

Coprecipitation of  $\text{NixMnyCoz(OH)}_2$  as precursor for ion lithium batteries: Influence of mixing and operating conditions

*Original*

Coprecipitation of  $\text{NixMnyCoz(OH)}_2$  as precursor for ion lithium batteries: Influence of mixing and operating conditions / Para, M. L.; Alidoost, M.; Shiea, M.; Buffo, A.; Boccardo, G.; Pisano, R.; Barresi, A.; Marchisio, D.. - ELETTRONICO. - (2021). (Intervento presentato al convegno 21st International Symposium on Industrial Crystallization tenutosi a online event nel 30 August-2 September 2021).

*Availability:*

This version is available at: 11583/2979712 since: 2023-07-04T13:47:52Z

*Publisher:*

DECHEMA

*Published*

DOI:

*Terms of use:*

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

(Article begins on next page)



# DECHEMA

Gesellschaft für Chemische Technik  
und Biotechnologie e.V.

## PROGRAMME

30 August – 2 September 2021 · Online Event

# ISIC 21

## 21<sup>st</sup> International Symposium on Industrial Crystallization

[www.dechema.de/ISIC\\_2021](http://www.dechema.de/ISIC_2021)



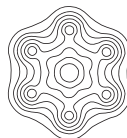
© Max-Planck-Institut, Magdeburg



EFCE

EFCE-Event-Nr. 751

SUPPORTED BY



FCI  
FONDS DER  
CHEMISCHEN  
INDUSTRIE



*crystals*

an Open Access Journal by MDPI

## Wednesday, 1 September 2021

Reactive Crystallization		Virtual Room 2
<i>Chair: B. Biscans, University of Toulouse, CNRS, INP, UPS, Toulouse/F</i>		
08:30	<b>Crystallization of (lanthanide, calcium) phosphate nanophosphors</b> J. Gómez-Morales <sup>1</sup> ; R. Fernández-Penas <sup>1</sup> ; C. Verdugo-Escamilla <sup>1</sup> ; D. Choquesillo-Lazarte <sup>1</sup> ; C. Drouet <sup>2</sup> ; F. Oltolina <sup>3</sup> ; M. Prat <sup>3</sup> ; M. Iafisco <sup>4</sup> ; J. Fernández-Sánchez <sup>5</sup> ; <sup>1</sup> Instituto Andaluz de Ciencias de la Tierra, Consejo Superior de Investigaciones Científicas, Armilla/E; <sup>2</sup> CNRS / University of Toulouse/F; <sup>3</sup> University of Piemonte Orientale, Novara/I; <sup>4</sup> CNR - National Research Council of Italy, Faenza/I; <sup>5</sup> University of Granada/E	
08:50	<b>Control of Reaction Crystallization of Organic Compounds Considering with Supersaturation Profile</b> H. Takiyama <sup>1</sup> ; <sup>1</sup> Tokyo University of Agriculture and Technology, Tokyo/J	
09:10	<b>A compartmental-based approach for the modelling of a vortex precipitation reactor for nuclear energy applications</b> C. Ruiz Vasquez <sup>1</sup> ; N. Lebaz <sup>2</sup> ; D. Mangin <sup>2</sup> ; M. Bertrand <sup>3</sup> ; E. Saikali <sup>4</sup> ; M. Rodio <sup>4</sup> ; G. Bois <sup>4</sup> ; U. Bieder <sup>4</sup> ; <sup>1</sup> CEA Marcoule, Villeurbanne, France/F; <sup>2</sup> LAGEPP, Université de Lyon, CNRS UMR5007, Lyon/F; <sup>3</sup> CEA, DEN, DMRC, Université Montpellier, Marcoule/F; <sup>4</sup> CEA, DEN, STMF, Saclay/F	
09:30	<b>Model-based design and control of precipitation processes in industrial applications</b> L. Metzger <sup>1</sup> ; M. Kespe <sup>1</sup> ; T. Beierling <sup>1</sup> ; M. Voges <sup>1</sup> ; <sup>1</sup> BASF SE, Ludwigshafen/D	
09:50	<b>Discussion with speakers</b>	
10:10	<b>Coffee Break</b>	
10:30	<b>Poster Session III</b>	
12:00	<b>Lunch Break</b>	
Plenary and Keynote Lectures		Virtual Room 1
<i>Chair: C. Melches, GEA Messo GmbH, Duisburg/D</i>		
12:45	<b>PLENARY LECTURE</b> <b>Recovery of critical metals from battery waste by leaching and precipitation processes</b> B. Biscans <sup>1</sup> ; <sup>1</sup> University of Toulouse, CNRS, INP, UPS, Toulouse/F	
<i>Chair: M. Stepanski, Sulzer Chemtech Ltd, Winterthur/CH</i>		
13:25	<b>KEYNOTE LECTURE</b> <b>Development of a Modelling Framework for the Co-Precipitation of NMC Hydroxide as Precursor for Lithium Battery Cathodes</b> M. Shiea <sup>1</sup> ; M. Para <sup>1</sup> ; G. Tronci <sup>1</sup> ; A. Buffo <sup>1</sup> ; G. Boccardo <sup>1</sup> ; D. Marchisio <sup>1</sup> ; <sup>1</sup> Politecnico di Torino, Turin/I	
13:50	<b>KEYNOTE LECTURE</b> <b>Combining reaction with crystallization for process improvement and intensification in continuous manufacturing of antibiotics</b> H. Salami <sup>1</sup> ; M. McDonald <sup>1</sup> ; P. Harris <sup>1</sup> ; C. Lagerman <sup>1</sup> ; M. Grover <sup>1</sup> ; A. Bommarius <sup>1</sup> ; R. Rousseau <sup>1</sup> ; <sup>1</sup> Georgia Institute of Technology, Atlanta/USA	
14:15	<b>Discussion with speakers</b>	
14:30	<b>Coffee Break</b>	
Battery Materials		Virtual Room 2
<i>Chair: M. Rauls, BASF SE, Ludwigshafen/D</i>		
14:50	<b>Coprecipitation of Ni<sub>x</sub>Mn<sub>y</sub>Co<sub>1-x-y</sub>(OH)<sub>2</sub> as precursor for ion lithium batteries: influence of mixing and operating conditions</b> M. Para <sup>1</sup> ; M. Alidoost <sup>1</sup> ; M. Shiea <sup>1</sup> ; A. Buffo <sup>1</sup> ; G. Boccardo <sup>1</sup> ; R. Pisano <sup>1</sup> ; A. Barresi <sup>1</sup> ; D. Marchisio <sup>1</sup> ; <sup>1</sup> Politecnico di Torino/I	
15:10	<b>Impact of Sulphate Intercalation on the Morphology of Co-Precipitated Battery Material Precursors</b> R. Berk <sup>1</sup> ; L. Metzger <sup>1</sup> ; T. Beierling <sup>1</sup> ; M. Rauls <sup>1</sup> ; <sup>1</sup> BASF SE Ludwigshafen/D	
15:30	<b>Recycling process of lithium from batteries by Li<sub>2</sub>CO<sub>3</sub> precipitation</b> M. Le Page Mostefa <sup>1</sup> ; C. Baumann <sup>1</sup> ; H. Muhr <sup>1</sup> ; <sup>1</sup> LRGP - UMR 7274 CNRS, Nancy/F	
15:50	<b>Discussion with speakers</b>	
16:05	<b>Short Break</b>	
Plenary Lecture		Virtual Room 1
<i>Chair: M. Rauls, BASF SE, Ludwigshafen/D</i>		
16:15	<b>PLENARY LECTURE</b> <b>Industrial crystallization – establishing solid state properties for both downstream processing and product performance</b> D. Green <sup>1</sup> ; <sup>1</sup> GlaxoSmithKline, Colledgeville/USA	
17:00	<b>End of third day</b>	

# Coprecipitation of $\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}(\text{OH})_2$ as precursor for ion lithium batteries: influence of mixing and operating conditions

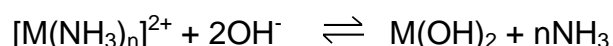
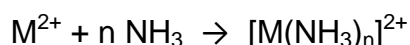
*M. L. Para; M. Alidoost; M. Shiea; A. Buffo; G. Boccoardo; R. Pisano, A. Barresi, D. Marchisio.*

*Dep. of Applied Science and Technology, Institute of Chemical Engineering,  
Politecnico di Torino, Torino, Italy.*

## Introduction

The Lithium ion cathode more widely spread is  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ , nevertheless more recently, research efforts have been targeted towards the development of new cathode compositions due to the high costs and toxicity associated with Cobalt.[1] The  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$  cathode has received much interest as it is associated with lower manufacturing costs, fewer toxicity, higher capacity. Such cathode can be obtained by calcination of the precursor  $\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}(\text{OH})_2$  (NMC hydroxide) mixed with LiOH. It was shown that NMC oxide maintains the morphological characteristics of the precursor, for this reason it is important to study the precipitation process that leads to formation of particles of  $\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}(\text{OH})_2$ , and the effects of the synthesis condition and mixing on the morphological characteristics of particles formed.

The NMC hydroxide can be synthesized by coprecipitation of the transitional metal salts, via wet synthesis, in presence of ammonia. This process consists of mixing the metal sulphate solutions with an ammonia solution and a basic solution.[2]



However, limited experimental data are available in the literature on this coprecipitation process and on the resulting primary particle characteristics, i.e. particle size distribution (PSD), surface area and porosity.

In this work we propose a systematic characterization of the coprecipitation processes to obtain  $\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y}(\text{OH})_2$  in order to investigate the nucleation and growth mechanism.

## Materials and methods

The NMC hydroxides were precipitated through a coprecipitation synthesis process which was carried out within a microscale multi-inlet vortex mixer. This micromixer

was fed up with the metal sulphates, ammonia and NaOH solutions; the outlet stream was collected and quenched for further characterisation. Different ratios between metal, ammonia and NaOH were tested; effects of initial conditions, such as total concentration of the chemical species as well as the flow rates synthesis were investigated.

## Results and discussion

The resulting particles were characterized to evaluate PSD, morphology and composition. The evolution of the mean particle size with initial solution concentration and different ratio  $[M^{2+}]:[NH_3]:[NaOH]$  were investigated.

Regarding the shape of the primary particles, it is observed in Figure 1, that at low initial total metal concentrations crystals are more spherical, while as the concentration increases the crystals tend to grow in one preferential direction. In fact, rod-like crystals formed at an initial total metal concentration of 2 M. This means that as the concentration increases, one-directional growth.

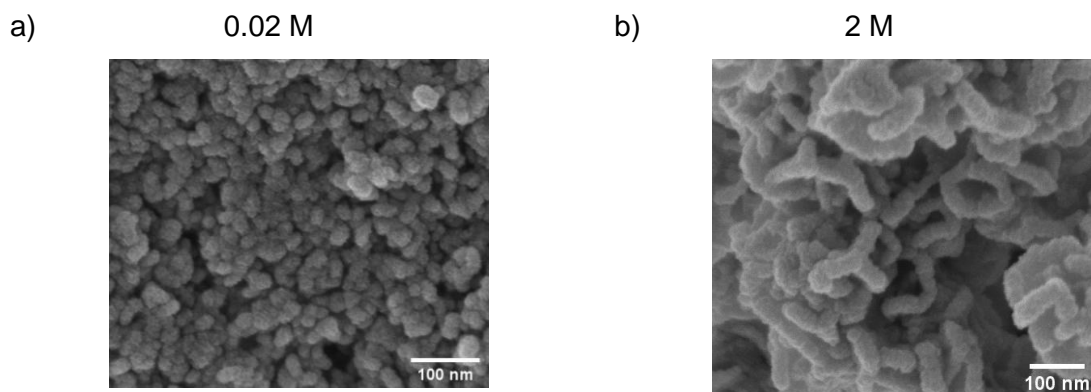


Figure 1: FESEM images for sample prepared at  $[M^{2+}]:[NH_3]:[NaOH] = "1:1:2"$ , at inlet flow rate of 70 mL/min and under different initial total metal concentration: a)  $[M^{2+}] = 0.02$  M and b)  $[M^{2+}] = 2$  M.

Regarding the flow rate, is observed that the mean secondary particle size decreases while increasing the flow rate. This can be explained by the fact that higher flow rates result in better and faster mixing, resulting in turn in higher nucleation rates and smaller particles, even if an increase in flow rate leads also to more aggregation. The resulting effect is the reduction of the mean secondary particle size with the flow rate. This trend is observed for the three different concentration ratios  $[M^{2+}]:[NH_3]:[NaOH]$  tested.

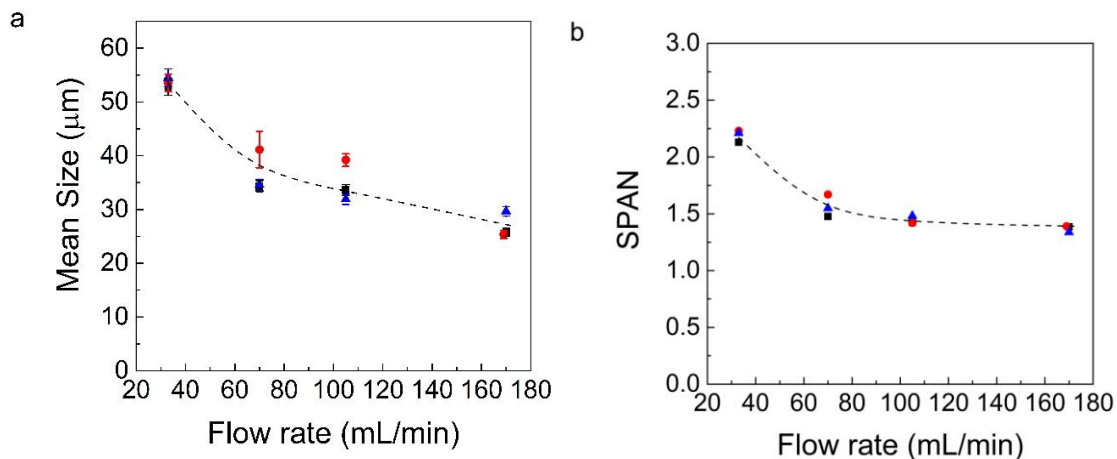


Figure 2: Mean secondary particle size (a) and SPAN (b) versus the flow rate for  $[M^{2+}]:[NH_3]:[NaOH] = "1:0.5:2"$  (black squares), "1:1:2" (red circles) and "1:2:2" (blue triangles). For all cases, the initial total metal concentration  $[M^{2+}]$  was equal to 1 M.

Additionally, the effect of the flow rate on polydispersity, the SPAN number is reported in Figure 2 b, the diminution represents a more monodisperse sample. The higher flow rates produce better and faster mixing within the micromixer, resulting in more uniform and spatially homogeneous supersaturation distributions, producing particles characterized by narrower PSD.

## Conclusions

Initial synthesis conditions have an important effect in this very fast coprecipitation process. Initial total metal concentration and turbulent mixing within the micromixer plays a crucial role in determining the effective concentration of free metal (i.e.  $Ni^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ) cations and of metal-ammonia complexes, i.e.  $Ni(NH_3)_n^{2+}$ ,  $Mn(NH_3)_n^{2+}$  and  $Co(NH_3)_n^{2+}$ , which in turn determines the actual supersaturation ratio.

Furthermore, the initial total metal concentration influences the relative importance of nucleation, molecular growth and aggregation rates, as this is directly related to the resulting supersaturation ratio.

In summary, the initial total metal concentrations influence predominantly in the shape of the primary particles, at higher concentration rod-like crystals are formed. While, faster mixing in the micromixer, leads to precipitates with a lower mean secondary particle size characterized by narrower PSDs (i.e. smaller SPAN numbers), due to a higher nucleation rates.

## **Acknowledgment**

The research reported in this paper was funded by European Union, Horizon 2020 Programme, SimDome Project, Grant Agreement No 814492. The views and opinions expressed in this publication are the sole responsibility of the author(s) and do not necessarily reflect the views of the European Commission/Research Executive Agency

## **Bibliography**

- [1] J. Li, H. Li, W. Stone, R. Weber, S. Hy, and J. R. Dahn, *Journal of The Electrochemical Society*, 2017, 164 (14) A3529-A3537.
- [2] A. van Bommel and J. R. Dahn, *Chem. Mater*, 2009, 21, 1500–1503.