Freeze Granulation

A multi-tool for enhanced ceramic processing

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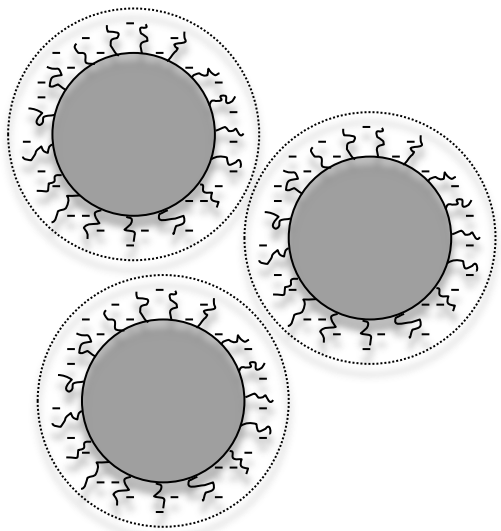
Outline

- Background and principle of Freeze Granulation (FG)
- Granule properties
- Applications
  - Pressing
  - Pre-preparation for dispersability in different applications
  - Powder synthesis
  - Particle preparation for different purposes
- Advantages and dis-advantages of FG
- Equipments
- Summary

Processing of advanced ceramics

Focus in the 80s and 90s



Colloidal processing
of fine powders

De-agglomeration - Stabilization

Liquid based shaping

Slip Casting

Tape Casting

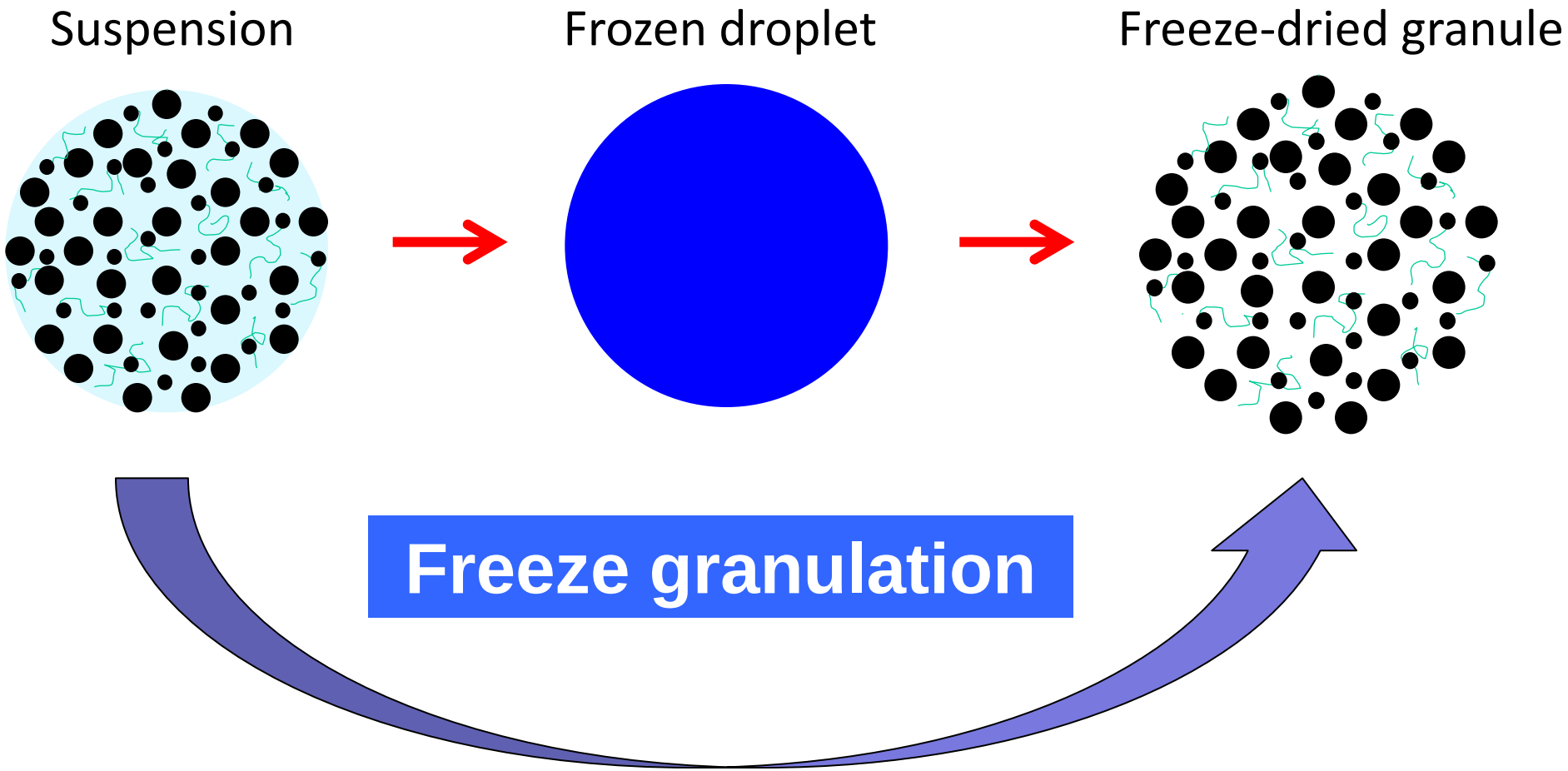
Gel Casting

Dry Pressing ?

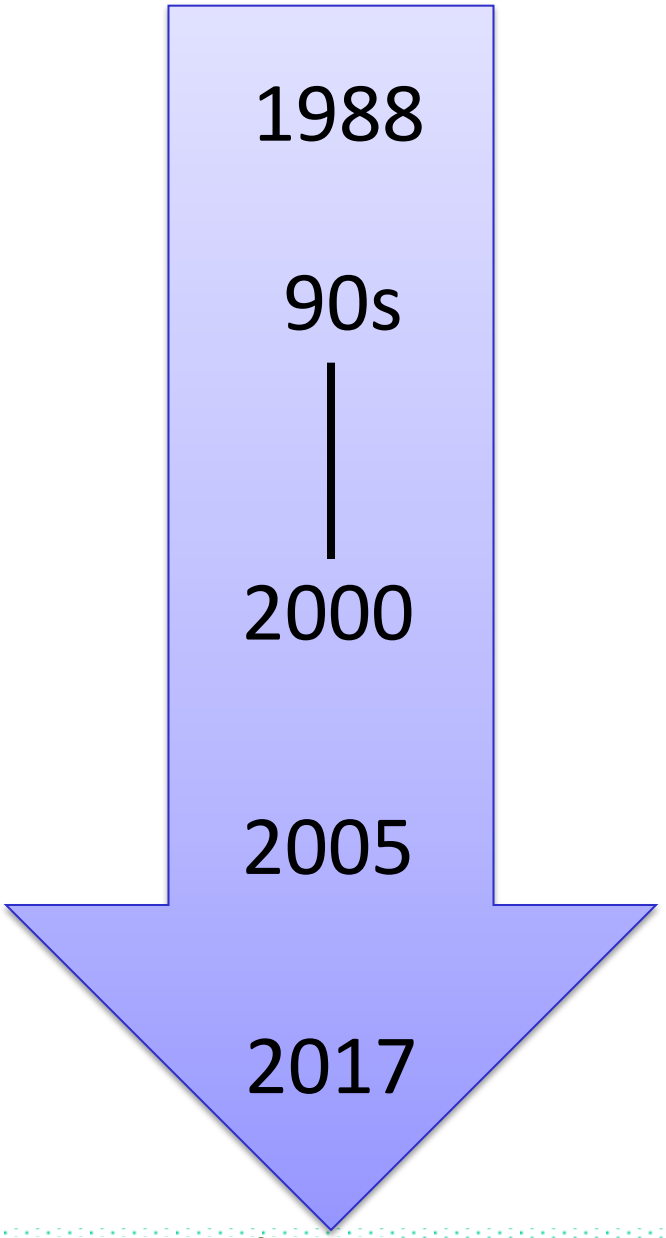
(Current granulation methods not satisfying)

Colloidal approach for pressing

Idea to lock and transfer suspension homogeneity into granules



Review



FG started at the Swedish Ceramic Institute (SCI) with focus on pressing

Successful research and development in many projects and contracted works

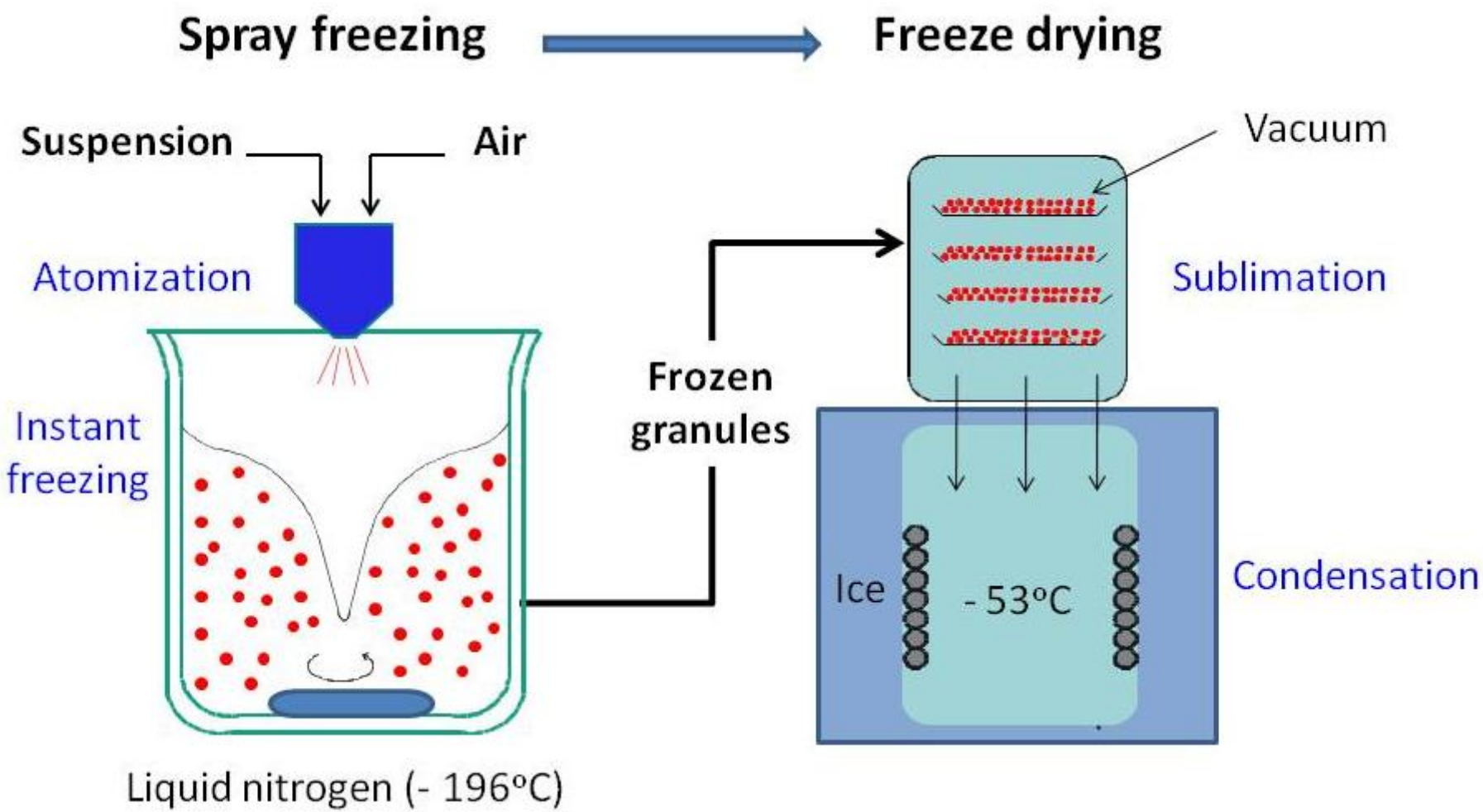
Other applications

Powderpro AB was established 2000 as a spin-off company to produce and sell FG equipment

SCI was incorporated with Swerea IVF

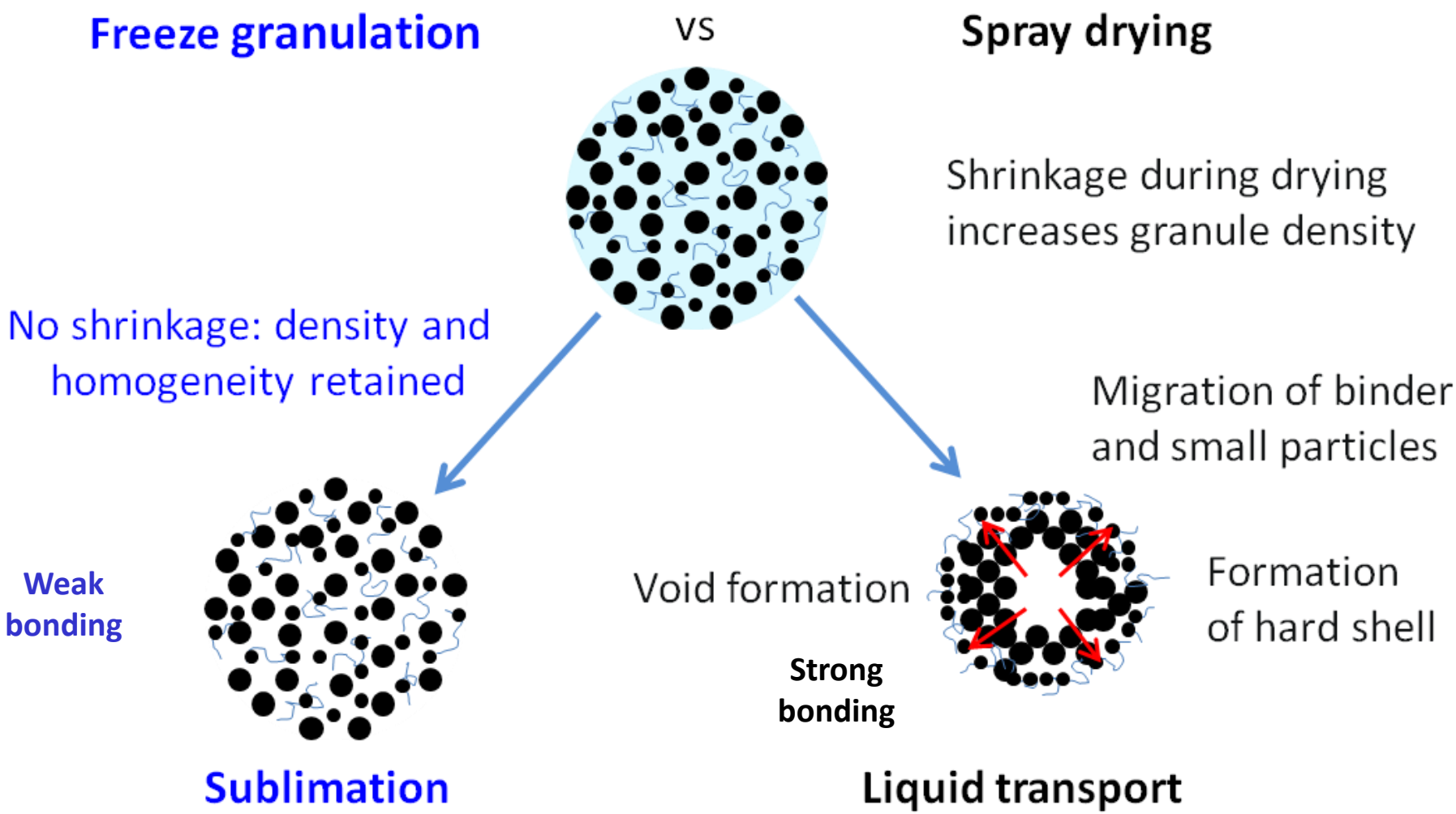
FG, a standard processing tool in material development in a variety of applications

Freeze granulation procedure



Instant freezing and subsequent freeze drying ⇒ homogeneity preserved

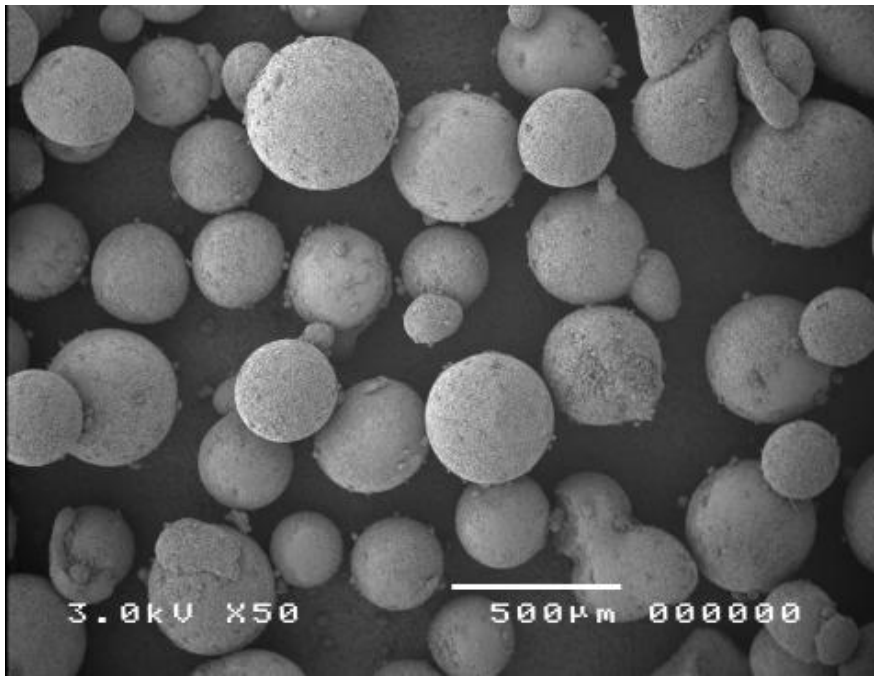
Freeze granulation (FG) vs Spray drying (SD)



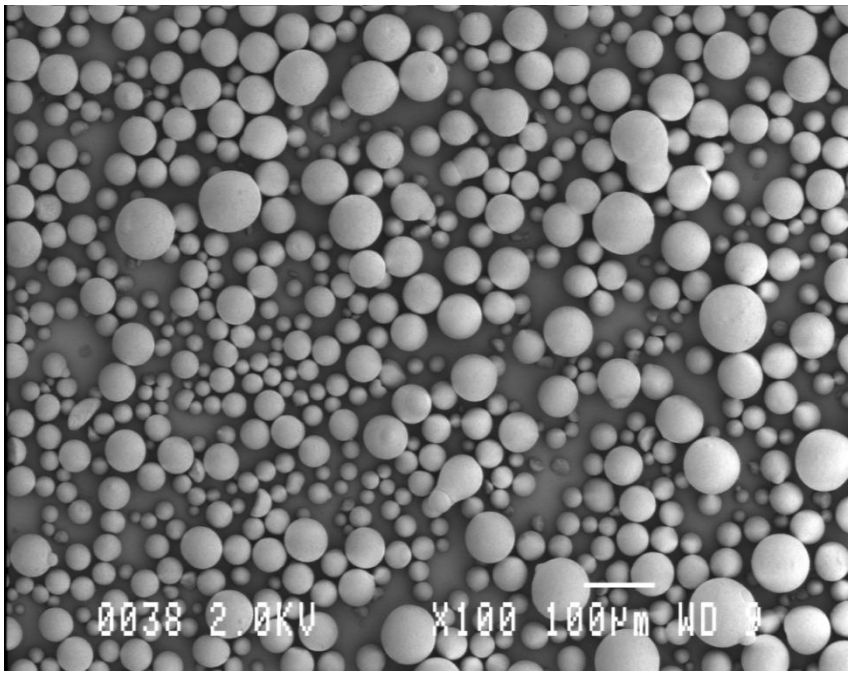
Granule properties - 1

Granules of composite materials

Diamond/Ceramic



Zirconia/Alumina

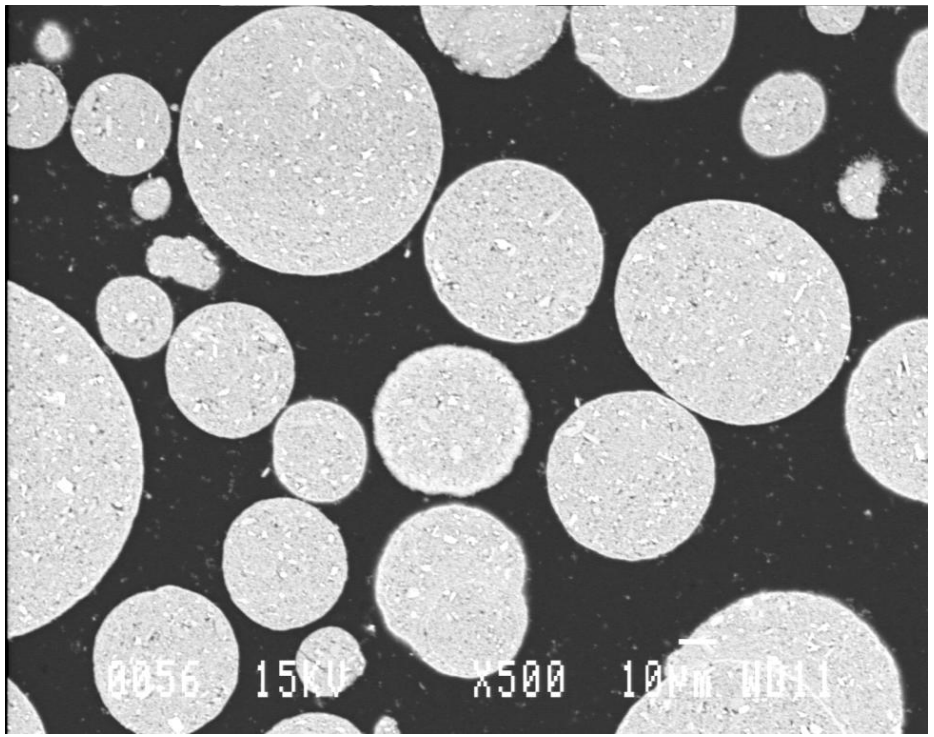


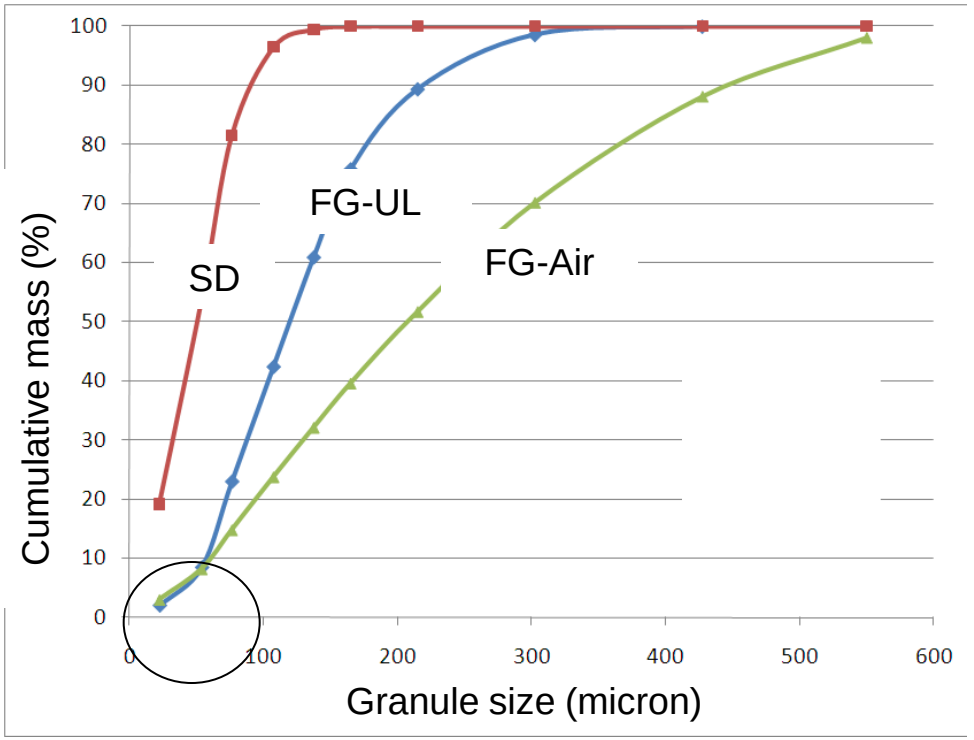
Free-flowing spherical granules

Granule size is controlled by suspension rheology, feed rate and atomizing air pressure

Granule Properties - 2

Homogeneous granules with low degree of fines vs spray drying



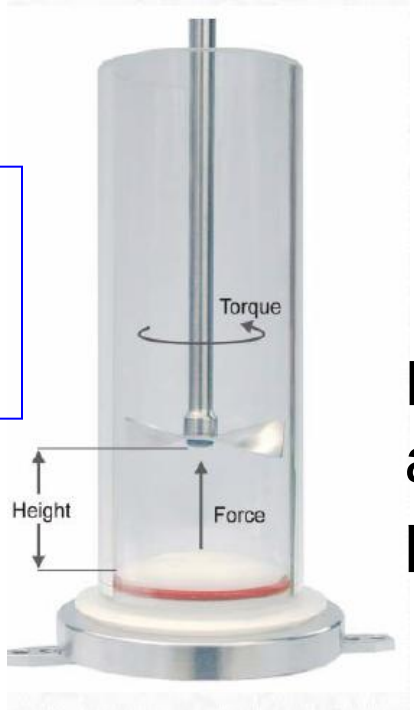


No cavities and equality in composition independent of granule size

Air atomization gives wide granule size distribution, can be fractionized and oversized is easy to recirculate

Flow properties

Granule flow is essential in automated pressing operations



Powder rheology (Flow Energy)

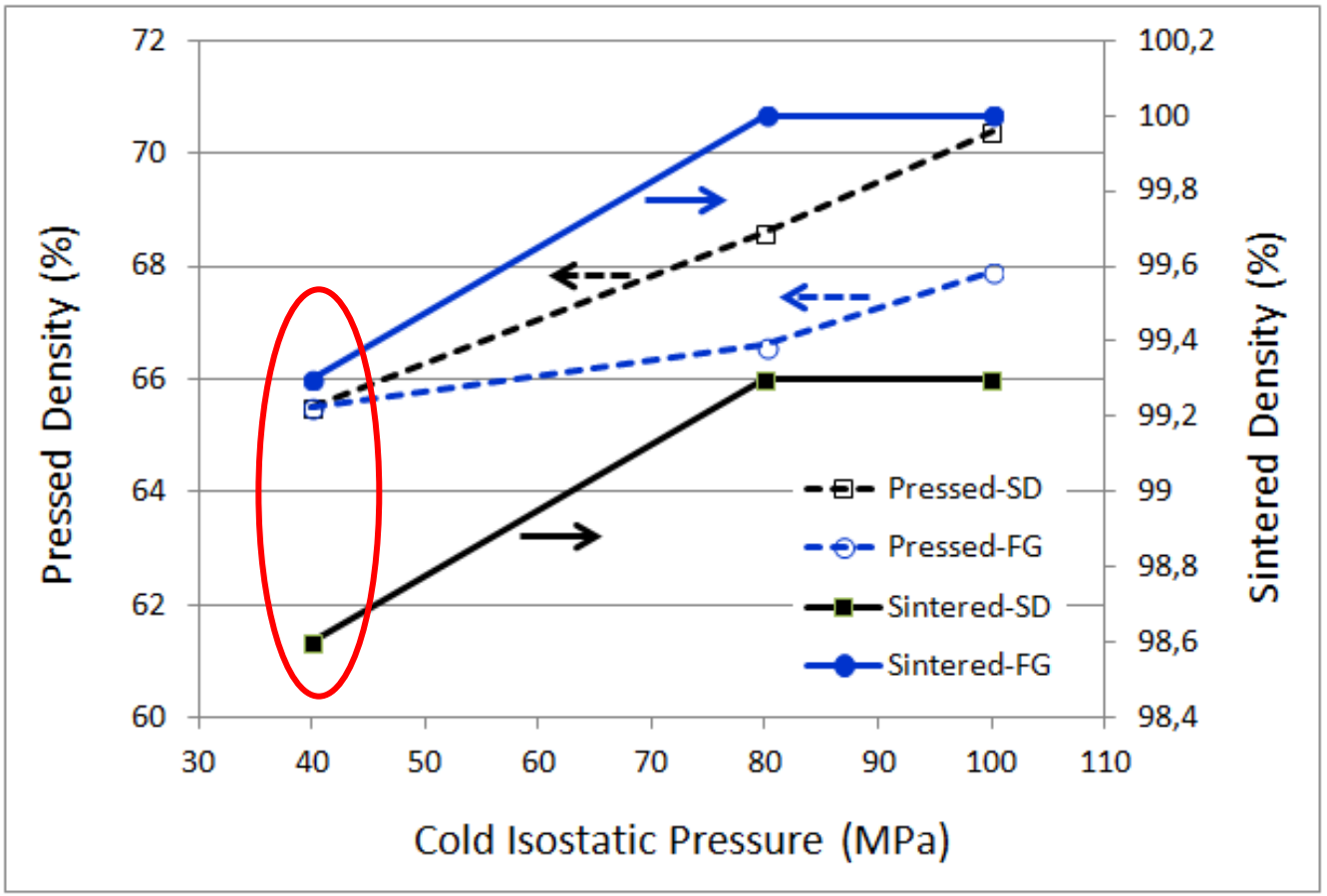
Measure the force to rotate a blade down and up in a powder bed

Zirconia granules	Flow Energy (mJ)	Bulk density (g/ml)
FG-PEG (-150 µm)	170	1.37
FG-Latex (-150 µm)	168	1.31
SD-Latex (-150 µm)	182	1.24

FG produced granules showed better flow and higher bulk density than a commercial SD version

Pressing

Cold Isostatic Pressing and sintering of alumina specimens



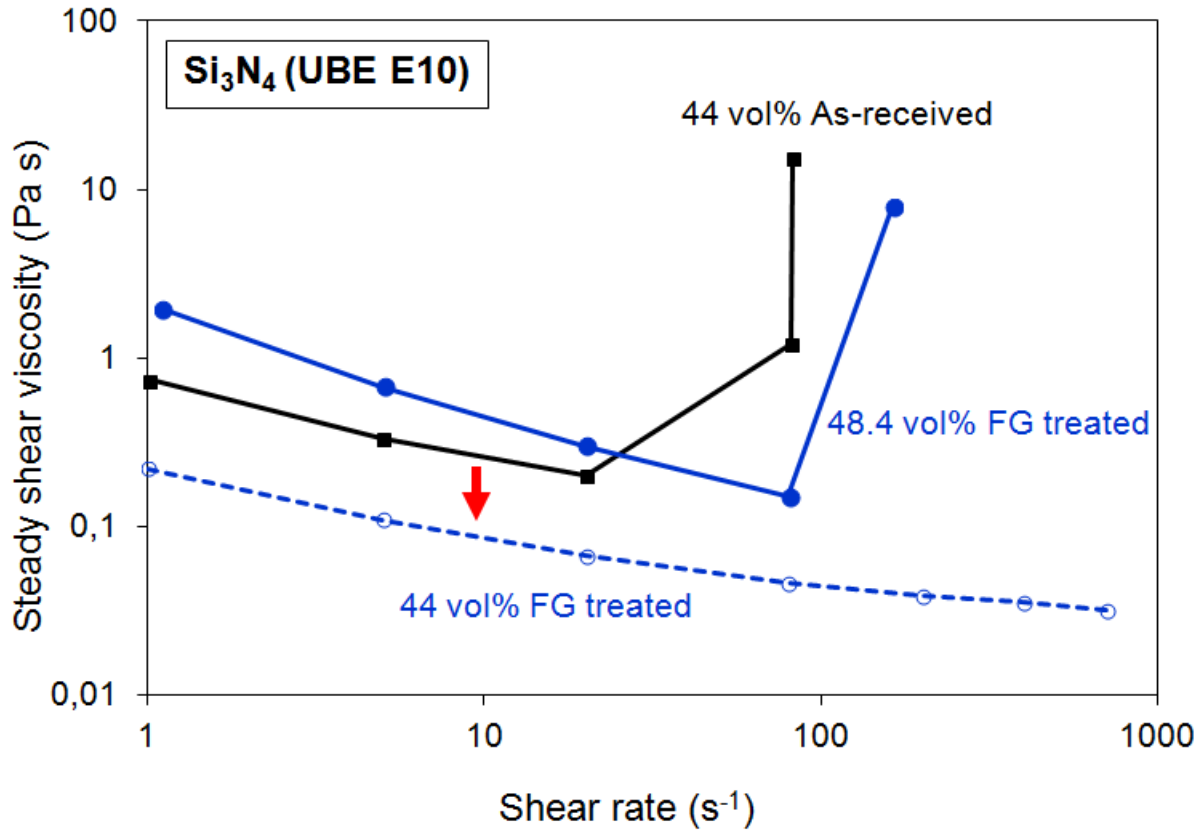
Spray-dried (SD)

Freeze-granulated (FG)

FG-granules required lower CIP pressure to reach higher sintered density vs SD-granules due to homogeneity

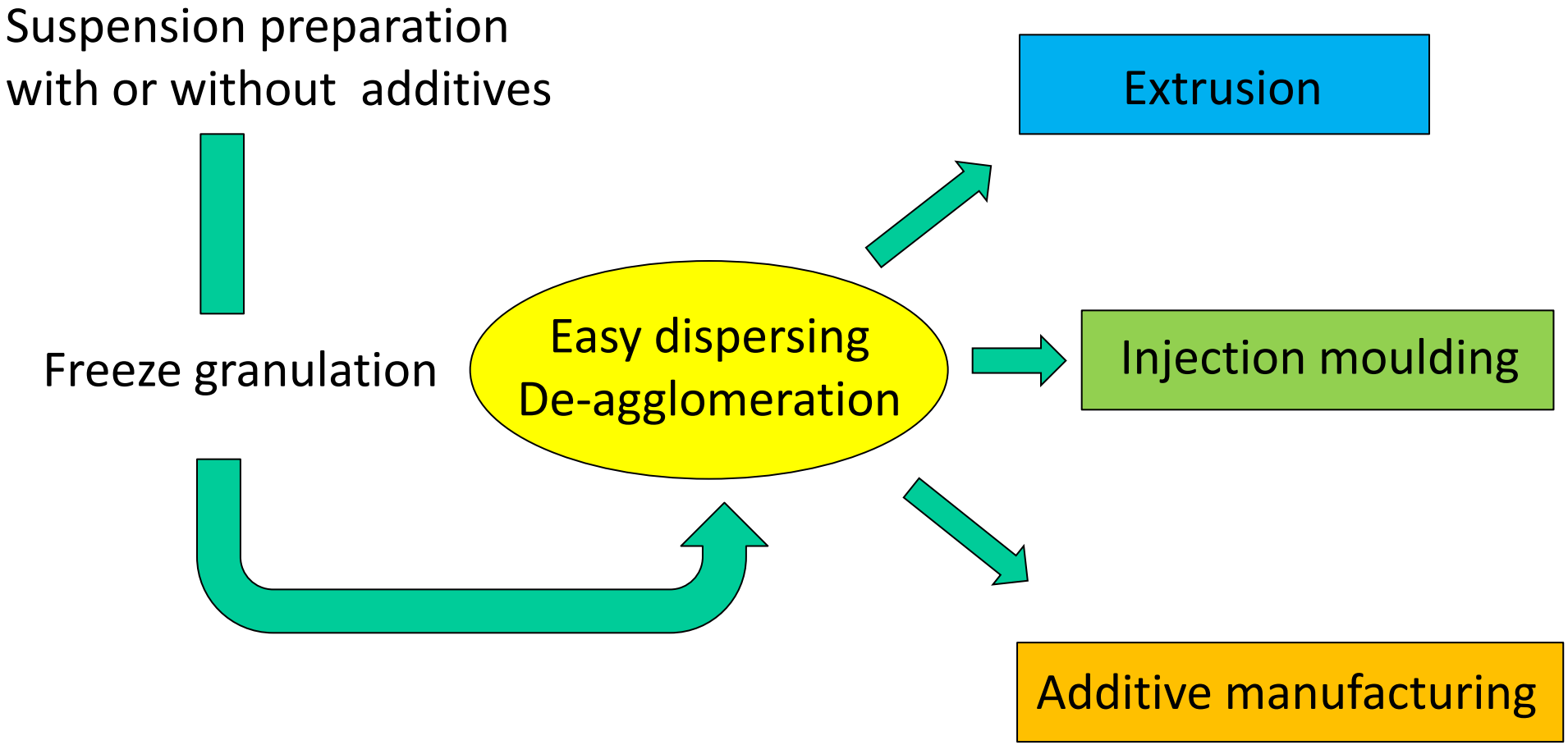
FG-granules – Easy to re-disperse

Powders that are difficult to deagglomerate can be dispersed at low concentrations, freeze granulated and re-dispersed at higher concentrations



Also favourable for pre-processing of nanopowders, graphene etc

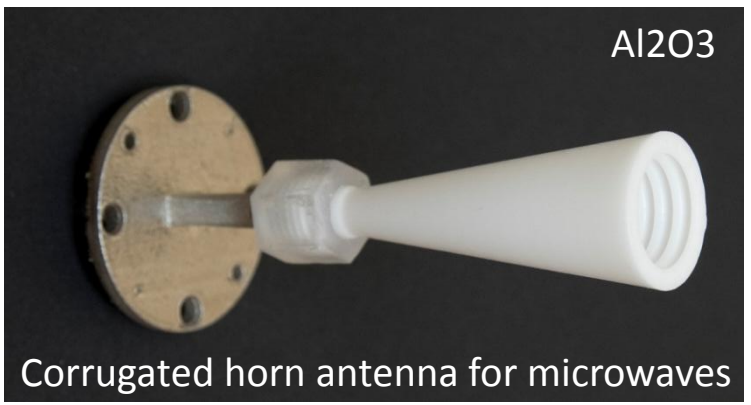
Applications with high powder loading



Additive manufacturing (Stereolithography)

- Suspension preparation by ball milling in organic media with dispersant compatible with the photopolymer system
- Freeze granulation ⇒ Easy and rapid re-dispersing into the photopolymeric resin with mild impeller stirring
- Larger batch of prepared powder can be produced and stored to be available

Components manufactured in Cerafab 7500 (Lithoz GmbH)



- Application of FG for other AM-methods are under development

Material/Powder Synthesis

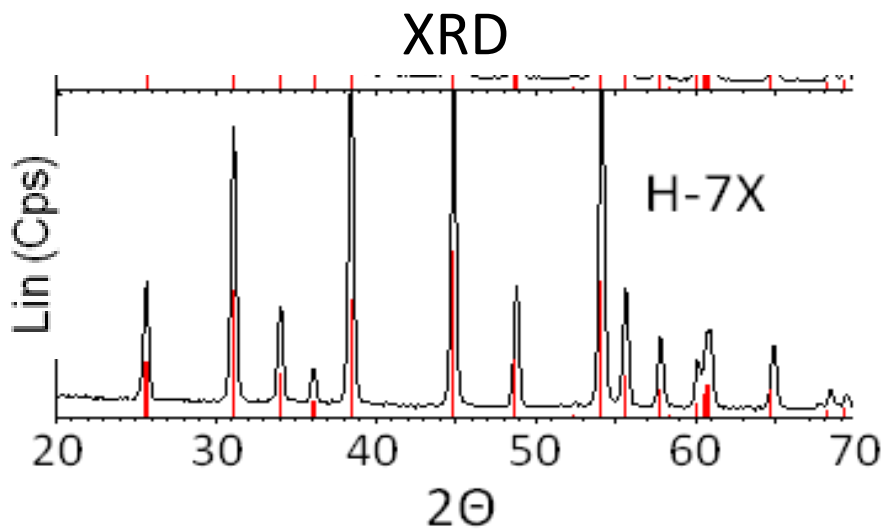
- Solids, salts and/or metal organic compounds are mixed and effectively homogenized in a liquid prior to FG
- Liquid medium depends on the material, reactivity to water requires organic solvent with suitable freezing point, in the range of -15 to +10°C
- Due to high degree of homogeneity, solid-state synthesis with high yield by calcination
- Further processing depends on application

Water based synthesis and processing of $LiFePO_4$

Solid Solid Dissolved

$Li_2CO_3 + 2\ FeC_2O_4{*}2H_2O + 2\ NH_4H_2PO_4 \Rightarrow 2\ LiFePO_4$ + Bi-products

Ball milling → **Stirring** →



High degree of pure crystalline $LiFePO_4$

Freeze granulation

Calcining
(600-800°C i reducing atm)

Evaluation

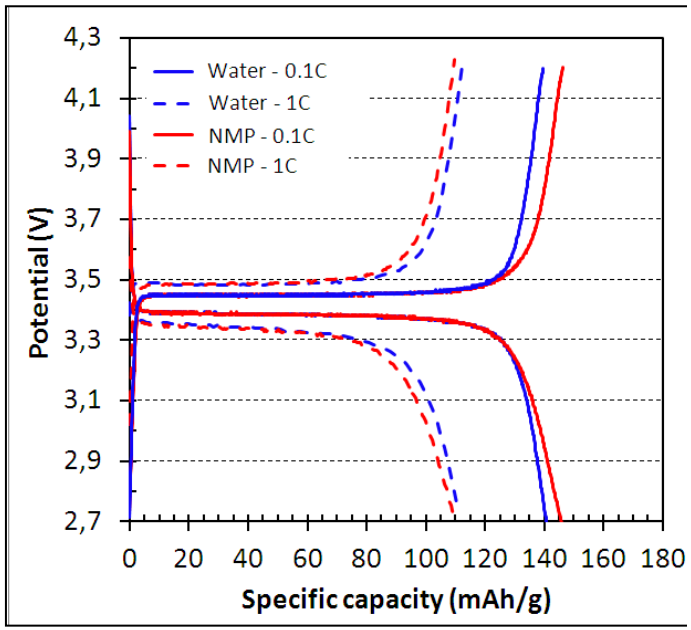
Milling and freeze granulation

Cathode manufacture

Electrochemical Performance

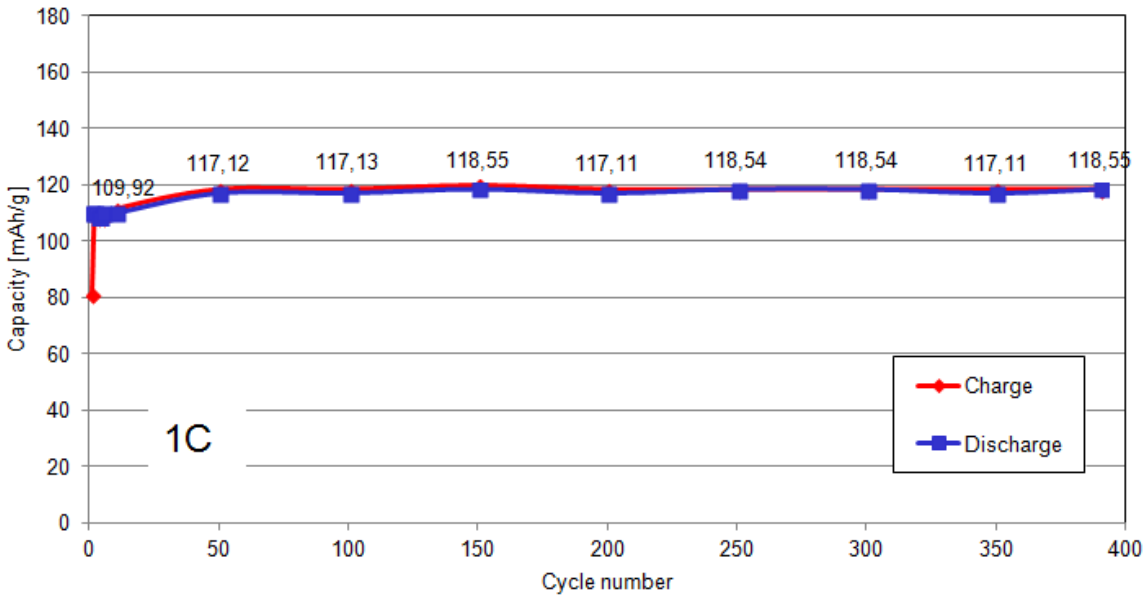
Water vs NMP (toxic solvent) produced cathode by tape casting

Charge and discharge curve



The obtained discharge capacity at the current rate 0.1C was 141 mAh/g, corresponds to 83% of the theoretical capacity (170 mAh/g).

Long term charge/discharge testing



Excellent long term performance with maintained capacity over 400 cycles

Publication: J. Orlenius, O. Lyckfeldt, K.A. Kasvayee, P. Johander, “Water based processing of LiFePO4/C cathode material for Li-ion batteries utilizing freeze granulation”, Journal of Power Sources 213 (2012) 119-127

Particle manufacture

- FG can be utilized to produce particles (aggregates) for
  - Catalytic purpose where porosity and high specific surface can be controlled
  - Thermal spraying where nano/micron sized particles can be utilized for improved coating performance
- Suspension of powder mix is prepared and FG processed
- FG-produced granules are calcined or pre-sintered to certain degree to obtain specific granule porosity and/or strength
- Size fractioning for the specific process

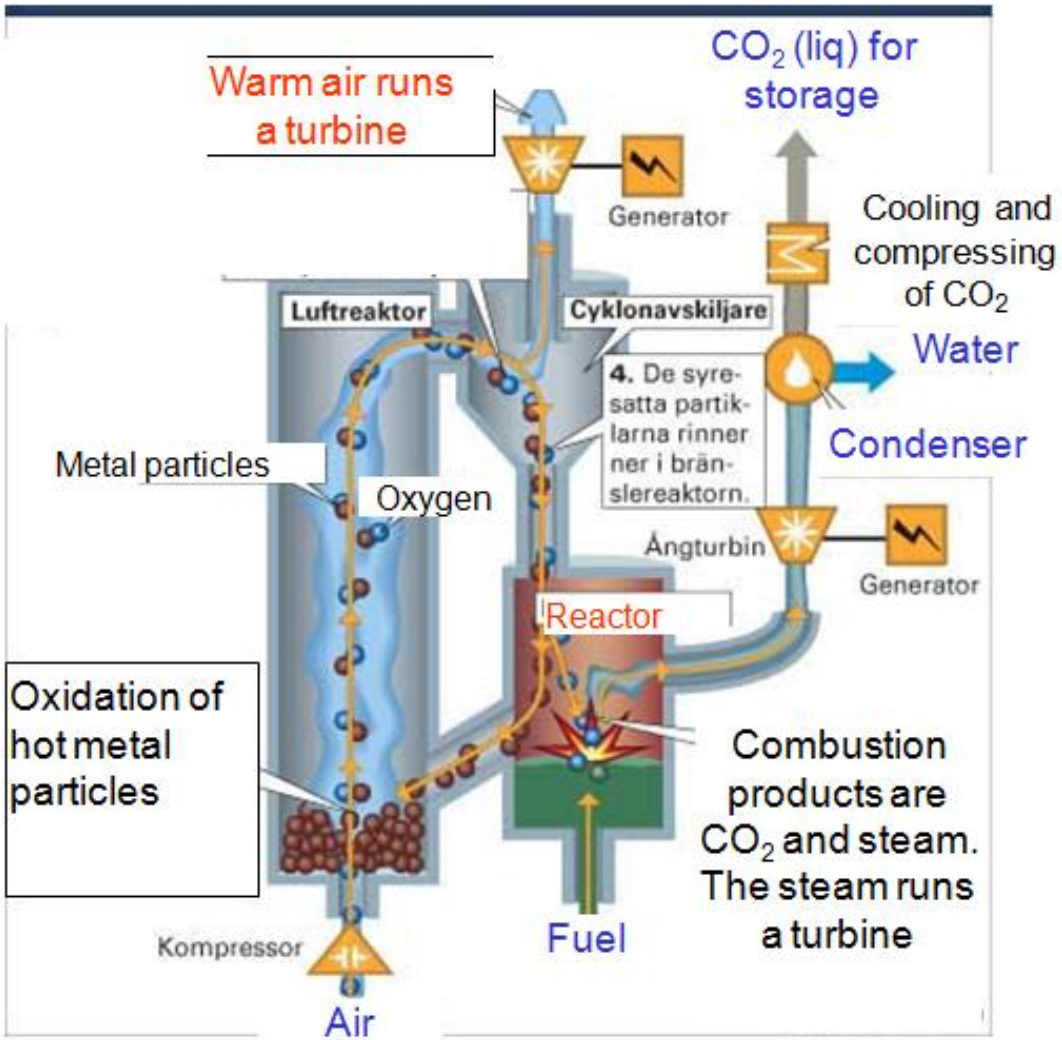
Medium for Two-Step Combustion

(Department of Energy Technology, Chalmers University of Technology)

- Particles (90–200 µm) of metal oxides catalyse combustion of natural gas via reduction to metal – the metal particles are re-oxidised by air and the process is restarted

- A lot of powder mixes of metal oxides have been freeze granulated, sintered and evaluated regarding reactivity and granule (particle) strength

⇒ The most promising materials have been processed in a 10 kW pilot plant with excellent results



Advantages of Freeze Granulation

- The granule density can be controlled (solid content of the slip)
- No cavities in the granules
- No migration of small particles and/or binder gives a high degree of granule homogeneity
- A mild drying procedure minimises oxidation of non-oxides and metals
- Lower specific granule density and evenly distributed pressing aids gives softer granules and ensure that all granules are broken during compaction
- Low waste of material (high yield)
- Not only larger quantities but also very small experimental batches (50–100 ml slip) can easily be processed
- The equipment is easy to clean (allows the use of latex as binder)
- Possibility of recycling organic solvents

Disadvantages of Freeze Granulation

- Two-step process: in-freezing and batch-wise freeze-drying
- Limitation in the choice of solvent, based on the freezing properties – a freezing point between –20 and +10 °C is recommended
- Limited scale capacity < ca100 kg granules (depends on material density) or processing of up to 80-100 liter suspension per day excludes processing of low-performance materials in large scale

Laboratory Granulator LS-6

- Impeller version (LS-6mns) for magnetic or heavy materials
- Capacity to pump feed up to 6 l powder suspension per hour – Processing of up to 3 l suspension per hour in practice
- Easy to set up and clean – many small samples can be prepared in a day
- Freeze-dryer with suitable capacity is required

Production granulator PS-20

Prototype developed and tested

Capacity to process up to 20 litre suspension per hour

No manual handling of liquid nitrogen

Frozen granules collected free from liquid nitrogen

Commercial version will be design and equipped according to costumers preferences

Freeze dryer Alpha 1-4 LSC plus

Heated trays for quick drying

Capacity to dry ca 2 litre of granules per day, achieved from ca 1 litre powder suspension

Ordinary household freezer can be used for storage of frozen granules

Driers with higher capacities are available on the market

The spread of FG

Globally, FG-equipments sold to 23 countries

Summary of Multi-purpose FG

Due to the homogeneity preservation, weak bonding within the granules, limited oxidation of sensitive materials, limited damage of organic compounds makes the use of this technique versatile

- Granulation for powder pressing (ceramic and metals)
- Pre-preparation for easy mix into formulation for PIM, extrusion, AM etc - supporting high powder loading
- Material synthesis with high yield
- Preparation of easy re-dispersible nanopowder or graphene
- Production of carrier particles for various catalysts
- Production of high performance particles for thermal spraying
- Pharmaceutical and biomaterial applications

Thanks for your attention!

Welcome to Powderpro’s exhibition stand for discussions

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