycle-life and C-rate performance of graphite/LFP-cells. Polymeric wetting & dispersing additives can further partially replace the conventional binder so that the energy density keeps constant. Wetting & dispersing additive (0.75 wt. %) partially substituted the Polyvinylidene Fluoride (PVDF) and was used for preparation of the LFP-cathode (90 wt. % LFP, 5 wt. % carbon, 5 wt. % PVDF/ wetting & dispersing additive).

**Cross-sectional SEM-images of LFP-cathodes**

Without wetting & dispersing additive  
With wetting & dispersing additive  

**Cycle-life and C-rate Performance of Graphite/LFP-cells – The Wetting & Dispersing Additive was Used in Cathode**

<table>
<thead>
<tr>
<th>Capacity [Ah]</th>
<th>C-Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>0.08</td>
<td>3</td>
</tr>
<tr>
<td>0.06</td>
<td>2</td>
</tr>
<tr>
<td>0.04</td>
<td>1</td>
</tr>
<tr>
<td>0.02</td>
<td>0</td>
</tr>
</tbody>
</table>

Graphite/LFP full cells:
- 1st cycle formation at 0.1C
- 50 cycles at 1C
- Rate capability (at 2C, 3C, 4C and 5C)
- Additional 50 cycles at 1C
- CC+CV charge
- CC+CV discharge

**Wetting & Dispersing Additives**

- Used for pastes of conductive carbon structures (carbon black, CNTs, etc.)
- Help to increase slurry solid content
- Shorten grinding time
- Reduce energy and labour cost
Additives for Electrodes – LAPONITE-RD

What is LAPONITE-RD?
LAPONITE-RD is a synthetic phyllosilicate of high purity that is delivered as white powder. LAPONITE has a layer structure which takes the form of nanosized disc-shaped crystals (figure 12).

In delivery form, the crystals are arranged into stacks which are held together electrostatically by the sharing of sodium ions in the interlayer region between adjacent crystals. A dilute dispersion of LAPONITE in deionized water may result in a low viscosity dispersion of non-interacting crystals for long periods of time.

Synergistic Effect with Organic Thickening Agents
When used in combination with polymer thickeners, the charged LAPONITE particles develop electrostatic associations with oppositely charged sections on the molecules of polymer co-thickener (figure 13). This additional bonding mechanism of particle to polymer interactions results in synergistic effects with carboxymethylcellulose (CMC) which enables the formulation of aqueous electrode slurries with high stability (figure 13). Furthermore, the interaction remains active in the dried electrode coating and results in improved adhesion strength of electrode coatings (figure 16).

Representation of a Single LAPONITE-RD Crystal – Product as Powder and Dispersed in H2O (From Left to Right)

Synergistic Effect with CMC

Composition of Graphite Anode Slurries

<table>
<thead>
<tr>
<th></th>
<th>CMC</th>
<th>CMC/LAPONITE-RD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC</td>
<td>1.5 g</td>
<td>1.2 g</td>
</tr>
<tr>
<td>LAPONITE-RD</td>
<td>-</td>
<td>0.3 g</td>
</tr>
<tr>
<td>H2O</td>
<td>100 g</td>
<td>100 g</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>1.7 g</td>
<td>1.7 g</td>
</tr>
<tr>
<td>Graphite</td>
<td>94.5 g</td>
<td>94.5 g</td>
</tr>
<tr>
<td>SBR</td>
<td>2.3 g</td>
<td>2.3 g</td>
</tr>
<tr>
<td>Solid content (%)</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>
Synergistic Effect with CMC Results in High Storage Stability

Synergistic Effect with CMC Results in Improved Adhesion Strength

LAPONITE-RD as an Additive in Electrodes

LAPONITE-RD can be used in aqueous electrode coating formulations in combination with conventional organic binders such as carboxymethylcellulose (CMC), poly acrylic acid (PAA) and styrene butadiene rubber (SBR).

Replacement of 20% of CMC by LAPONITE-RD in graphite anode slurries (figure 14), which corresponds to 0.3% in the coating, can lead to distinct improvements of cycle-life as shown in figure 17.

Furthermore, in second generation anodes with silicon, the expansion of the active material during lithiation causes severe mechanical stress to the coating. The reinforcement of binder with LAPONITE-RD has proven to improve the cycle-life of Si-anodes (figure 19).

Capacity Retention of Graphite-anodes Formulated with and without LAPONITE-RD

Properties of LAPONITE-RD

- High purity
- Improved slurry stability
- Improved adhesion strength
- Improved electrode wettability
- Improved cycle life

Anode loading: 2.5 mAh cm², Cathode: NCM-111 coins from Custom Cells Itzehoe
A/C-ratio: 1.1, CCCV/CC: 1C (0.1C cut-off for CV), 3–4.3 V, room temperature
Additives for Electrodes – LAPONITE-RD

Reinforcement of Binder Due to LAPONITE-Polymer Interaction

![Diagram showing reinforcement of binder due to LAPONITE-polymer interaction.](image)

Capacity Retention of Si-C/NCM-cells with Anodes of Following Composition

![Graph showing capacity retention of Si-C/NCM-111.](image)

- **CMC/LAPONITE-RD**
- **CMC**

Anode loading: 2.6 mAh cm⁻², Cathode: NCM-coins from Custom Cells Itzehoe
A/C-ratio: 1:1, CCCV/CC: C/2 (C/20 cut-off for CV), 3–4.2 V, room temperature
CMC/LAPONITE-RD: Si-C: 87 %, Graphene: 5 %, CMC: 3.4 %, LAPONITE-RD: 0.6 %, SBR: 4 %
CMC: Si-C: 87 %, Graphene: 5 %, CMC: 4 %, SBR: 4 %
Additives for Ceramic-coated Separators

Product Groups Applied in Separator Coating
Polymer separators or electrodes are coated with a thin layer of ceramic particles in order to improve the safety of Li-ion cells. BYK supplies additives that work on the different interfaces in order to improve the production process and properties of the coating. As shown in figure 20, surface additives work at the ceramic coating-separator-interface, defoamers at the air-dispersion medium-interface and wetting & dispersing additives at the ceramic particle-dispersion medium-interface.

Surface Additives
These additives can be applied in order to improve the wetting of hydrophobic surfaces with aqueous ceramic slurries, the levelling of the thin coatings, and to adjust the surface energy of the coating in order to provide good wetting with the electrolyte. The combination of a non-polar polydimethylsiloxane and a hydrophilic polyether group in silicone surfactants (figure 18) significantly reduces the surface tension of aqueous slurries. This improves the coating speed and adhesion of the coating (figure 22, 23 and 24).

In addition to silicone surfactants, BYK offers silicone-free wetting agents that are based on alcohol alkoxylates.

Product Groups Applied in Separator Coatings – Working at the Interfaces

Surface additives
Defoamers
Wetting & dispersing additives

Structure of a Silicone Surfactant

Improved Wetting of an Aqueous Ceramic Coating Slurry on a PP-separator Due to the Addition of a Wetting Agent

Dewetting
Partial dewetting
Homogeneous wetting
Additives for Ceramic Coated Separators

Defoamers
The dispersion process of ceramic particles is often accompanied by the formation and stabilization of foam (figure 25). Prior to coating, defoaming of the ceramic dispersion is required to ensure a defect-free coating without pinhole formation due to encapsulated foam bubbles.

BYK supplies different types of defoamers (e.g. mineral oil defoamers, silicone defoamers, and silicone-free polymer defoamers) that help to minimize foam formation and improve the defoaming process.

Influence of Wetting Agent on Adhesion Strength

![Figure 23: Improved adhesion strength with different wetting agents.](image)

<table>
<thead>
<tr>
<th>Wetting agent</th>
<th>0.3%</th>
<th>0.6%</th>
<th>0.9%</th>
<th>1.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetting agent</td>
<td>Improved adhesion strength</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Influence of Wetting Agent – Composition of Separator Coating Slurries

![Figure 24: Composition of separator coating slurries.](image)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boehmite</td>
<td>60.00 %</td>
<td>60.00 %</td>
<td>60.00 %</td>
<td>60.00 %</td>
</tr>
<tr>
<td>Water</td>
<td>36.90 %</td>
<td>36.60 %</td>
<td>36.30 %</td>
<td>36.00 %</td>
</tr>
<tr>
<td>Dispersant</td>
<td>1 %</td>
<td>1 %</td>
<td>1 %</td>
<td>1 %</td>
</tr>
<tr>
<td>Binder</td>
<td>1.60 %</td>
<td>1.60 %</td>
<td>1.60 %</td>
<td>1.60 %</td>
</tr>
<tr>
<td>Defoamer</td>
<td>0.20 %</td>
<td>0.20 %</td>
<td>0.20 %</td>
<td>0.20 %</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>0.30 %</td>
<td>0.60 %</td>
<td>0.90 %</td>
<td>1.20 %</td>
</tr>
</tbody>
</table>

Defoaming of Ceramic Slurries

![Figure 25: Comparison of ceramic slurries with and without defoamer.](image)

Without defoamer
With defoamer
Wetting & Dispersing Additives
BYK's polymeric wetting & dispersing additives result in a fine and homogeneous distribution of solid particles in liquid media and ensure the long-term stability of such systems.

Dispersing additives adsorb onto the particle surface and therefore maintain proper particle spacing through electrostatic repulsion and/or steric hindrance, thus reducing the tendency towards agglomeration. In some systems, a connection between the dispersed particles can be advantageous, e.g. to prevent sedimentation of the particles. Controlled flocculating wetting & dispersing additives can build up a 3D network in dispersions to prevent particle sedimentation (figure 26 and figure 27). Linking particles with organic molecules may also increase the mechanical flexibility of the ceramic coating.

Ceramic Slurries with Different Types of Wetting & Dispersing Additives

Controlled Flocculation

Controlled flocculating additive  Deflocculating additive  Ammonium polyacrylate

figure 26

figure 27
For more information about our additives and instruments, as well as our additive sample orders please visit:

www.byk.com

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