Optimizing a LTO synthesis process for an industrial up scaling

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MAT4BAT Summer School, EIGSI La Rochelle, 02-04/06/2015

- **World leader** in the production of **phosphoric acid and phosphates**, for **food and technical** applications

- **Products** and **technical services**

- Headquarters in **Engis, Belgium**, 4 production sites (BE, FR and USA), 1.400 people

- Total turnover > 800 M€

- 2008 : **Technology transfer from CEA for LFP**

PRAYON + cea liten → praylion

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- 2012 : **Joint venture with Umicore for LFP**

- Joint Venture by Umicore (49%) and Prayon (51%)
- Phosphate based cathode materials for use in Li-ion batteries
- Industrial pilot plant located in Engis, Belgium.

- Production, R&D and analysis in Engis, Belgium
- Lab pilot plant : 300 kg/month
- Industrial pilot plant : 100 t/year
- Design capacity : 2500-3000 t/year

SEVENTH FRAMEWORK PROGRAMME

PRAYON

- AMELIE, 2011-2014

Advanced Fluorinated Materials for High Safety, Energy and Calendar Life Li-Ion Batteries

- ELIBAMA, 2011-2014

European Li-Ion Battery Advanced Manufacturing for electric vehicles

HORIZON 2020

beLife by Umicore & Prayon

- BASMATI, 2015-2018

Bringing Innovation by Scaling up Nanomaterials and Inks for Printing

- SPICY, 2015-2018

Silicon and Polyanionic Chemistries and Architectures of Li-Ion Cell for High Energy Battery

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Silicon and Polyanionic Chemistries and Architectures of Li-Ion Cell for High Energy Battery

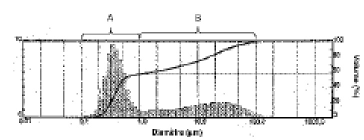
Starting point : CEA process for LTO at lab scale

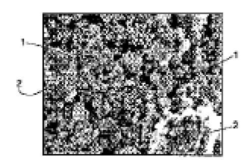
Patent FR 2 874 603 (2004)

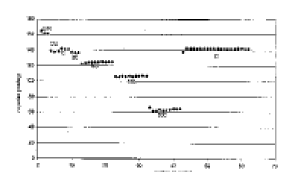
Carole Bourbon, Séverine Jouanneau, Frédéric Le Cras, Hélène Lignier

(54) COMPOSE PULVERULENT D'OXYDE MIXTE DE TITANE ET DE LITHIUM DENSE, PROCEDE DE FABRICATION D'UN TEL COMPOSE ET ELECTRODE COMPORTANT UN TEL COMPOSE.

(57) Un composé pulvérulent d'oxyde mixte de titane et de lithium, de préférence, utilisé comme matériau actif d'une électrode pour accumulateur au lithium est constitué de particules (1) ayant un diamètre inférieur ou égal à 1µm et d'au moins 10% en volume de grains (2) ayant un diamètre inférieur ou égal à 100µm et formés par agglomération desdites particules (1). Le procédé de fabrication d'un tel composé consiste, de préférence, à broyer, l'oxyde synthétisé, pendant une durée comprise entre 24 heures et 48 heures, dans un broyeur planétaire, puis à réaliser un traitement thermique à une température comprise entre 450°C et 600°C.







FR 2 874 603 - A1

Starting point : CEA process for LTO at lab scale (100-200g)

$$2\ Li_2CO_3 + 5\ TiO_2 \rightarrow Li_4Ti_5O_{12} + 2\ CO_2$$

Operation	Equipment	Duration
Wet milling	Planetary mill	1 h
Drying, 60°C	Oven	12 h
Firing 1, 500°C	Muffle furnace	17 h
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Planetary mill : no large size, batch only

Wet milling : expensive drying

Firing : too long

Multiple firings : expensive

Muffle furnace : ok, batch only

Overall duration : way too long

Possible improvements for industrial up scaling

Lab machine/process	Industrial solution	Advantages	Disadvantages

Possible improvements for industrial up scaling

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Planetary mill	High energy horizontal ball mill	High energy, low milling time	High cost of large machines, high temp.
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Multiple firings	Single firing	Cheaper	Lower product quality?

Lab process VS industrial process

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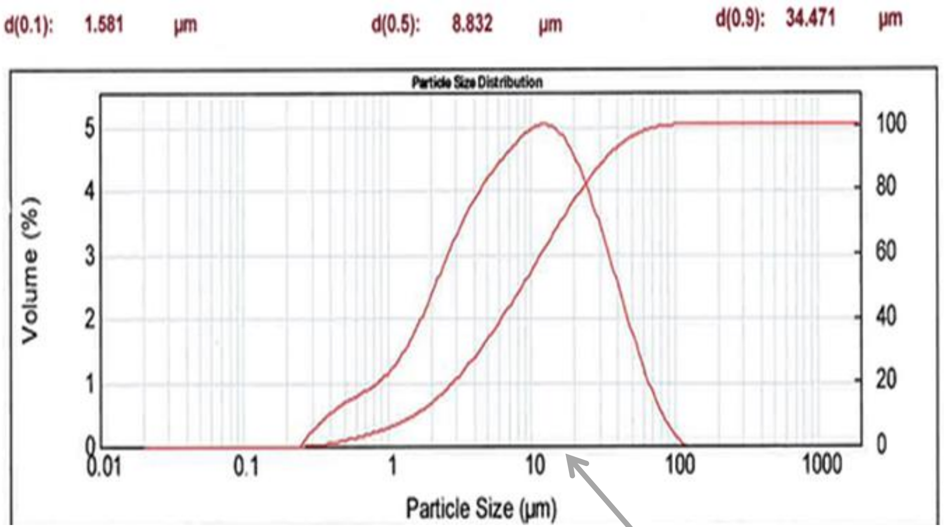
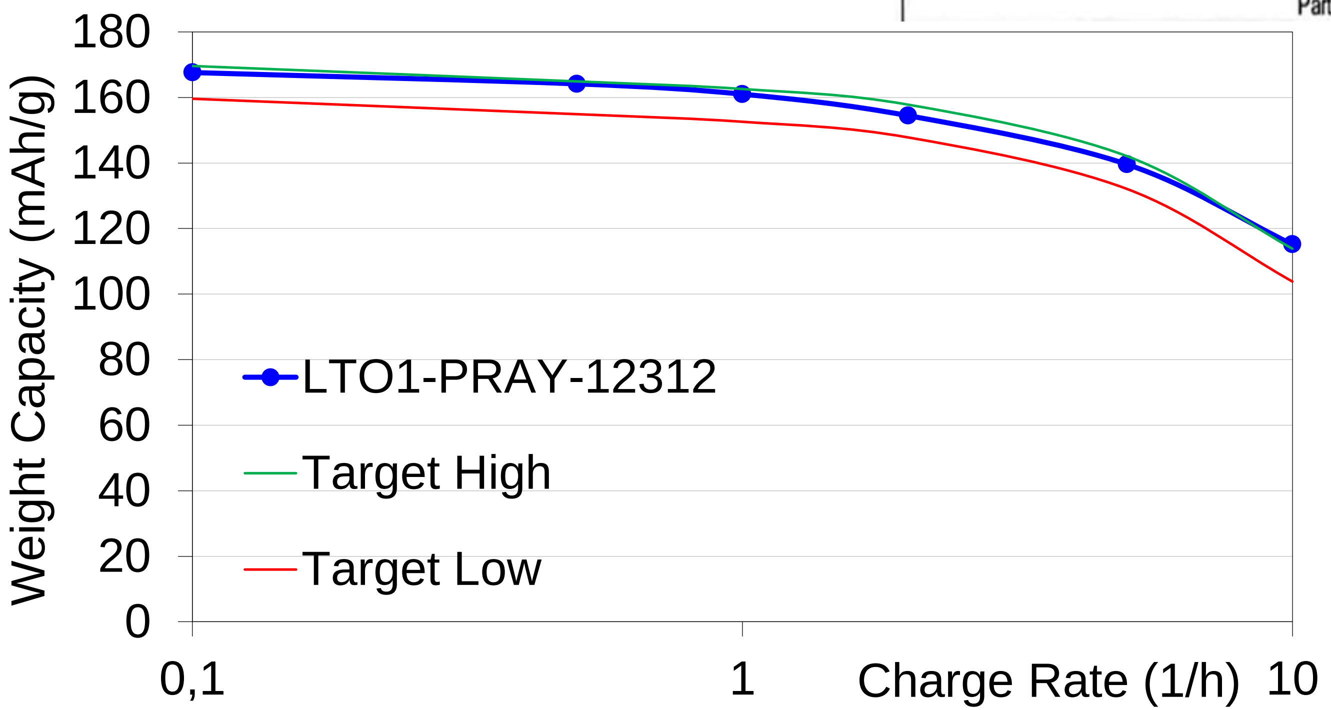
LTO after firing in rotating tube furnace

Performance is inline with ELIBAMA targets



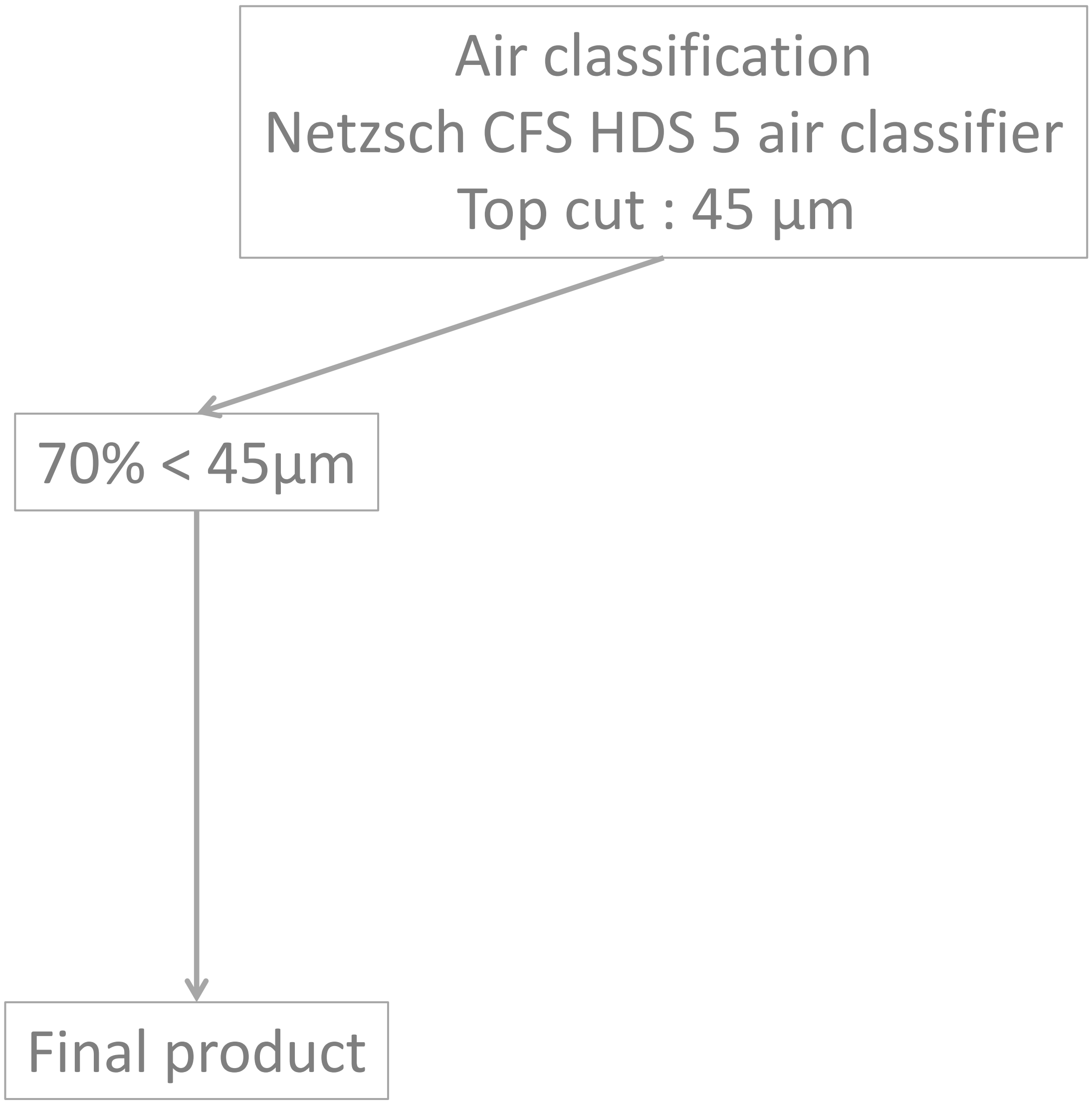


PSD's too coarse

Bad electrode coating with scratches

Classification/milling required

LTO after firing in rotating tube furnace



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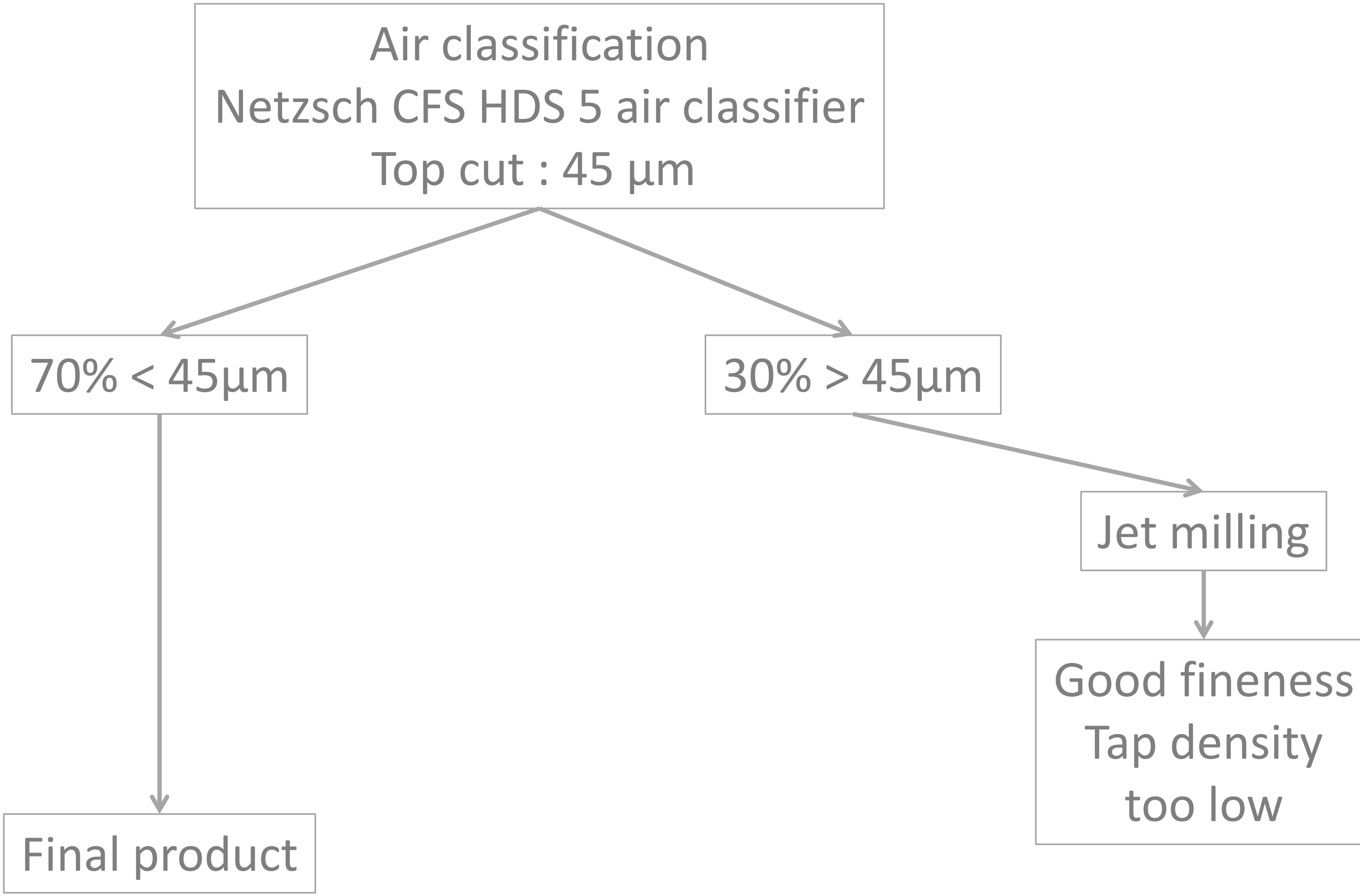

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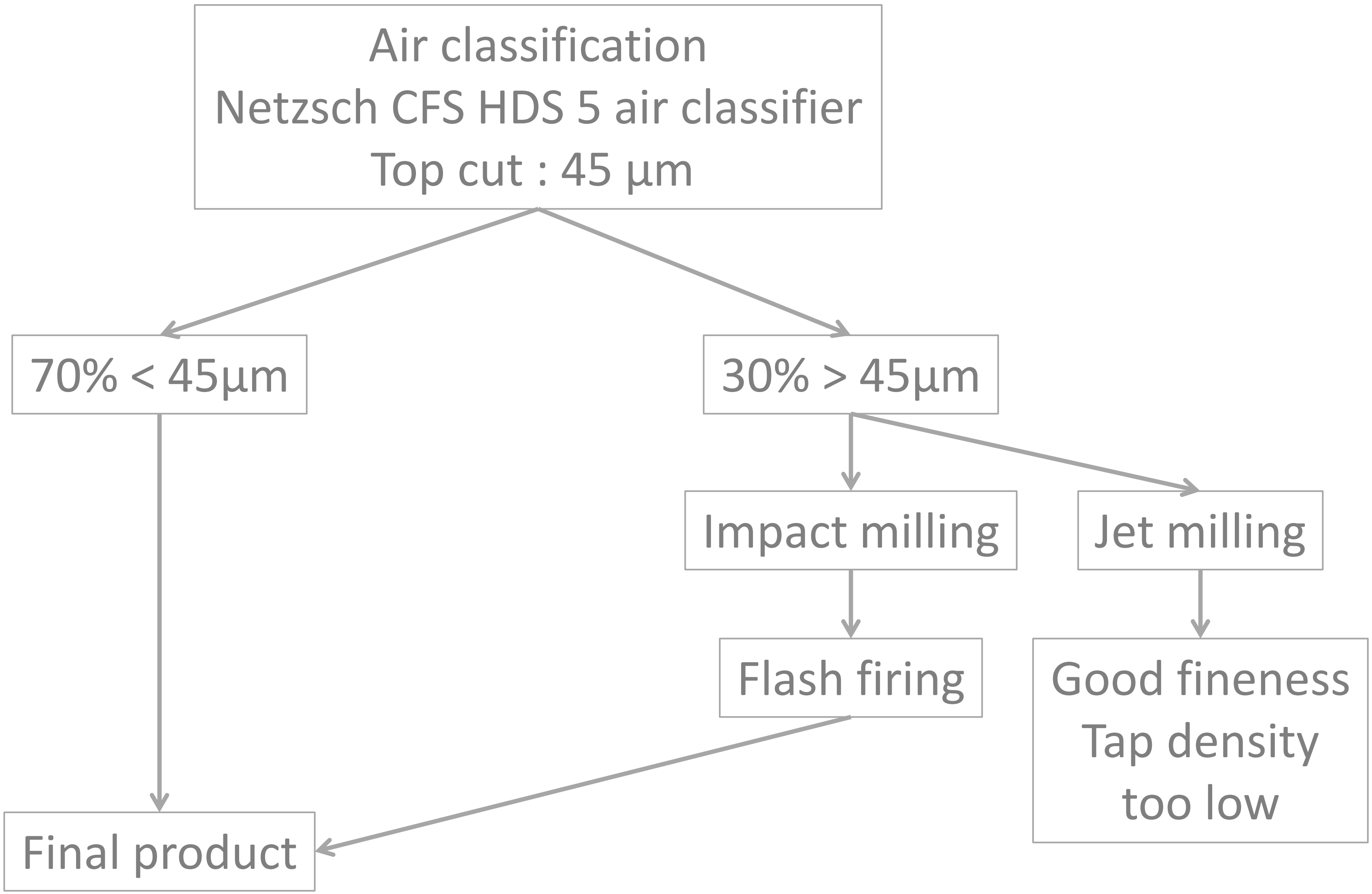
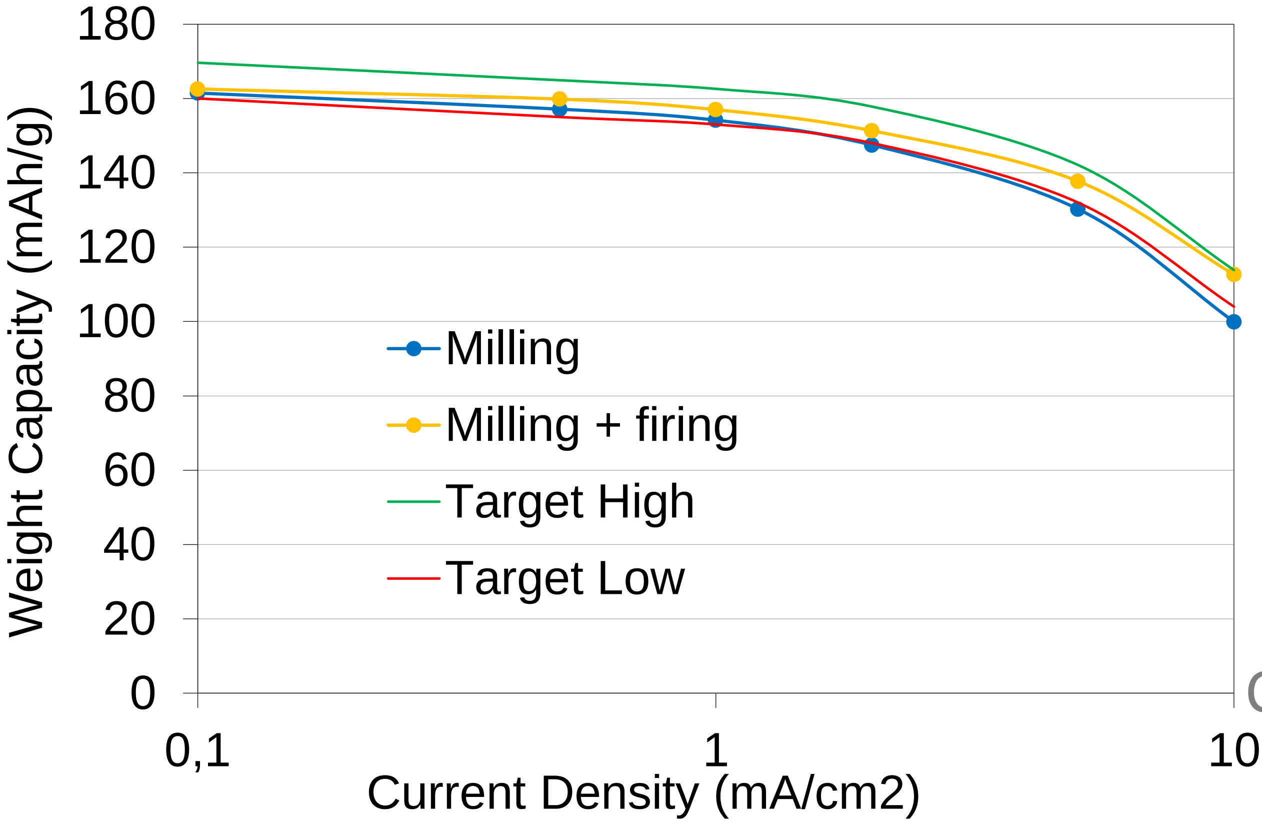


LTO after firing in rotating tube furnace

Air classification
Netzsch CFS HDS 5 air classifier
Top cut : 45 µm



30% > 45µm

Impact milling

Flash firing

Good performance after firing

Classification/milling is still to be optimized

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Firing 4, 900°C	Muffle furnace	8 h			
Dry milling	Planetary mill	24 h	Dry milling	Impact mill with classifier	TBD
Firing 5, 500°C	Tube furnace	0 h 15	Firing 2, 500°C	Rot. Tube furnace	0 h 15
10 steps	**4 machines**	**98 h 45**	**4 steps**	**4 machines**	**5-6 h**

Conclusions

The **lab process** (100-200 g) was successfully **upscaled** to a **small pilot** scale (2 kg)

The duration of the synthesis was reduced from **100 h to 6 h**

All technologies involved are **available** at an **industrial scale**

Perspectives

The final impact milling – classification step is still to be optimized

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