SimDOME

# User Story: Predicting the crystal size distribution of NMC precursor particles produced via wet-phase synthesis

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| Aims | • Predict the crystals size distribution of $Ni_xMn_yCo_z(OH)_2$ precursors particles produced by co-precipitation |
| Methodology | • Couple CFD with chemical and population balance models |
| Results | • Predict the equilibrium concentration of species in liquid solution<br>• Predict the crystal size distribution of solid particles formed by co-precipitation |

## Summary


$Ni_xMn_yCo_z(OH)_2$ precursor particles constitute the first solid product in the value chain of Li-ion batteries cathode materials. One of the most common approaches to produce these particles at industrial scale is via a co-precipitation also known as wet-phase synthesis.

Because the electrochemical performances of NMC-based batteries depend on the characteristics of these precursor particles, being able to predict the final precursor population properties using the reactor operating conditions as sole inputs is key to:

(a) understand the effect of process parameters on the crystals population,
(b) adapt these parameters to obtain the desired product specs.

The comprehensive approach developed by POLITO in the framework of the SimDOME project couples Computational Fluid Dynamics (CFD) with a chemical equilibrium solver and Population Balance Modelling (PBM) to predict the liquid mixture mixing, the equilibrium concentrations of the most important species in solution and the formation and evolution of the solid particles population [1].

The model is now being used by Umicore to predict the particles size distribution of NMC precursor materials produced at industrial scale to design new reactors and optimize their process conditions.



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## Case Description

The coupled CFD-PBM model has been used to simulation a co-precipitation process carried out in a multi-inlet vortex mixer (MIVM) at POLITO (see Fig. 1) [1]. It consists of four inlet pipes of 1 mm diameter, a mixing chamber with a diameter of 4 mm and height of 1 mm, and an outlet pipe of 2 mm diameter and 41 mm length. Two inlets are used to inject sodium hydroxide, one to inject ammonia and the last one is used for metal sulphates. The metal mix is set to 80% nickel, 10% cobalt and 10% manganese (NMC811). In addition, the temperature is set to 25 °C, and the flow is assumed to exit at atmospheric pressure. The total inlet flow rate is set to 70 ml/min and the inlet metal concentration is varied between 0.01 and 1 M. The inlet concentration of ammonia and sodium hydroxide is set such that the ratio between them and the inlet metal concentration is $[M^{2+}]:[NH_3]:[NaOH]=1:1:2$. Additional details about the simulation setup can be found in [1].

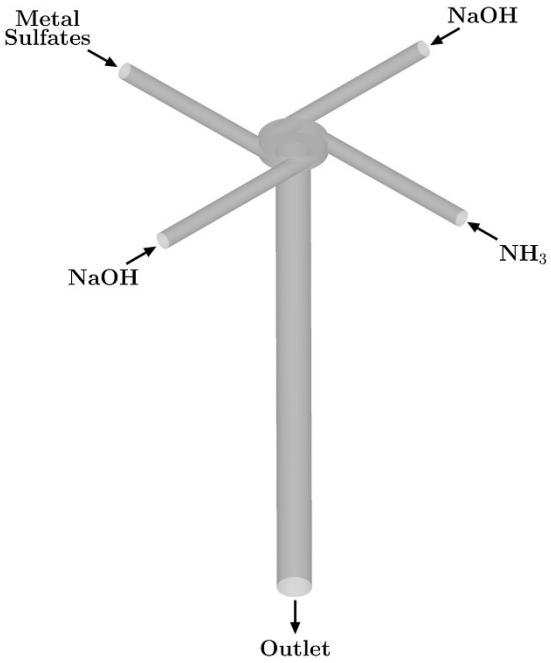


*Figure 1: Sketch of the MIVM.*

## Results

The spatial distribution of Sauter mean diameter which can be seen as the average diameter of the particles population is shown in a vertical cross-section plane in Fig. 2. This contour plot illustrates the evolution of the average particles diameter as liquid species are injected in the MIVM.

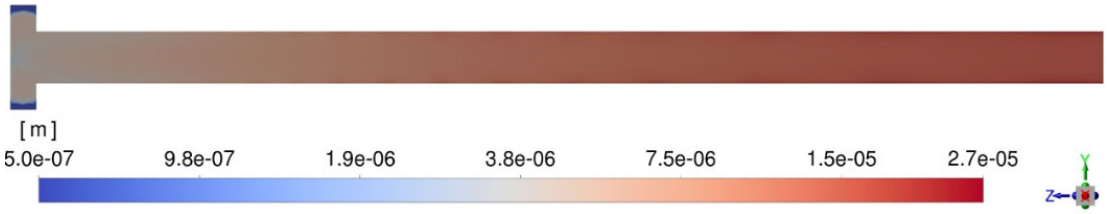


*Figure 2: Contour plot of Sauter mean diameter (m) for an inlet metal concentration of 0.1 M.*

The results show that NMC precursor particles tend to first precipitate in the mixing chamber, where their diameter quickly grow from 0.5 µm to 5-6 µm. Then, because the supersaturation is not completely consumed in the mixing chamber, particles tend to grow and agglomerate as they flow downward in the outlet pipe. At the end of the pipe, the mean diameter is significantly larger than in the mixing chamber and can reach values up to 27 µm.

The influence of the inlet metal concentration on the final particles size distribution can be assessed by averaging the particles properties over the MIVM outlet surface and by reconstructing the particle size distribution using an assumed log-normal shape. The PSDs corresponding to the different inlet metal concentrations are shown in Fig. 3.

Contact us:
emanuele.ghedini@unibo.it

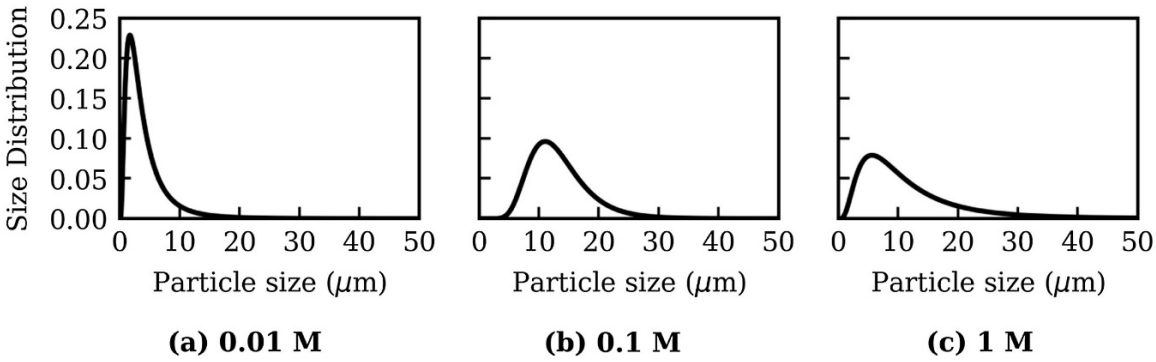


*Figure 3: Particle size distribution (number density) at the outlet of the micromixer for three inlet metal concentrations (assumed log-normal shape).*

The results show that increasing the inlet metal concentration tends to widen the outlet particles size distribution, which can be explained by the strong effect of particles aggregation at higher concentrations [1].

## Conclusion

The CFD-PBE model developed in the framework of the SimDOME project is an iteresting tool that allows to predict the size distribution of solid particles produced by co-precipitation in liquid solution. The model has been applied to the MIVM system and predicted realistic particles sizes that were in relatively good agreement with experimental data. This model is now being used to predict the properties of NMC precursor particles produced at industrial scale in CSTRs operated by Umicore.

Link to download the software: https://github.com/mulmopro/wet-synthesis-route

## References

[1] M. Shiea, A. Querio, A. Buffo, G. Boccardo, D. Marchisio. *CFD-PBE modelling of continuous Ni-Mn-Co hydroxide co-precipitation for Li-ion batteries*. Chemical Engineering Research and Design **177** pp. 461-472 (2022).

Contact us:
emanuele.ghedini@unibo.it