Pioneering Process for Groundbreaking Particle Synthesis

J. Wagner

Future materials such as high-energy and safe battery components, more economical membranes, orthopaedic ceramics, functional additives or high-performance pigments must provide more than the current properties of existing material components. A common issue within each of these applications is the high levels of powder performance that are required. Therefore, completely new products or novel innovations require powder materials that must first be developed and then manufactured in the necessary quantities. With APPtec®, plant manufacturer Glatt/DE has succeeded in overcoming these challenges and established a mature continuous process technology to produce future materials at both laboratory scale for research purposes and at industrial levels. Time-consuming and risky scale-up procedures are eliminated because of the size-independent conditions – fluid mechanic and thermodynamic – that exist from lab- to commercial-scale production. With APPtec®, primary particles can be provided with an almost freely adjustable chemical and mineralogical composition and previously unattained properties.

Traditional synthesis processes

An issue, though, is the fact that the particle size of high-performance powder materials can only be produced under extremely accurate and reproducible process conditions. Common processes with which nanoscale or submicron powders in various compositions can be produced are chemical, mechanical and thermophysical synthesis. Wet chemical methods (hydroxide precipitation, sol-gel-syntheses, hydrolysis, hydrothermal processes) lead to so-called precursor powders.

Only post-treatment calcination delivers the desired crystal formation, whereby the particle structure and size must be controlled by carefully monitoring the reaction. By contrast, large quantities of pure powder can be produced with this old and simple method. However, the time-consuming process of grinding the particles is only really suitable as a way to homogenize the reaction components. Hugh amounts of energy are required to grind a nanoscale ceramic powder.

In addition, the grinding method can lead to undesired phase transformations, including amorphization, abrasion and contamination. Thermophysical methods use evaporation-based techniques to condense fine particles from solid, liquid or gaseous starting compounds. They are widely used in the synthesis of nanocrystalline powders and known processes include, for example, laser evaporation, flame pyrolysis, plasma and microwave-assisted evaporation. These techniques require complex technical prerequisites and usually generate low throughput quantities. Whether combustion or thermal decomposition is used, if the heat treatment is too intense or not homogenous, as can occur during flame pyrolysis, plasma reactor technology or rotary kilns, hard aggregates or hot spots form.

Hard aggregation is generally caused by the fact that the very high local temperatures induce a partial melting phase. Hence, colliding particles remain directly attached to this phase and, during cooling, a hard chemical bond is formed. When the powder is transferred to the application matrix, the particles not only have to be distributed uniformly, but also often have to be dispersed. If the powders are not or only lightly agglomerated (physical surface bonds), this is generally easier to achieve.

But in the case of hard aggregations (chemical bonds), this is virtually impossible. Last but not least, another challenge in the production of future materials is to establish a more economical and scalable process for reproducible quality.

Rethinking spray calcination

APPtec® is a thermal powder synthesis process that is particularly suitable for the production of fine or nanostructured materials with homogenous chemical properties. The abbreviation APPtec® stands for Advanced Pulse Powder technology, the process belongs to the thermophysical class. This pioneering spray calcination development makes it possible to produce completely new powder types in a hot gas reactor.

Compared with other methods, this is a more homogenous thermal treatment,

Jörg Wagner
Glatt Ingenieurtechnik GmbH
99427 Weimar
Germany

E-mail: joerg.wagner@glatt.com
www.apptec-glatt.com

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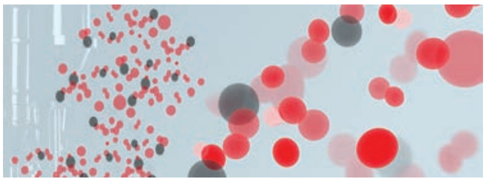

Fig. 1 **Targeted particle size adjustment**

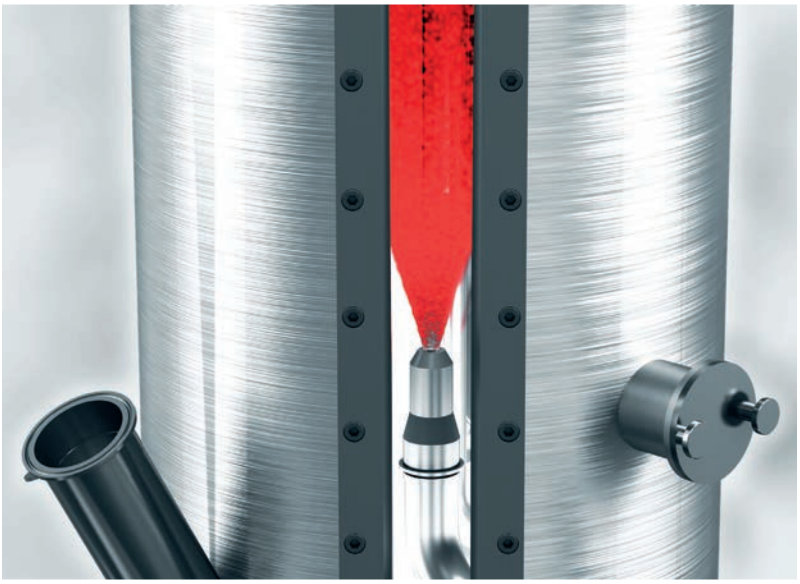

Fig. 2 **In the synthesis reactor, only the gas flow pulsates in a controlled manner in the specially designed reaction chamber; for particle production, fine droplets of a raw material solution are sprayed into the gas stream to form particles**

providing a wider range of material applications, fewer hard aggregates and easier scale-up.

Ceramic materials are particularly suitable candidates because of their unique performance characteristics. From batteries, LEDs and coating systems to catalysts, corrosion protection components or cathode materials for fuel cells, this wide range of applications requires increasingly complex material systems. APPtec® enables the development and manufacture of highly complex powder systems within which particle distribution is homogenous.

One of the advantages of the process is that the particle size can be specifically adjusted by controlling the spraying parameters and the process conditions used (Fig. 1). In addition, APPtec® can accommodate a wide range of raw materials, which means that low-cost ingredients can be processed into higher-value products with specific or customized properties.

Furthermore, doped components and systems can be used, making spray calcination ideal for the production of oxide, nitride and sulfide ceramic and other product groups, such as metal oxides. Using the innovative spray calcination method, a particle size and morphology can be fine-tuned to provide specific properties.

The required stoichiometry can also be configured for highly complex systems. This ensures that any doping elements are optimally distributed. In addition, both the mineralogical and chemical composition can be precisely defined. For example, mixed oxides such as spinel, perovskite or titanate can be produced; and, owing to the adjustable phase composition, particles can also be produced from high-temperature phases such as corundum or mixed oxides such as mullite.

At the pulse of the reactor

APPtec® builds on established spray calcination technology, wherein calcination refers to altering the chemical composition of a substance by thermally expelling any volatile components. The heart of the technology is a specially designed elongated process chamber in the synthesis reactor ProAPP® 500 (Fig. 2).

A strictly controlled hot gas flow pulsates in this chamber, providing unique fluid dynamics. In fact, owing to the high degree of turbulence, pulsating gas flows do not demonstrate the temperature and speed gradients that would typically be found in continuous gas flows.

As a result, all particles undergo the same thermal treatment (Fig. 3). With constant flow and increasing pulsation intensity, the layer of air that forms in the gas flow and surrounds the particles is almost completely eliminated. As a result, the heat transfer rate from gas to particle can be up to five times faster, which means that the particles heat up very quickly and cool down just as rapidly at the end of the reaction (Fig. 4). This extremely accelerated particle formation and phase transformation provides the

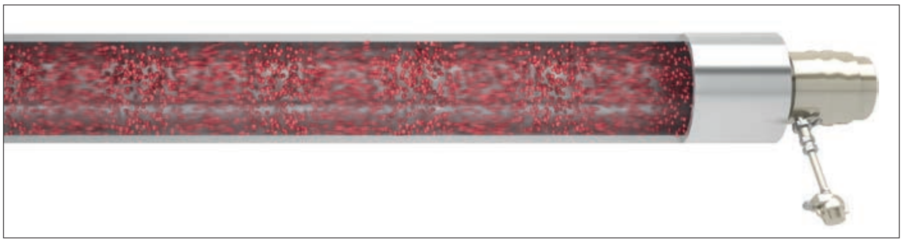

Fig. 3 **Compared with continuous gas flow, the pulsating gas flow has no temperature and speed gradients because of the high degree of turbulence; therefore, all particles experience the same thermal treatment**

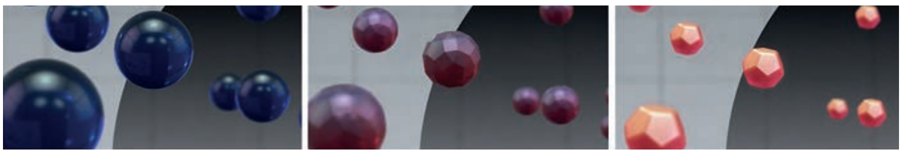

Fig. 4 **For chemical and mineralogical reactions, the particles are rapidly heated and cooled; the schematic representation shows the conversion of the injected raw material solution over the crystal-forming structures up to the calcined particle**

desired reaction states and the subsequent formation of unique structures.
When raw materials are added to the process, two effects are triggered. Using silicate-based powder (conventional SiO_2) as an example, any substances with which the surface of the raw material has already reacted are removed (the OH-groups in the case of SiO_2). The raw material thus becomes "purer." Secondly, pore size and specific surface area of the particles can be manipulated, contributing to the functionalization of the particle. This process is very fast; the solvent or water is evaporated and the particles are formed very rapidly.
In addition, process steps such as drying, calcining, particle formation or coating can be combined in a single step. If needed, functional core shell particles with application-specific layer thickness, porosity and activity characteristics can be produced (Fig. 5). Because of the absence of local hot spots in the reactor, no sintering takes place. As a result, the individual particles are easily separated and dispersed.
With APPtec® technology, those thermodynamic conditions that can be easily adjusted by targeted process control. Process conditions such as temperature, residence time, frequency and amplitude can be set as accurately as the pulsating gas flow speed. Additionally, the gas atmosphere – oxidizing or oxygen-free – can be chosen according to the application.

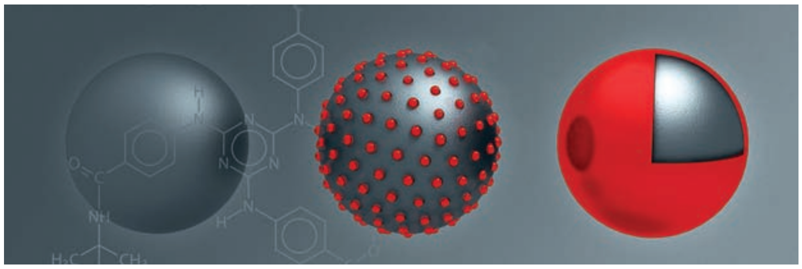

Fig. 5 Functionalization of particles using core-shell-principle

Test batches and product samples in hours

This unique thermal treatment opens up many possibilities for the customisation of particle properties in an application-specific manner and to produce novel, not currently available additive systems. Test batches for material and reaction analyses or product samples can be generated under industrial conditions and recipes or product ideas – from raw material to a usable amount of powder – can be brought to fruition in a short time, so that pilot projects or the marketability of a product can be assessed quickly.
To cite a joint research project example, the Fraunhofer Institute for Ceramic Technologies and Systems IKTS/DE has been working on thin, supported membrane layers for oxygen generators. To put it simply, the new membrane tubes are intended to lead to a considerable increase in O_2 permeation while, at the same time, the required number of membranes produced decreases significantly. Ceramic components such as membranes, storage materials and catalysts are to be optimised with regard to their process-relevant properties. This involves geometry, layer thickness, porosity and cell thickness. The aim is to develop smaller and more cost-effective O_2 generators with asymmetrical MIEC membranes, which can be used both in medical technology and industrial applications.
Given the importance of the particle morphology, the powder raw materials for the membrane are being produced with APPtec®. And, having successfully completed the preliminary tests, IKTS has now ordered a ProAPP® lab-scale reactor to capitalize on the manufacturing opportunities.

Fig. 6 **ProAPP® 500 plant for the production of high-performance powders (Source: Glatt Ingenieurtechnik)**

Process without disposal risk

Considering the procurement and disposal costs that the manufacturing industry usually has to contend with, processing in hot gas reactors is a truly economical alternative. Once the right raw material or blend has been identified and the process established, there is no waste. Production can be started immediately after the successful evaluation of practical tests.
Shaping technology is one of Glatt's core competences. As one of the world's market leaders in fluid bed technology, Glatt has more than 60 years of experience in pioneering solutions for the development, refinement and production of solids. The plant manufacturer accompanies its customers from the initial idea through process development to the construction of turnkey production plants. At Glatt's Technology Center in Weimar, materials for research

Tab. 1 APPtec® and ProAPP® reactor respectively, in a nutshell

Process temperature	200–900 °C (higher temperatures on request)
Pulsation frequency	10–300 Hz
Pulsation amplitude	0–50 mbar
Residence time	100 ms–10 s
Gas atmosphere	oxidizing or O_2-free (other atmospheres on request)
Suitable materials	solutions, suspensions or solids
Capacity	100 g/h–300 t/a (higher capacities on demand)

projects are developed and produced in hot gas reactors as well as novel powders for its customers (Fig. 6).

Summary

The demand for high-performance powder materials is increasing worldwide, combined with extremely high requirements for narrow particle size distribution and application-specific properties such as chemical composition, phase structure, morphology and surface chemistry.

With APPtec®, Glatt introduces a continuous powder synthesis method that makes it easy to adjust these properties and enables cost-effective production of the desired quantities. Spray calcination in a pulsating hot gas reactor enables a wide range of powder synthesis applications under unique and homogenous conditions with numerous advantages for the adjustment of particle properties.

At Powtech, hall 3, booth 3-249, Glatt will be presenting the APPtec® and the ProAPP® reactor (Tab. 1).