FUMED METAL OXIDES

ENERSIL® SILICA ADDITIVES

FUMED SILICA PRODUCTS FOR LEAD BATTERIES

CABOT

Delivering battery performance through particle science expertise

Cabot Corporation is a global performance materials company and we strive to be our customers' commercial partner of choice. We have been a leading manufacturer of carbon black, fumed silica and other specialty chemicals for more than 135 years, and our global reach enables us to partner closely with customers to meet the highest standards for performance, quality, innovation and service. We are a key player in the provision of high-performance materials and technology to many sectors of the energy industry, including lead and lithium-ion batteries as well as fuel cells. We have 45 manufacturing locations globally, including 21 manufacturing and sales locations in the Asia-Pacific region.

Lead batteries

As demand grows for advanced lead acid batteries in the automotive, industrial and grid storage applications, battery manufacturers are looking for performance materials companies like Cabot to enable the next generation of lead batteries.

Lead batteries are the most mature and recyclable battery technology available today and continue to be the most widely used batteries in energy storage applications. Currently more than 98% of all consumer and commercial vehicles use lead batteries to provide basic start-lighting-ignition (SLI) functionality. Electric scooters, popular in China, are most often powered by lead batteries. Fork lifts, telecom towers and variety of backup and power storage applications use lead batteries as the most convenient and affordable battery solution. Emerging applications, such as micro-hybrid cars and storage for renewables are strongly demanding improved cycleablity and charge acceptance. These existing and emerging applications are pushing lead battery manufacturers to deliver advanced products with increasing levels of performance and durability, while at the same time reducing total system cost. Engineers and designers of advanced lead- batteries can use carbon and silica additives to improve the durability and performance of their products.

Lead battery applications for silica additives

Use of fumed silica additives in valve regulated lead acid (VRLA) gel batteries is well known, delivering significant benefits for cycle life and high temperature durability due to reduced acid stratification and stability of gel structure. Typically, 5-6% of fumed silica is dispersed in the electrolyte and allows formation of a porous gel structure that enables the VRLA oxygen recombination cycle.

In addition to VRLA gel batteries used for back up and stationary energy storage applications, fumed silica additives are also incorporated in the so-called hybrid AGM-gel batteries, where typically <1% of fumed silica dispersed in electrolyte is filled into an AGM battery to extend battery lifetime. Fumed silica can increase the cycle life in deep discharge by increasing acid absorption capacity of the AGM and forming a protective layer between the AGM and electrodes thus minimizing the formation of shorts. Such hybrid batteries are typically used in e-bikes or low speed electric vehicles, especially popular in China.

Figure 1: Lead battery applications

ENERSIL® silica additives

ENERSIL silica additives are designed specifically for use in lead battery applications. There are two types of lead batteries in which they are typically used: traditional gel batteries and hybrid AGM-gel batteries.

Hybrid AGM-gel batteries: ENERSIL 2030 silica additive is one of the most widely used additives in hybrid absorbent glass mat (AGM)-gel batteries since its launch in 2015. Due its unique morphology, it is easier to disperse compared to competitive fumed silica products; its dispersion viscosity remains stable during the battery filling process, providing uniform gel distribution along the AGM separator and at the interface with battery electrodes. ENERSIL 2030 silica additive performs best when the silica is dispersed in water and the dispersion is then mixed with a sulfuric acid electrolyte during manufacturing.

Gel Batteries: The densed version of ENERSIL silica additives, ENERSIL® 2030 KD, enables excellent gel strength when used at relatively low silica loadings versus competitive densed silica products. The ENERSIL 2030 KD product is best suited for direct dispersion of silica in sulfuric acid electrolyte.

For valve-regulated lead-acid (VRLA) battery gel batteries, ENERSIL 2030 KD silica additive is used as a gelling additive to immobilize the electrolyte solution, which reduces risk of spills and minimizes stratification thus improving battery life and safety. The porous structure formed in the gel via the incorporation of fumed silica can facilitate the oxygen recombination cycle and enable higher cycle life versus conventional flooded batteries and less high temperature sensitivity versus AGM-VRLA batteries. Fumed silica is typically incorporated at 4-6% loading in sulfuric electrolyte solutions.

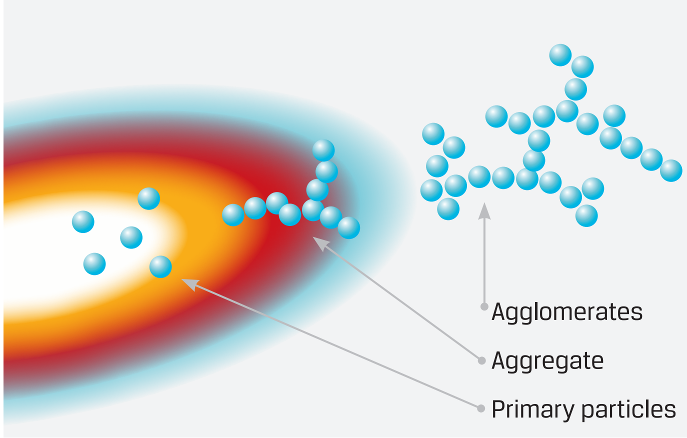
ENERSIL® 2030 silica additive for lead batteries

Morphology and surface chemistry

ENERSIL 2030 fumed silica additive has a surface area of about 200 m^2/g and is manufactured by high temperature hydrolysis of chlorosilanes in a hydrogen/oxygen flame as illustrated in Figure 2. Molten spheres of silica are formed during the flame process. The diameters of the silica spheres are varied by adjusting the process conditions to average size of around 12 nm. These primary particles collide, attach and sinter with one another to form three-dimensional branched chain aggregates with an average size of approximately 160 nm. As the aggregates cool below the fusion temperature of silica, further collisions result in some reversible mechanical entanglement or agglomeration. Further agglomeration takes place in the collection system and during the densification process.

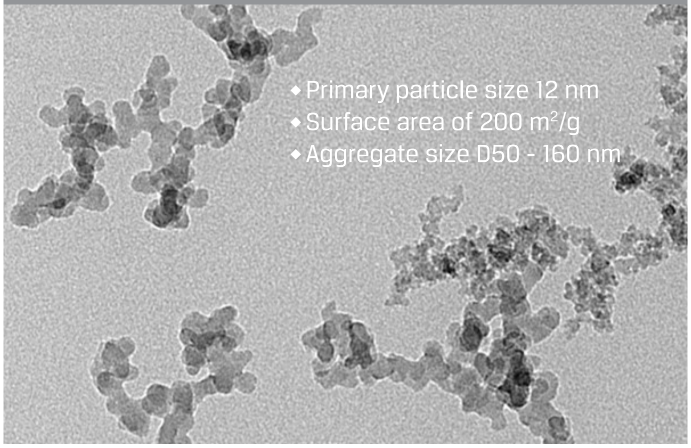
Manufacture of ENERSIL® 2030 silica additive

Figure 2: Manufacture of CAB-O-SIL® Fumed Silicas



$SiCl_4 + 2H_2 + O_2 \rightarrow SiO_2 + 4HCl$

Figure 3: Structure of fumed silica aggregates



Transmission Electron Micrograph 200,000×

The chemical groups on the surface of ENERSIL 2030 fumed silica are predominantly isolated silanol and hydrogen bonded silanol groups, which are both hydrophilic. Surface properties of ENERSIL 2030 fumed silica are tailored to ensure ease of dispersion and gelling characteristics suitable for lead battery applications.

Particle size distribution

Compared to many other fumed silica products on market, ENERSIL 2030 silica additive has a very narrow particle size distribution when dispersed in water with a majority of its aggregate diameters close to 0.160 microns (see Figure 4).

Due to its unique morphology, ENERSIL 2030 silica additive is easier to disperse compared to other silica products and its dispersion viscosity remains stable during the battery filling process, which is essential to achieving manufacturing consistency.

Rheology

For hybrid AGM-gel batteries, the rheological behavior of the water-silica dispersion over time is critical to allow enough gel time before it is used. Cabot conducts regular proxy testing of our ENERSIL 2030 silica additive production lots for dispersion stability characteristics to ensure quality consistency for that application.

In our laboratory, ENERSIL 2030 silica additive is dispersed in deionized (DI) water at 15 % loading to check the viscosity stability, viscosity of the fresh dispersion is recorded, and changes in viscosity are tracked at 24 hours, 48 hours, and 72 hours and after seven days after it is prepared.

As Figure 5 shows, viscosity of the water-based ENERSIL silica dispersion remains relatively stable over time to allow enough shelf life before being filled into batteries.

Product portfolio and key properties

In order to better accommodate the requirements of different types of lead batteries, ENERSIL products will be offered in two forms: ENERSIL 2030 silica additive in fluffy form, best suited for use in water-based dispersions for hybrid AGM-gel batteries, and densified ENERSIL 2030KD silica additive best suited for use in gel batteries.

Figure 4: Particle size distribution of ENERSIL® 2030 silica additive vs. other fumed silica products

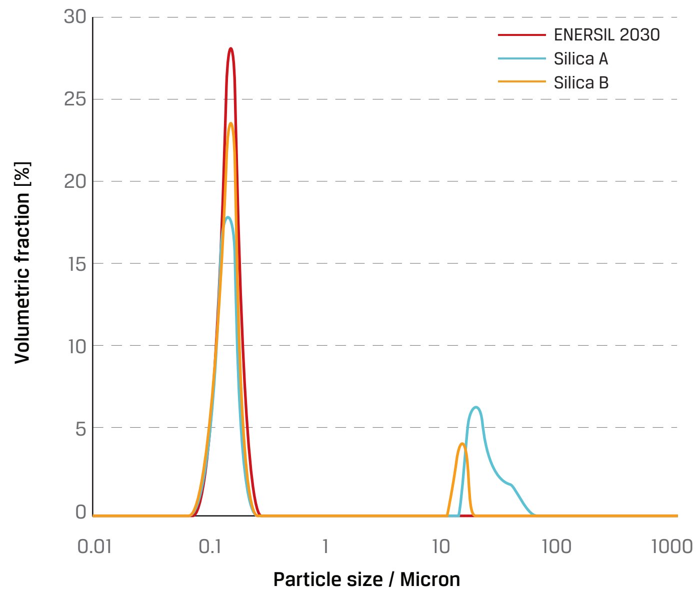


Figure 5: Stability of water-based dispersion

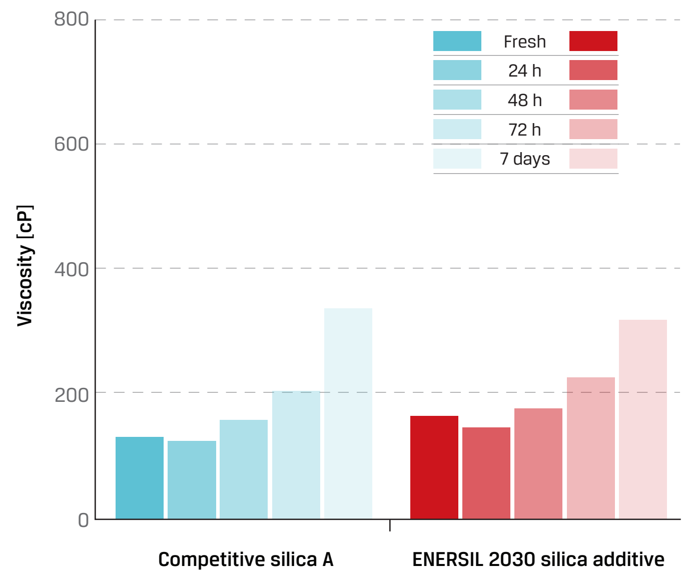


Table 1: Typical properties of ENERSIL fumed silica products

Property	Test method	Unit	ENERSIL 2030	ENERSIL 2030KD
BET nitrogen surface area	ISO 9277	m^2/g	**175-225**	**175-225**
pH	ASTM E70-77	-	**3.8 – 4.3**	**3.8 – 4.3**
325-mesh residue	ASTM D-1514	%	**<0.02%**	**<0.02%**
Tamped Density*	Cabot Test Method	g/L	**40**	**60**

The data in the table above are typical test values intended as guidance only and are not product specifications. Product specifications are available upon request from your Cabot representative.

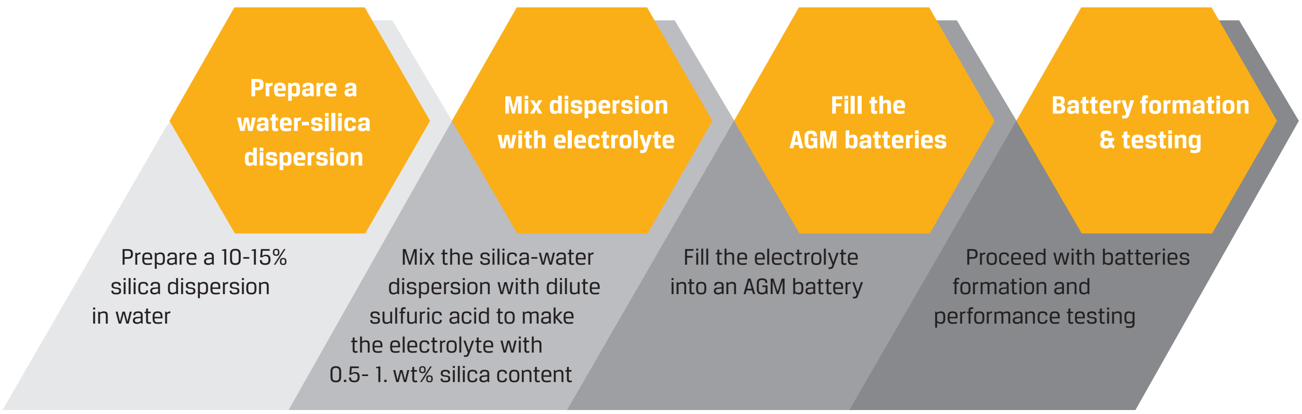
Handling and processing of ENERSIL® products

The below methods and procedures are provided as examples for informational purposes. Different applications may require different battery designs resulting in different handling and processing procedures.

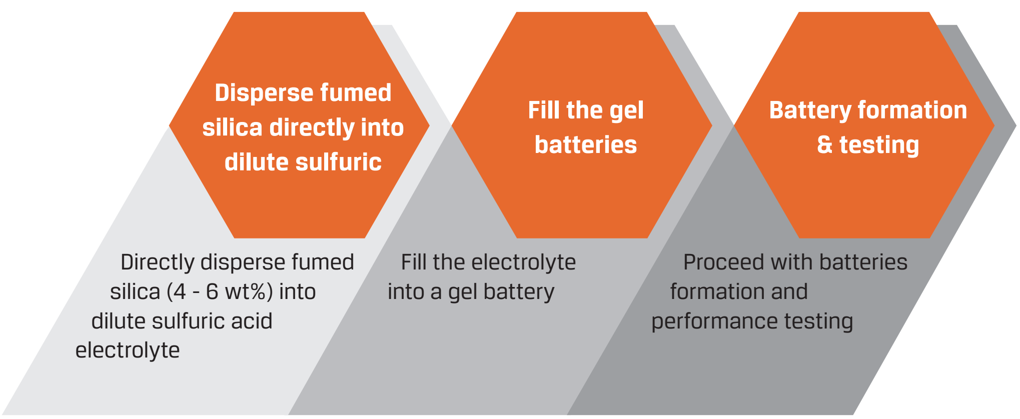
Typically, when making hybrid AGM-gel batteries for e-bikes, tricycles, and low speed electric vehicles, it is common practice to first disperse the ENERSIL 2030 silica additive in water and then mix with the sulfuric acid electrolyte.

Densified ENERSIL 2030KD silica additive can be mixed directly in dilute sulfuric solution (H_2SO_4) to make gel batteries with minimized heat generation. Typically, the sulfuric acid electrolyte used in both cases needs to be chilled to appropriate temperatures to minimize the risk of gelling.

HYBRID AGM-GEL BATTERIES



GEL BATTERIES



As the fumed silica is dispersed into water or sulfuric acid, the agglomerates are broken down to nanometer-sized aggregates. When properly dispersed, the fumed silica aggregates can begin to interact and form an intermediate chain like structure. Eventually, enough of these structures interact to form the desired network to form an electrolyte gel. Care must be taken during this step because applying an excessive amount of dispersion energy may result in over dispersing without gelling or in poor gel strength.

Gel time and gel strength testing

To internally test gel time and strength in our laboratories, the electrolyte is added into a 15 mm diameter glass tube. A lead ball (4.5 mm in diameter, 0.5 g in weight) is dropped from a height 23 mm above the tube to see if it can reach the bottom of the tube.

Gel time: the elapsed time from when the electrolyte is prepared to the point when the lead ball could no longer reach the bottom of tube.

Gel strength: the depth of the lead ball's penetration in the electrolyte is measured 24 hours after the electrolyte is prepared. A smaller displacement of the lead ball means higher gel strength.

Gel time and gel strength for ENERSIL® 2030 KD silica additive used in VRLA gel batteries

Sulfuric acid is diluted. Fumed silica is directly added into the diluted sulfuric acid and stirred at 10000 rpm for 1 min to get the electrolyte at 37.4% sulfuric acid. Density of electrolyte is 1.280 g/ml.

Figure 6 illustrates that electrolyte with 5% ENERSIL 2030 KD silica additive has similar gel time as other fumed silica additives at 6% loading. As shown in Figure 7, ENERSIL 2030 KD silica additive can achieve a good gel strength even at a reduced loading (5% compared to 6% using other fumed silica additives).

Figure 6: Gel time test

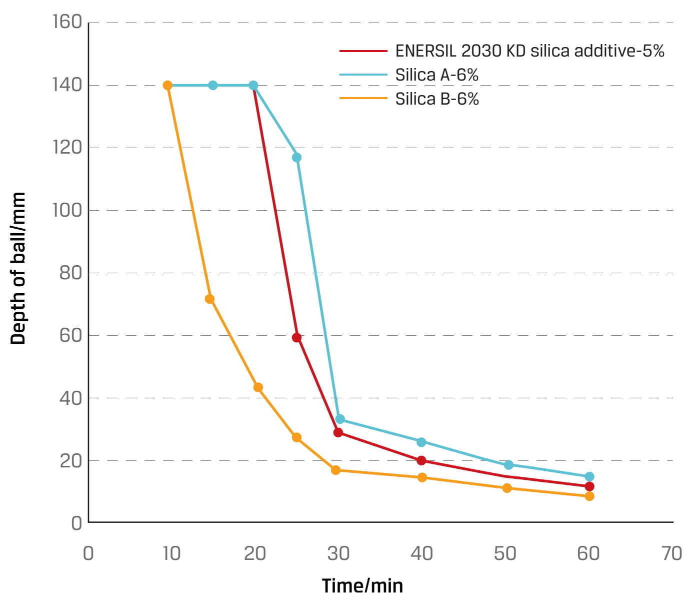
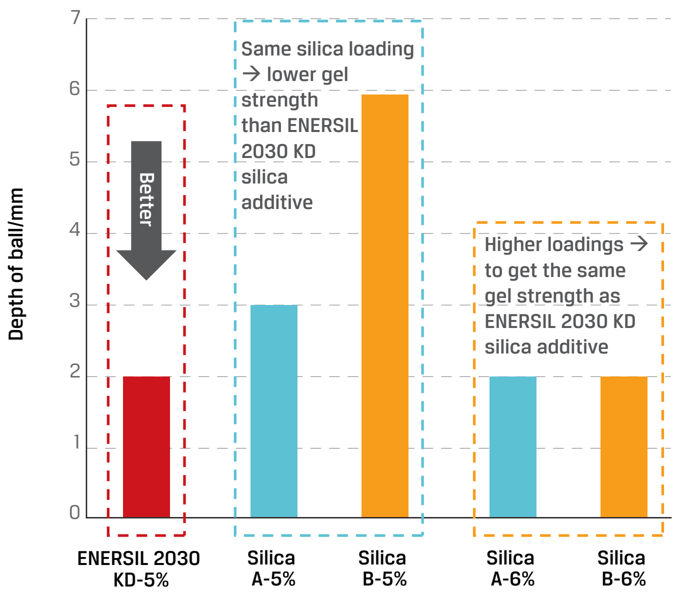


Figure 7: Gel strength after 24 hours



Health and safety

For safety, health, and regulatory information, please refer to the applicable Safety Data Sheets (SDS) available from your Cabot representative or at **cabotcorp.com**.

Corporate Responsibility

Cabot is committed to build a healthier, safer and more sustainable future. Sustainability is a core pillar of our global business practices. In Asia, Cabot was the first chemical manufacturer in China to have successfully certified manufacturing facilities in accordance with the Responsible Care Management System and RC14001 standard by British Standards (BSI), the authorized registrar in China.

RC14001 is the globally recognized gold standard for safety & health, environmental and security management systems established by the American Chemistry Council's (ACC) Responsible Care program.

To read more about Cabot's commitment in sustainability, please visit **cabotcorp.com/sustainability**.

Our commitment to energy

The world depends upon energy to drive industry, support commerce and care for communities. The world's energy consumption continues to increase, despite planned energy saving initiatives. Satisfying this demand while also striving for a sustainable environment will require not only reliable and safe energy production and distribution from today's technology, but novel solutions to enhance our power generation, storage, transmission and consumption into tomorrow's world.

We are committed to supporting that goal, and we maintain development programs with industry bodies, institutes and universities across the world. We will continue to use our expertise in small particle science to deliver solutions that meet the energy needs of today and the challenges of tomorrow.

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