Products for batteries

Industry information 2244

Evonik. Power to create.

Contents

1. Introduction

The world of rechargeable batteries is changing. For the last decades, lead acid starter batteries have been the most prominent type of battery on the market. But since the greenhouse effect and global warming are regarded as global threats and since energy costs are increasing significantly, scientists and technicians are worldwide looking for new energy concepts. Battery technology plays an important role in solving the current problems and in making energy available in a better way.

Renewable energy sources, like wind and solar energy, are becoming more and more important and the necessity for efficient intermediate storage is increasing. This can be solved, for example, by lead acid gel batteries or lithium-ion batteries (Li-ion).

New high-voltage and high-power Li-ion batteries also play an important role for new concepts for automotive drive trains. Hybrid electric vehicles (HEV) as well as full electric vehicles (EV) need these new battery technologies, which are currently being developed intensively.

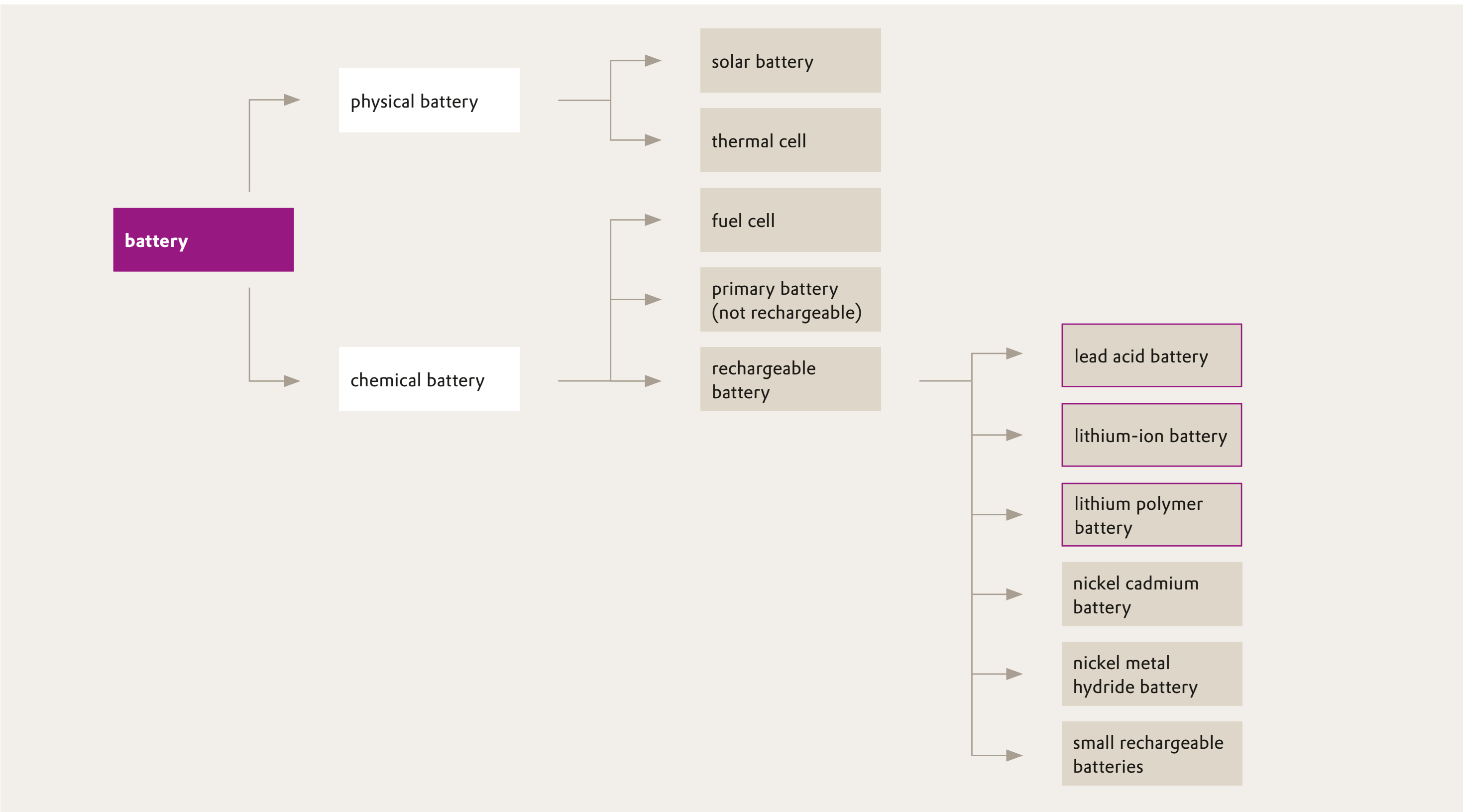
But also the new bike generation (e-bikes) needs an efficient energy source: AGM (Absorbent Glass Mat), gel or Li-ion batteries.

These are just a few examples to demonstrate the growing demand for new materials and technologies for efficient and environmentally friendly batteries. Evonik Industries, as one of the most important chemical suppliers to the battery industry, provides many highly sophisticated solutions for current and future battery systems.

Precipitated silica and fumed alumina for separators for lead acid or Li-ion batteries, fumed silica for gel batteries, fumed titania for anodes of Li-ion batteries, and conductive carbon blacks for all types of electrodes – these are just a few examples from Evonik's extensive portfolio for the battery industry. Ask us, challenge us – we will find the right solution for your application. Our applied technology experts will provide optimum solutions for your advanced battery technology.

Description of different battery types
Batteries can be divided into physical and chemical batteries. Physical batteries are solar batteries and thermal cells, while chemical batteries include fuel cells, non-rechargeable batteries (often referred to as primary batteries) and rechargeable batteries (secondary batteries).

There are various types of rechargeable batteries:
- lead acid batteries
- nickel cadmium batteries
- nickel metal hydride batteries
- lithium-ion batteries



Lead acid batteries are constructed of
a) electrodes (anode / cathode) and
b) separators

which are surrounded by
c) electrolyte (sulfuric acid).

Evonik products are present in all these battery components

	Carbon Black	AEROSIL®	SIPERNAT®
Electrode	●		
Separator	●		●
Electrolyte (gel)		●	

Lithium-ion (Li-ion) batteries consist of
- cathode-active material and anode-active material
- (cathode and anode collector)
- separator
- electrolyte

Evonik products are present in the following battery components

	Carbon Black	AEROSIL® / AEROXIDE®	Dynasylan®
Electrode	●		
Active material		●	
Separator	●	●	●
Electrolyte		●	●

2. Electrolyte

2.1 AEROSIL® and AERODISP® for lead acid gel batteries

Nowadays, in our modern lives, many power sources and energy storage systems are needed for a huge variety of applications.

Lead acid batteries are one of the oldest types of rechargeable batteries. Even though their energy-to-weight ratio is low, the ability of the cells to supply a high surge current results in a high power-to-weight ratio.

Due to the relatively low costs for lead acid batteries, they are still gaining market shares where new battery systems are either too expensive or too demanding as regards maintenance.

Lead acid batteries are still the most cost effective battery type for the following applications:
- starter batteries for automotive engines
- traction batteries for golf caddies, fork-lifts, wheelchairs, cleaning machines
- stationary batteries as power back-up for telecommunication and data centers, power plants, hospitals, renewable energy systems, emergency lighting, green energy plants

History of lead acid gel batteries

Conventional flooded cell lead acid batteries are usually not secure regarding acid containment and should be used only in an upright position in order to prevent leaking or spilling of the electrolyte (sulfuric acid), which is highly corrosive.

In the late fifties, a new class of advanced lead acid battery based on gel technology was introduced.

The gel battery (also known as gel cell) is a type of valve-regulated lead-acid battery (VRLA). In VRLA batteries no water needs to be added during their lifetime and the battery is sealed with valves. The acidic electrolyte is either fixed in the form of a gel or is absorbed in a glass fleece.

The advantages of gel batteries are:

- almost maintenance-free
- spillage-free
- can be used in different positions / no need to be kept upright / operation irrespective of its position
- possibility of high discharge currents
- resistance to vibration, shock, extreme temperatures
- no acid stratification
- deep discharge

Fumed silica is used to gelify the sulfuric acid. The requirements for the gel forming agents are challenging:

- high purity
- chemical stability to sulfuric acid, lead oxide and lead
- thickening and thixotropic behavior
- medium to high surface area

AEROSIL® fumed silica fully meets these demands and provides our customers with the following benefits:

- highly effective thickening
- specific thixotropic behavior
- electrochemically and chemically inert
- stable viscosity
- high purity
- dispersions of AEROSIL® available (AERODISP®)
- prevention of acid stratification

2.2. Dynasylan® for Li-ion batteries

Due to their special properties, organofunctional silanes act as highly efficient surface modifiers, as water and HF scavengers, and as solvents. Furthermore, in combination with lithium salts, they can act as electrolytes for potential use in Li-ion batteries. In addition to increased reliability due to higher thermal stability and the lower risk of hydrogen and oxygen formation, increased durability and a higher number of load cycles can also be expected.

3. Separators

3.1. SIPERNAT®, PRINTEX®, HIBLACK® and AROSPERSE® for PE separators in lead acid batteries

The functional parts of a lead acid battery are the positive and negative electrodes and the separator between them.

The functions of the PE separator are to separate the electrodes to avoid short circuits and consequently, total damage of the battery and, on the other hand, to contribute to the electrical circuit to enable the battery to provide electrical energy.

To fulfill these contradicting properties, the material of the PE separator consists of non-conducting PE and silica which provides the separator's high porosity. The separator is also highly porous.

Due to the high porosity, sulfuric acid and lead ions can migrate from one electrode to the other and close the electrical circuit. Because of the non-conducting separator the electrodes have no direct contact with each other.

PE separators are used in lead acid batteries, which are used and specifically produced for many purposes, such as starter batteries for cars, stationary batteries in power stations and hospitals, fork lift trucks, wheelchairs, submarines, etc.

PE separators vary regarding design (thickness, ribs), porosity and composition of ingredients so as to fulfill specific requirements.

The main raw materials are PE, silica and oil. Selected additives are used, such as lubricants, wetting agents, carbon black, etc. carbon blacks like PRINTEX®, HIBLACK®, AROSPERSE® are used as colorants for PE separators.

Benefits of the PE separator compared to other materials are: puncture resistance, flexibility, ability to be folded and sealed, oxidation resistance and low acid displacement. These properties account for the replacement of PVC separators, for example.

The function of the silica is to make the separator porous. This is achieved by mixing the raw materials and by extruding the mixture to form a sheet. The oil is extracted from the sheet and the sheet becomes porous. The silica remains in the porous sheet and makes the surface of the PE separator hydrophilic and wettable for sulfuric acid – allowing the sulfuric acid and the lead-ions to pass through the separator.

Silica for battery separators needs to be tailor-made to achieve the following properties: low electrical resistance of the separator material, good processing properties for the manufacturing process, specific morphology to control the separator shrinkage behavior during manufacturing and in service, and specific requirements for purity and trace elements.

The Evonik grades SIPERNAT® 325 C, SIPERNAT® 325 AP, SIPERNAT® BG-2 and possibly new grades fulfill these market requirements excellently.

3.2. Separators for Li-ion batteries (AEROSIL®, AEROXIDE®)

Like in lead acid batteries, the basic function of the separator is to prevent physical contact of the anode and the cathode while allowing lithium-ions to move between the electrodes.

The separator itself is made of electrically insulating materials that have been engineered to have pores that allow lithium-ions to move back and forth between the battery's electrodes during the battery's charging and discharging processes. The separator itself does not participate in the chemical reaction.

Various separator types are known for Li-ion batteries, including:

1. Microporous polymer membranes (wet/dry process)
2. Supported liquid membranes/composite polymer electrolytes
3. Inorganic composite membranes (ceramic separators)

The performance of the battery, including energy and power density, cycle life and safety is affected by the separator.

Important requirements for Li-ion separators

Parameter	Goal
Thickness	< 25 µm
Porosity	> 40 %
Pore size	< 1 µm
Electrical resistance	2 ohms cm^3
Wettability	Complete wetting by typical battery electrolytes
Mechanical and chemical strength	
Dimensional stability	

Inorganic fillers like AEROSIL® and ceramic layers with AEROXIDE® greatly influence the characteristics and properties of the polymer electrolyte:

- Increase porosity
- Enhance mechanical stability
- Improve ion conductivity
- Decrease activation energy for ion transport
- Improve thermal stability

The basis of all microporous membranes is a thermoplastic material, such as polyolefin that prevents short circuiting by separating the electrodes and blocking ionic conductivity in case of thermal runaway.

These microporous membranes can be coated with a gel-forming polymer (e. g. PVDF) for use with lithium polymer batteries or with a ceramic layer for advanced protection against dendrite growth and enhance the thermal stability.

The inorganic filler can either be integrated into the thermoplastic material or into a separate layer that is coated, laminated or coextruded on top of the thermoplastic material, or infiltrated / soaked into the pores of the porous membrane.

Carbon black in Li-ion separators
For separators with advanced behavior in case of sudden thermal runaway, conductive carbon black is added to enhance electrical and thermal conductivity of the membrane.

4. Electrodes

Apart from lead acid batteries, carbon black is also used in Li-ion and lithium polymer batteries.

While in lead acid batteries the carbon black is used only for the anode, in lithium-based batteries the carbon black is used for both electrodes.

4.1. Electrodes for lead acid batteries (Lamp Black, PRINTEX®, HIBLACK®, DERUSSOL®)

Carbon black is one component in the expander mass spread onto the anode grid. In general, the expander mass is formulated from the following materials:
a. lead sponge / lead sulfate
b. barium sulfate
c. organic (lignin sulfonate)
d. carbon black
e. others

Sulfation of the negative electrode of lead acid batteries causes loss of capacity especially if the battery is left partially charged. This is attributed to large lead sulfate crystals that have formed in re-crystallization processes.

The carbon black has three main functions:
1. to improve conductivity
2. to reduce pore radii
3. to add color for better differentiation of anode and cathode

Improved conductivity facilitates electron transport and reduced pore radii limits crystal growth.

4.2. Electrodes for Li-ion batteries (AEROXIDE®, PRINTEX®, HIBLACK®)

4.2.1. Additives (PRINTEX®, HIBLACK®)

In Li-ion batteries, conductive carbon black is added to both electrodes – to the anode and as well as to the cathode. The amount of conductive carbon black added depends on the conductivity of the active material.

In general, the electrodes are formulated from the following materials:
a. active material
b. conductive carbon black
c. binder
d. solvent
e. others (like graphite)

The carbon black has two main functions:
1. to make the active component conductive
2. to act as buffer for the volume change during intercalation / decalation of the Li-ion

4.2.2. Raw material for active mass (AEROXIDE®)

Lithium titanates (e. g.: $Li_4Ti_5O_{12-x}$)

Lithium titanates are used as anode materials besides graphite as a host for the Li ion.

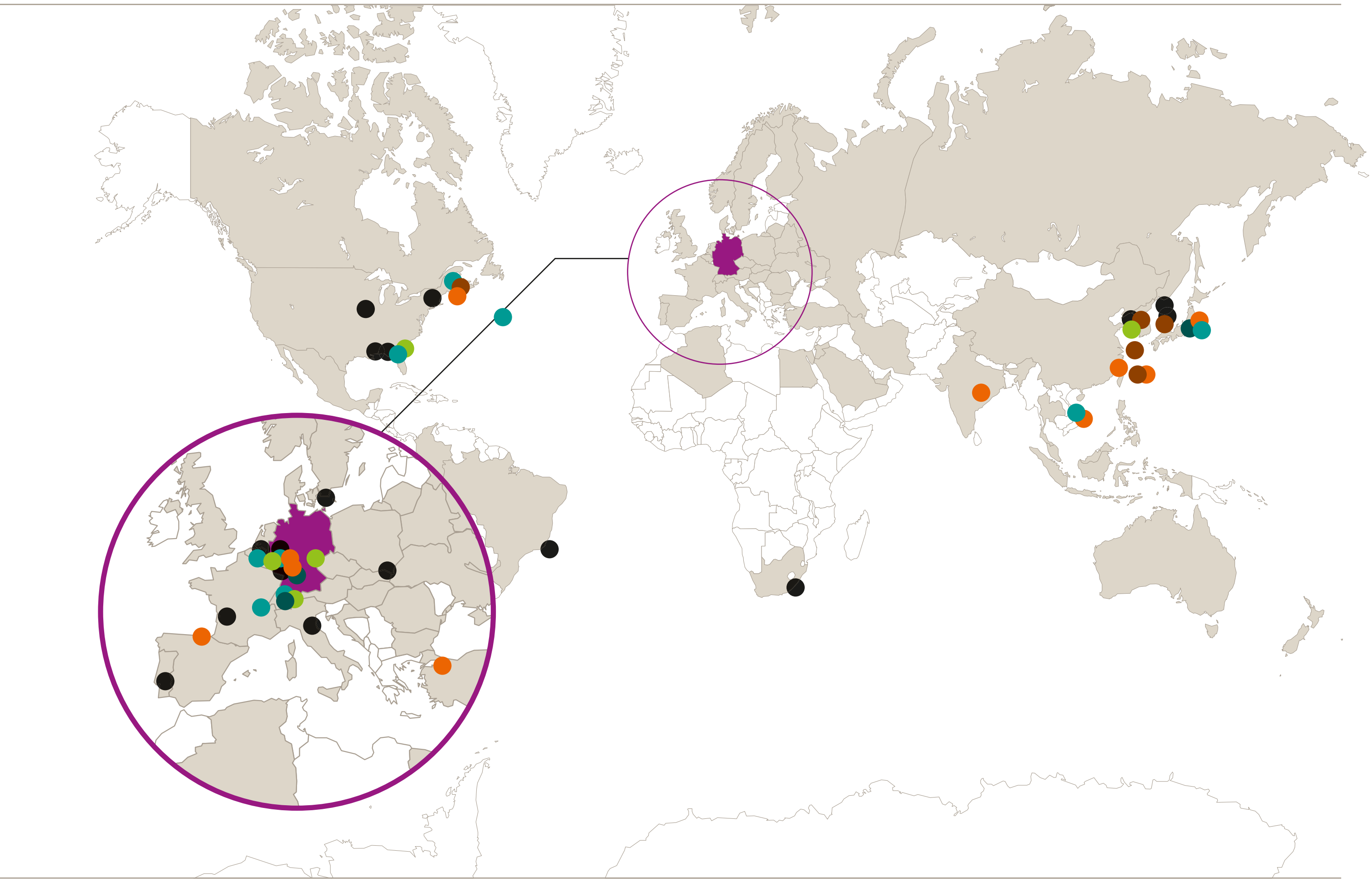
Lithium titanates have the advantage of low volume change during charging / discharging, excellent cycleability and a flat discharge curve (meaning: the electrical potential is not dependent on the lithium concentration).

The very low conductivity can be improved by doping with transition metals or carbon coating.

Different synthesis methods are used, such as

Method	Ti source	Li source (examples)
Sol-gel	$Ti(OR)_4$, $TiCl_4$	Li_2CO_3, Li(COOR), Li(OR)
Electrochemical insertion	TiO_2	$LiClO_4$, $LiAsF_6$, $LiCF_3SO_3$
Solid-state reaction	TiO_2	Li_2CO_3, LiOH, Li_2O
Electrochemical	TiO_2	LiCl (molten)
Hydrothermal	TiO_2	LiOH

5. Global presence



- Carbon Black Plants
- Silane Plants
- Silica and Matting Agent Plants
- AEROSIL® Plants
- Applied Technology Centers
- Research & Developement

6. Literature from Evonik Degussa

- Specialty Silica, Product Overview
- AEROSIL® Product Overview
- What is Carbon Black?, Brochure
- Pigment Blacks, Technical Data
- Industry Brochure Dispersions
- Dynasylan® Product Range
- Technical Bulletin Fine Particles No. 11, Basic Characteristics of AEROSIL®

7. Product recommendation

Lead acid batteries

	Carbon black	AEROSIL®	SIPERNAT®
Electrode	Lamp Black 101 PRINTEX® G AROSPERSE® HIBLACK® DERUSSOL®		
Separator	Colcolor E 20/60 AROSPERSE® HIBLACK® PRINTEX®		SIPERNAT® 325 C SIPERNAT® 325 AP SIPERNAT® BG-2 SIPERNAT® 22 S
Electrolyte (gel)		AEROSIL® 200 AEROSIL® 200 V AEROSIL® 200 VS AERODISP® W 7520N	

Li-ion batteries

	Carbon black	AEROSIL® / AEROXIDE®	Dynasylan®
Electrode	HIBLACK® 40 B2		
Active material		AEROXIDE® TiO_2 P25 AERODISP® W 740 X AERODISP® W 630	
Separator	PRINTEX® L6 HIBLACK® 40 B2	AEROSIL® AEROXIDE® Alu C AEROXIDE® TiO_2 P25 AERODISP® W 740 X AERODISP® W 630	Dynasylan® VTMO
Electrolyte		AEROSIL®	Dynasylan® (aminofunctional silanes for HF)

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