KYNAR® BY ARKEMA

LITHIUM ION BATTERY

PVDF electrode binders & separator coatings

Contents
DISCOVER OUR BATTERY SOLUTIONS

2–3. Battery solutions overview

4–7. Electrode binders
HSV series

8–11. Separator coatings
LBG series

KYNAR® PVDF
BATTERY SOLUTIONS OVERVIEW

By nature, Kynar® PVDF is designed for extreme environments. The evidence is in its outstanding track record in use for high durability skyscraper coatings (>50yrs), subsea pipes for oil & gas (>25yrs), and solar panel backsheet protection (>10yrs).

The electrochemical environment in lithium ion batteries is extreme as well. Where oxidation and high voltage threaten the integrity of the every material that is exposed, it is critical for engineers to design with purpose and caution when in the material selection process.

As one of the pioneers in the evolving lithium ion battery market, Arkema has quickly grown through intense innovation to its position today as a global reference and a leading supplier of high quality resins. Kynar® PVDF battery solutions are represented by two flagship ranges:

- Kynar® HSV series for electrode binders
- Kynar Flex® LBG series for separator coatings

NOT ALL RESINS ARE CREATED EQUAL

For decades now, PVDF resins have proven themselves to be the best choice for highly stable binder resins – particularly for the cathode. The choice of PVDF resin is driven by two main factors: proof of extreme performance under extreme conditions and peace of mind. But, not all PVDF is created equal. Kynar® PVDF continues to stand out for its characteristic emulsion polymerization process. This process creates PVDF particles with very high surface area that translates to quicker dissolution and faster processing for cell manufacturers. Arkema is a committed global partner, providing customers peace of mind with assurance of global supply, quality, compliance, and commitment to developments for next generation batteries. With global resources and regional manufacturing, service, and R&D, our global team is dedicated to helping our customers succeed.

COST DOWN, PERFORMANCE UP

The popularity of lithium ion batteries is growing at a rapid pace. While the market's initial growth came from consumer electronics for use in phones, tablets, and power tools, today's big boom comes from electric vehicles. The demanding automotive industry requires costs to be driven down and performance of batteries to significantly improve, while emphasizing the need for a consistent global supply chain – a challenge the Arkema team is ready for.

ELECTRODE BINDERS – KYNAR® HSV SERIES

Electrode binder material choice is paramount in producing higher performance lithium ion batteries. The Kynar® HSV series is a tailor-made range of PVDF grades providing fast dissolution, easy processing, high adhesion/lower loading, lower swelling in electrolyte, lower electrode resistivity, and high voltage stability. *See pages 4–7*

SEPARATOR COATINGS – KYNAR FLEX® LBG SERIES

As the industry evolves to even larger and higher power cells, high performance separators are required to improve battery abuse tolerance. The Kynar Flex® LBG series features a range of PVDF grades that provide great electrode adhesion (wet & dry), high voltage stability, high dimensional stability, controlled crystallinity, and nano-ceramic compatibility for both solvent and water-borne technologies. *See pages 8–11*

KYNAR® HSV SERIES

The Kynar® HSV series of PVDF binders offer fast dissolution, easy processing, high throughput, stable slurry viscosity, and very high adhesion through many cycles and wide temperature fluctuations. Lower binder loading can be achieved while maintaining high adhesion through Arkema's careful control of **functionalization** of the binder resin. This allows for higher concentrations of active materials, lower internal resistance, and high cohesion across the electrode. The HSV series also exhibits very low swelling in electrolytes, which can be tailored by **fine tuning crystallinity**. These grades offer best-in-class capacity retention and electrochemical resistance with stability over a wide voltage range (up to 5V Li+/Li). Thermal stability is also stable across this range. With nearly 20 years of experiene in the battery industry, we understand the importance of not only innovation but consistent quality and supply. Through many years of global experience in chemical processing industries (e.g. semiconductor, nuclear, potable water, healthcare), our team has developed industry-leading proficiencies in lot-to-lot consistency of very high purity PVDF.

- **KYNAR® HSV 900** – the industry reference
- **KYNAR® HSV 1800** – the 2nd generation
- **KYNAR® HSV 1810** – the 3rd generation

> **"Cathodes typically account for 25% of lithium ion battery costs. Building a better cathode is the key driver for the continued success of the lithium ion revolution."**
> *Lithium Investing News, 2017*

With high adhesion at lower loading levels, the Kynar® HSV series enables higher energy densities due to the increased active material content. HSV series binders also demonstrate low swelling levels in common solvents and electrolytes (even at high temperatures – up to 80ºC). Binder swelling can have serious consequences in a lithium ion battery, so Kynar® HSV resins can ensure peace of mind.

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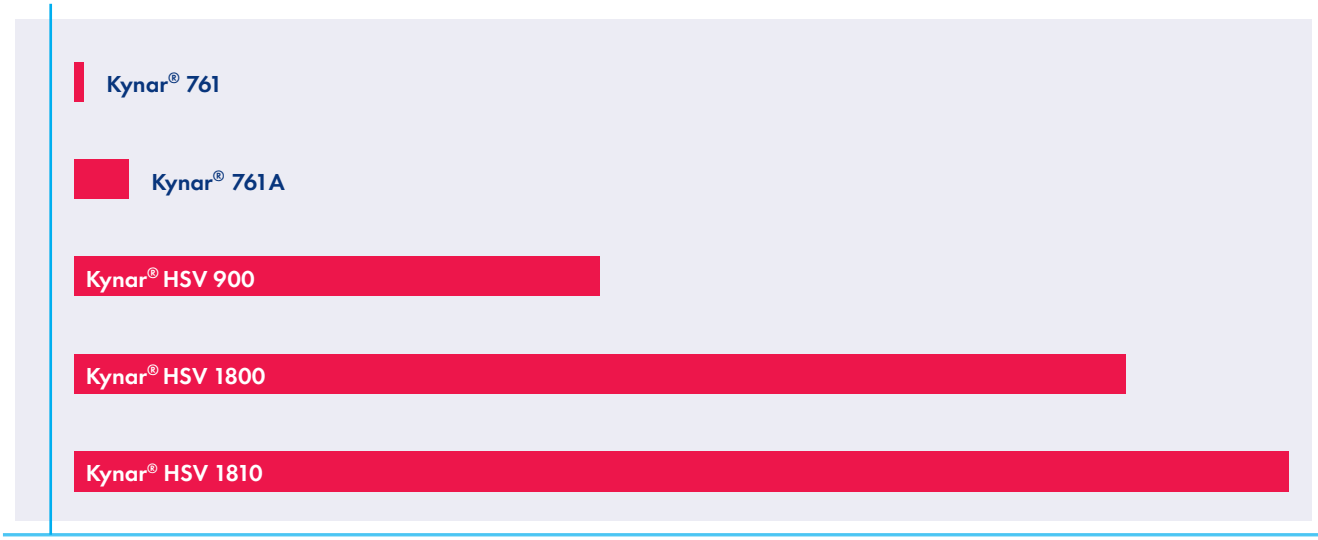
Active materials are constantly changing in the evolution of ever-more efficient batteries. It is critical for binder solutions to provide high adhesion properties no matter what active material is being used. The Kynar® HSV series maintain excellent adhesion properties with: LCO, LFP, LMO, NMC, and NCA. Please contact our team for other materials.

Binder innovation is at the core of our strategy in the battery market. Arkema is committed to an exciting future in binder development that will drive safer, higher performing cells. Arkema's King of Prussia, PA battery **innovation hub** in the USA leads the way and we invite customers to collaborate with us as we push the boundaries of cutting-edge technologies (e.g. high nickel binders, waterborne solutions, dry process prototypes). Our team is also eager to assist from our **satellite technical centers in China, France, Japan, and Korea**.

CONTINUOUS BINDER INNOVATION

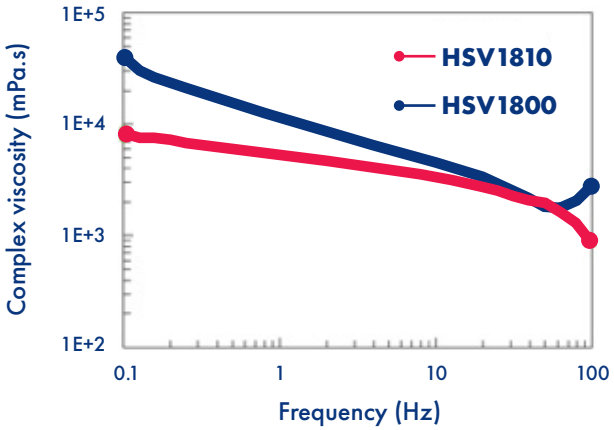
Adhesion is of course one of the most important properties of electrode binders, and over the years our team has continued to improve adhesion of our binders. But the Kynar® HSV series really stands out by retaining performance and adhesion in a variety of scenarios (i.e. bending, electrolytes, heat exposure), and also improving the **processing** qualities that we know are extremely important to efficiently produce lithium ion battery cells.

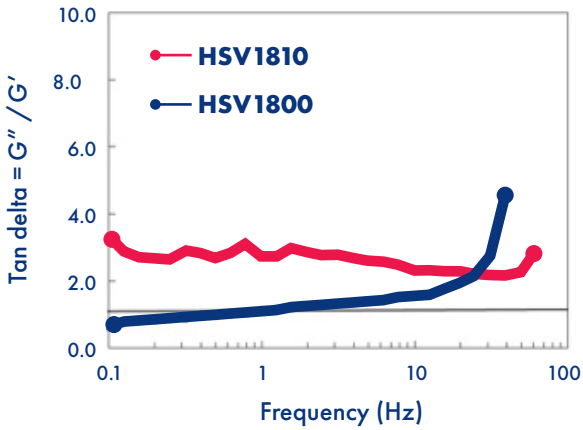
Relative adhesion on aluminum substrate



NEXT GENERATION KYNAR® HSV 1810

Slurry processing window



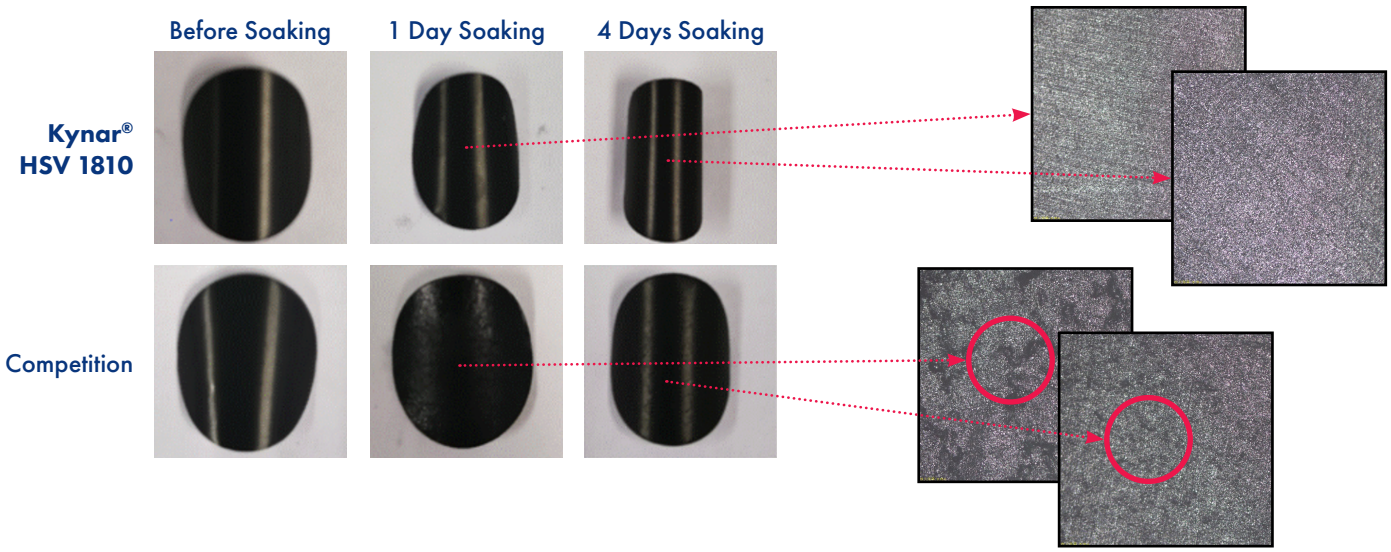


A wider processing window enables battery manufacturers to tune their processes and construct their cells using the most efficient methods possible. In the end, easier and faster processing can lead to cost reduction and higher throughput, and the new Kynar® HSV 1810 can help manufacturers achieve their stretch goals in operations.

HSV 1810 – BALANCED ADHESION & FLEXIBILITY

Retained performance after exposure to electrolyte is extremely important for the long-term performance of the battery cell. Batteries are also subjected to many mechanical stresses so binders that can maintain adhesion without cracking after being flexed are critical to serving the battery market of the future. Kynar® HSV 1810 exhibits outstanding flexibilty compared to competitive binders on the market.

In the test below, electrodes using Kynar® HSV 1810 and competitive binders were bent then soaked in electrolyte (EC: DEC: DMC=1:1:1) for 4 days and evaluated for cracking. The resulting pictures illustrate that after only 1 day the competitive binder formulation begins to crack, while the Kynar® HSV 1810 binder formulation shows no signs of cracking even after the full 4 days.



In China each and every day, electric buses powered by batteries containing Kynar® PVDF travel more than 51,000 km!

ADVANTAGES OF ARKEMA'S EMULSION PVDF

PVDF is commonly produced by free-radical polymerization via **emulsion** or **suspension** processes. Both technologies are water-based. In the emulsion process, a surfactant (emulsifier) is used to stabilize the VF2 monomer droplets and typically a water-soluble, inorganic initiator is used. In the suspension process, dispersing agents are needed to stabilize the VF2 droplets, where polymerization takes place. The initiator is typically organic in this case.

Thanks to the emulsifier, the PVDF particles generated by VF2 polymerization are physically stable, even in the absence of mixing, thus remaining evenly dispersed in water, as seen in Figure 1.

In typical suspension polymerization, the PVDF particles are much bigger. Under shear, the use of the dispersing agent is still necessary to maintain a uniform dispersion. However, when the mixing is stopped, the particles settle as seen in Figure 2.

Suspension PVDF is by definition emulsifier free but often contains a lot of dispersing agents like cellulose or polyvinyl alcohol.

To isolate and recover the PVDF polymer from the aqueous phase, a drying step is necessary in both polymerization technologies. In the case of the emulsion process, a spray drying step allows an agglomeration of the primary latex particles (~200nm) into larger particles (~10µm). As shown in Figure 1, the final powder is comprised of a multitude of smaller ones.

In the case of the suspension process, the PVDF recovery is typically made by settlement where the dispersing agent remains associated with the particles. The mean diameter of the suspension beads is typically much bigger and on the order of hundreds of microns. This size is typically 10 times bigger than spray dried powder recovered from the emulsion process.

Figure 1. Arkema Emulsion Polymerization

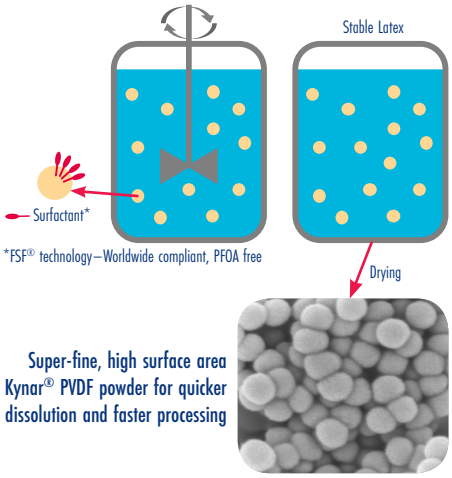
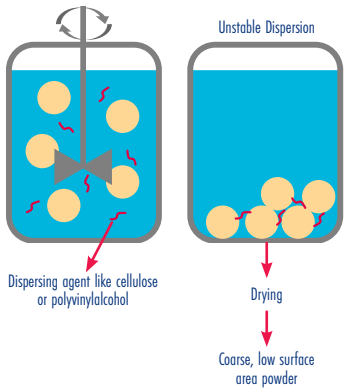


Figure 2. Suspension Polymerization



KYNAR FLEX® LBG SERIES

The Kynar Flex® LBG copolymer series provides a wide range of performance similar to the HSV series, but this range is dedicated specifically to separator coatings. With an accelerating market, productivity to meet growing demand is under high pressure. One way to dramatically reduce the cell assemby time and lower overall production costs is to use adhesive-type separators. The LBG separator coating series demonstrates outstanding adhesion while maintaining a high degree of flexibilty. Regardless of being combined with ceramics, Kynar Flex® LBG grades allow an excellent balance between phase separation, adhesion to electrode (dry and wet), cohesion of the coating, and electrolyte uptake. With separator coatings being somewhat of an "art," Arkema provides the most comprehensive range of polymers, allowing a broad selection of tailored solutions.

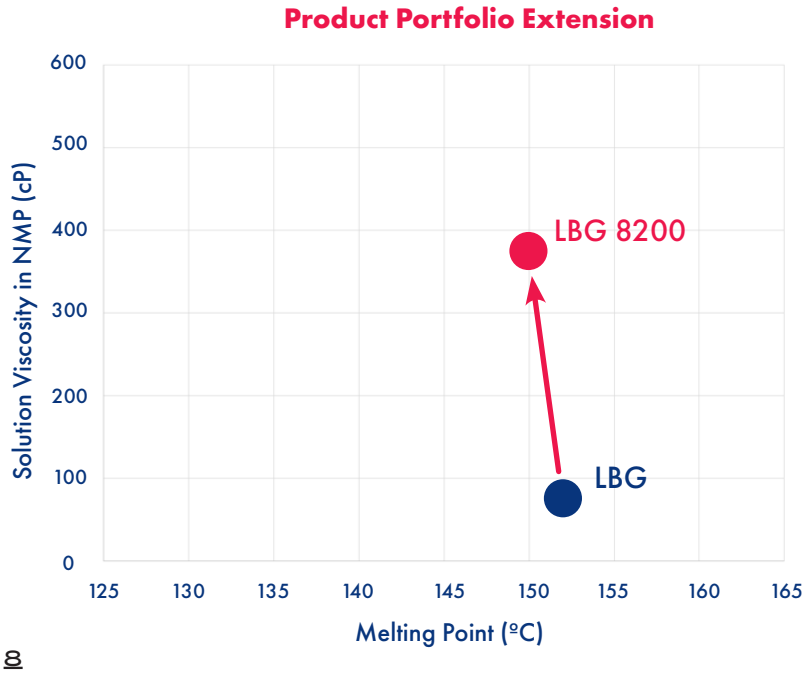
- **KYNAR FLEX® LBG** – the first separator coating solution
- **KYNAR FLEX® LBG 8200** – the portfolio extension
- **KYNAR FLEX® LBG 2200 LX** – the water-borne solution

HIGH PERFORMANCE SEPARATOR COATINGS

The Kynar® LBG series has served the separator coatings application for many years, and after much R&D, the range is extending to even higher performance solutions.

> **"By 2025, more than 50% of global lithium ion power will be driven by automotive and e-bus markets"**
>
> *Avicenne Energy*

EXTENDING THE RANGE



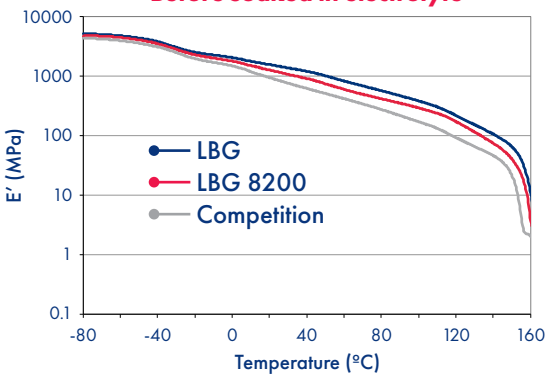
Kynar Flex® LBG 8200 effectively increases adhesion by 50% compared to the original Kynar Flex® LBG. With an increased molecular weight and subtle functionalization, Kynar Flex® LBG 8200 extends the performance range of the LBG series for separator coatings.

Property	LBG	LBG 8200
Molecular weight	Medium	High
Functional	No	Yes
Melting point	152ºC	150ºC

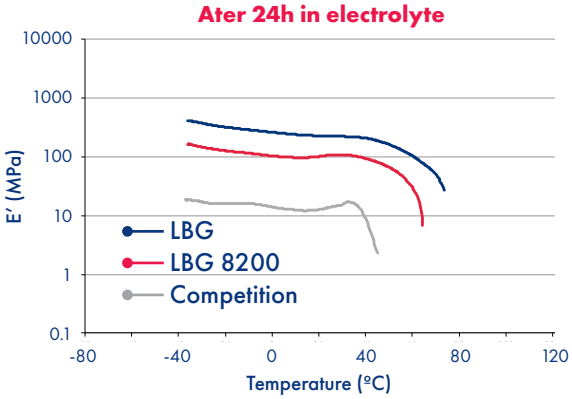
Dynamic mechanical thermal analysis of separator coatings soaked in electrolyte

Thermal-mechanical behavior in flexion at 1Hz-2°C/min

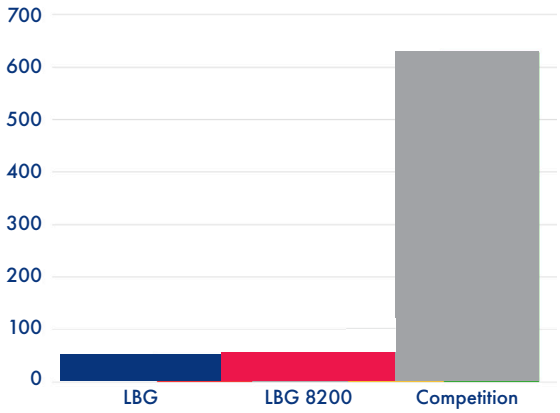
Before soaked in electrolyte



Ater 24h in electrolyte



Swelling (%) in EC/DMC/PC= 1:1:1 at 60ºC



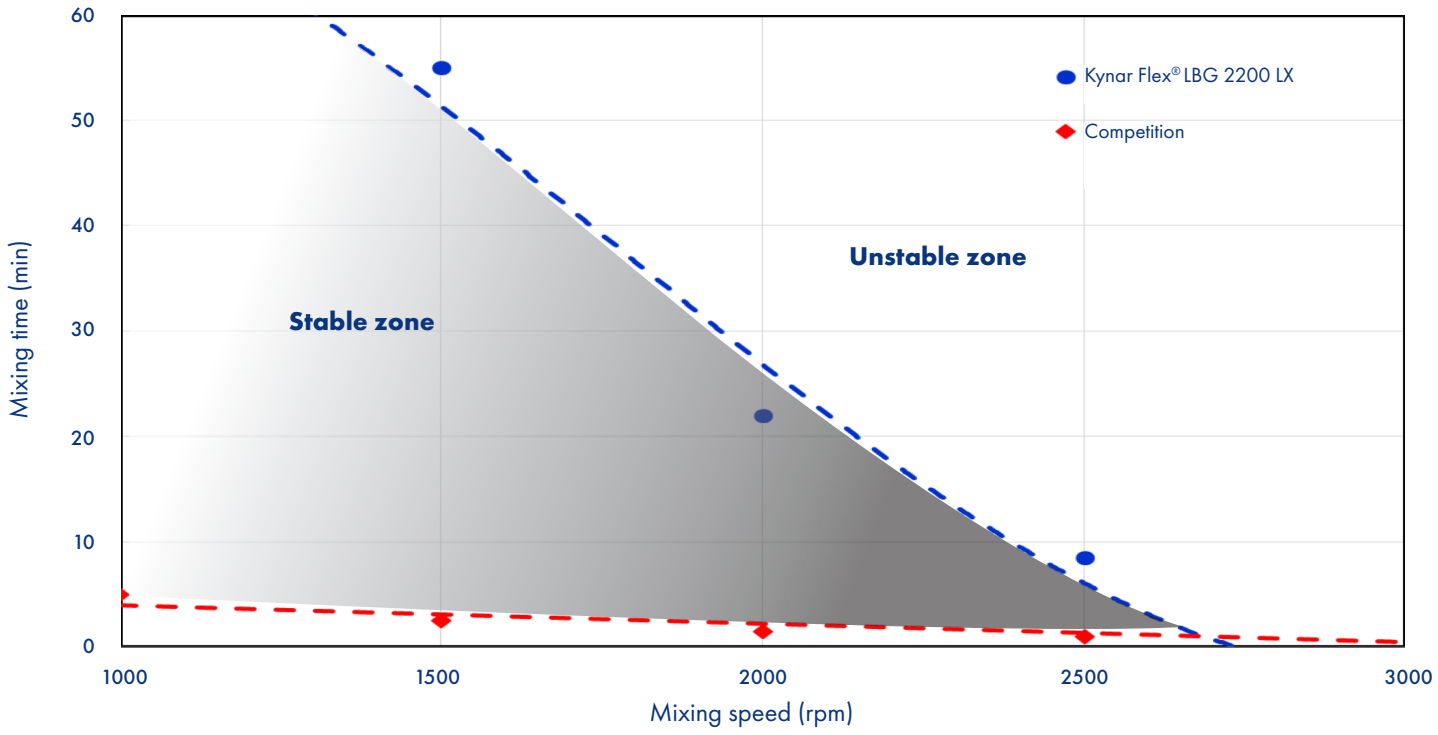
Swelling correlates with the thermal-mechanical behavior of the separator coating, as seen in the graph above. The competitive separator coating evaluated essentially dissolves completely in electrolyte when exposed to 60ºC heat. Therefore, when high performance is required at elevated temperature, the Kynar® LBG series is a better option.

WATER-BASED SOLUTIONS

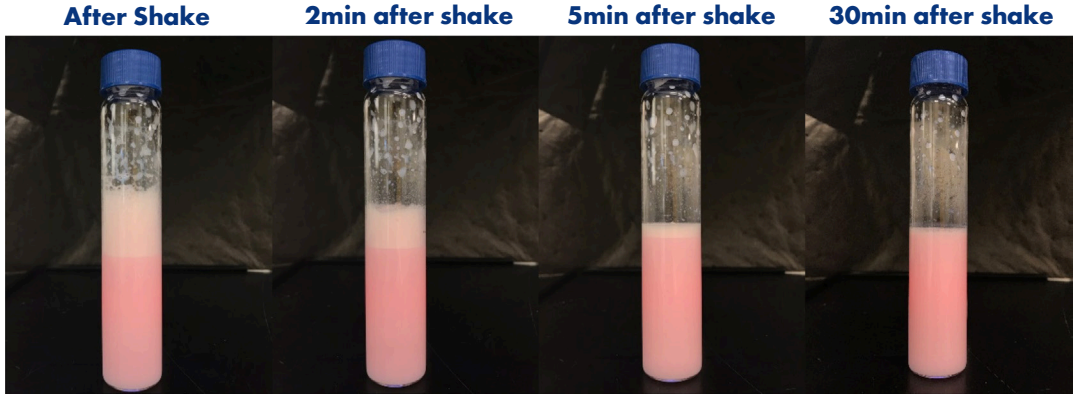
KYNAR FLEX® LBG 2200 LX (LATEX)

LX technology is the most stable PVDF latex that can be shipped all over the world. With Arkema's decades of expertise in water-borne, latex coatings (Kynar Aquatec®), our researchers now extend the LBG separator coating series to water-based Kynar Flex® LBG 2200 LX. This new grade also has unmatched shelf-life stability with very high solids content. Arkema is committed to developing sustainable solutions and this new water-based technology for lithium ion batteries is the result of our dedication.

Latex shear stability – Onset of thickening



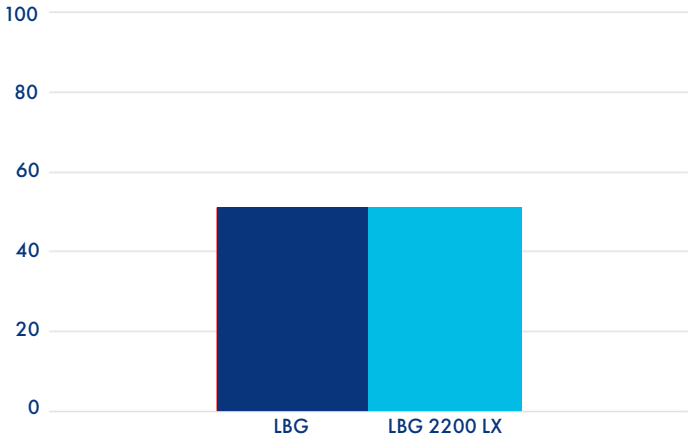
Low foaming after shaking



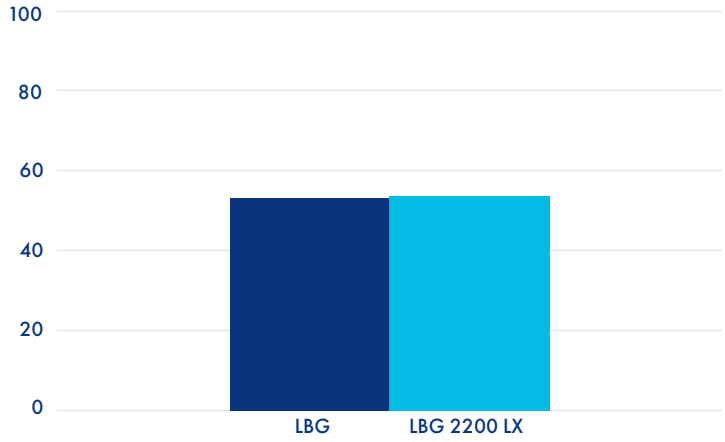
The colored latex, as seen in the images above, illustrates that after only 5 minutes, foaming is almost entirely gone, and then after 30 minutes foaming has completely subsided.

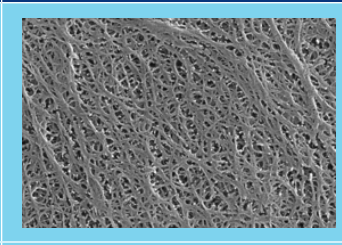
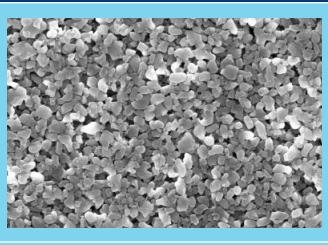
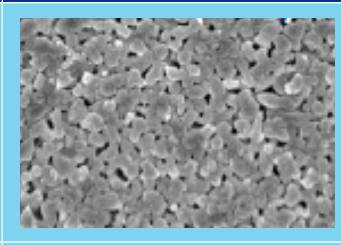
SIMILAR PERFORMANCE TO LBG

Weight Gain (%) in EC/DMC/PC=1:1:1 at 60ºC

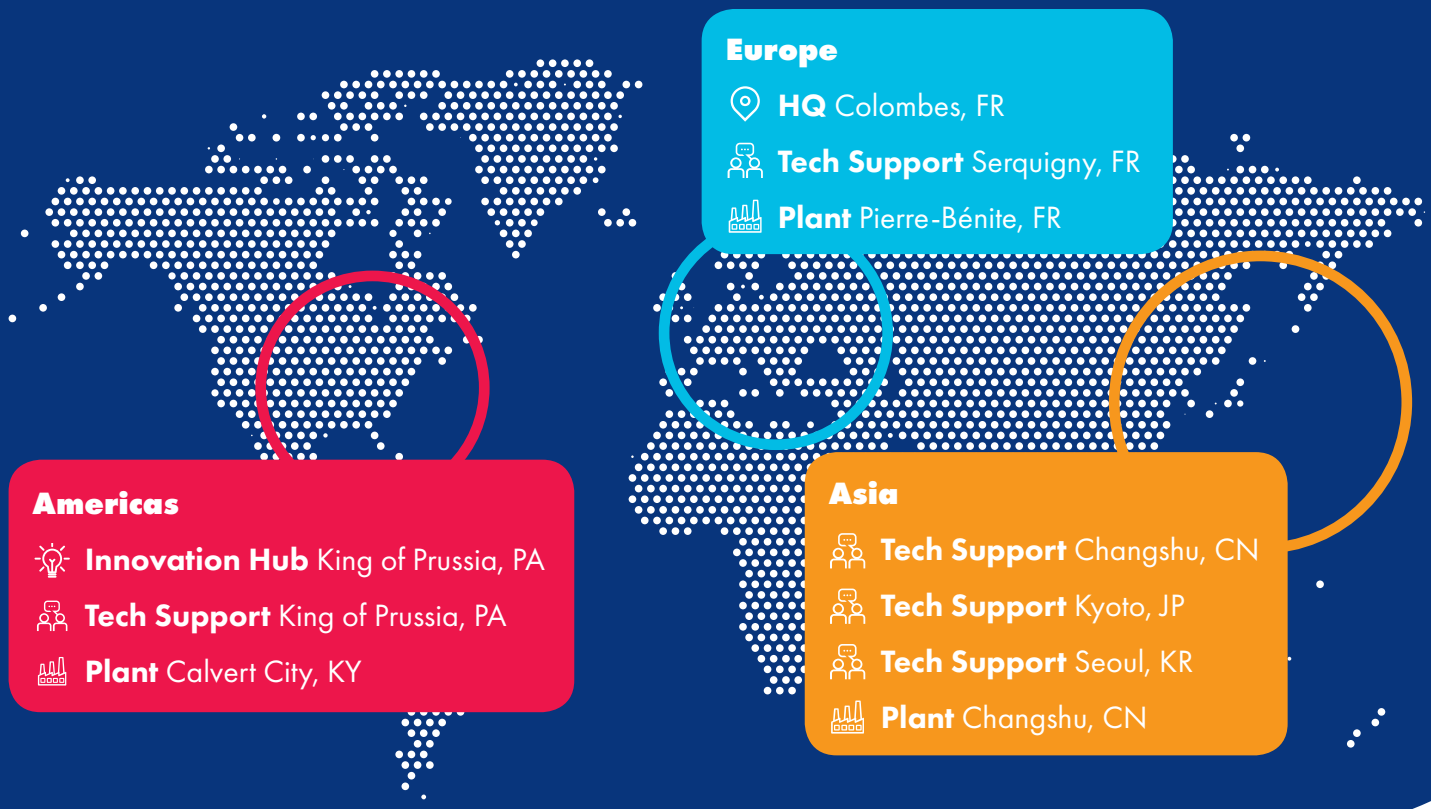


Swelling (%) in EC/DMC/PC=1:1:1 at 60ºC



Property	Non-coated separator	Al_2O_3/LBG	Al_2O_3/LBG 2200 LX
SEM image			
Thickness (μm)	20	25	26-28
Gurley value (sec/ 100cc air)	250	391.2	301.2
Resistance	1.211	1.485	1.535
Ionic conductivity	0.821	0.837	0.875
Conductance (S)	0.826	0.673	0.651

Global Manufacturing, Technical Support, and R&D



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