

# **Nucleation kinetics and flow-driven crystallization of lithium phosphate**

Theses of doctoral (Ph.D.) dissertation

**Michael Emmanuel**

Supervisors:

Dr. Ágota Tóth  
Dr. Dezső Horváth

Doctoral School of Chemistry

University of Szeged  
Department of Physical Chemistry and Materials Science

2022



# 1 Introduction and Aims

The development of rechargeable batteries and the high demand for electric cars in the recent years have led to an increased popularity of lithium ion. It not only is useful in the battery technology but also has gained a widespread industrial interest. It is an effective desiccant for ceramics and glass due to the high hygroscopy of its bromide and chloride salts. The hollow shaped lithium phosphate catalyzes propylene oxide isomerization; lithiated esters are high temperature resistant lubricants, and various lithium salts are used as medicine for the treatments of mental illnesses.

With all these applications of lithium, the common source depends on its mining from minerals, certain soil, underground or geothermal waters. This activity is costly and detrimental to the environment, hence recovery from spent lithium ion batteries is a very important step in using a completely environment-friendly source of energy. In 2021, 74% of the world's total lithium mined was consumed in battery production. At this rate of consumption, recycling must be taken seriously to balance the increasing demand. Therefore, to improve and make the recycling process more effective, we must first understand how the final product, which is lithium phosphate, is formed, thereby optimizing the conversion process. During the precipitation process, factors such as supersaturation, temperature, presence of foreign materials, and mixing condition play a role in determining the quality and quantity of the final products formed.

During precipitative crystallization, nucleation and growth are very important processes to investigate. Change in solution properties such as turbidity, pH, conductivity and temperature, could be employed as pointers towards nucleation process. It is feasible to use systems like microfluidics to study the growth of a single crystal through flow-driven or droplet-based techniques. The bulk characteristics of a well-defined architectural buildup can be effectively described using a precipitation system in the form of chemical garden or hydrothermal vent structures.

In this work, three major segments of lithium phosphate precipitation are covered and presented. First, the effect of concentration on the nucleation of lithium phosphate is investigated in a well-stirred system. Secondly, a quasi 2-dimensional microfluidic setup is employed to describe the growth behavior of polycrystalline lithium phosphate. Finally, a 3-dimensional lithium phosphate precipitate structure resembling a chemical garden and its growth characteristics in a flow-driven system are thoroughly explored.

## 2 Experimental Section

The turbidity of a mixture of  $\text{LiCl}$  and  $\text{Na}_3\text{PO}_4$  at stoichiometric ratio of reactants concentration was measured in a thermostated UV-vis spectrophotometer coupled with a magnetic stirrer (Fig. 1) at a wavelength of 340 nm and at constant room temperature. The turbidity of the reaction at a given chemical composition was also measured at various temperatures.

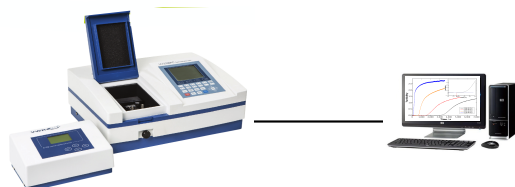


Figure 1: Schematic illustration of the experimental setup used in the measurement of turbidity.

The formation of polycrystalline lithium phosphate precipitate and the investigation of the growth of the polycrystals were carried out using a fully automated microfluidic setup (Fig. 2). By injecting solutions of  $\text{LiCl}$  and  $\text{Na}_3\text{PO}_4$  into the microchannel from separate reservoirs in the injection rate ranges of  $0.2\text{--}5\ \mu\text{L}/\text{min}$ , the growth of the polycrystalline particle was monitored under a microscope and time-dependent images were saved for further analysis.

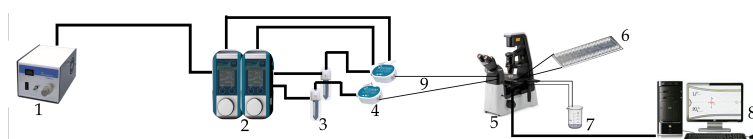


Figure 2: Fully automated microfluidic setup (not to scale): 1. Pressure generator, 2. Pressure controller - dual lineup series, 3. Reservoirs, 4. Flow sensors, 5. Microscope with camera, 6. Microreactor, 7. Drain reservoir, 8. Computer/readout, and 9. PTFE tube connectors

The formation of  $\text{Li}_3\text{PO}_4$  chemical garden was performed using a cuvette of  $1 \times 1 \times 10\ \text{cm}^3$ , by injecting a  $\text{Na}_3\text{PO}_4$  solution into a  $\text{LiCl}$  solution in the injection ranges of  $0.01\text{--}0.05\ \text{mL}/\text{min}$ . The chemical garden structure was monitored using a digital camera focused on the cuvette (Fig. 3).

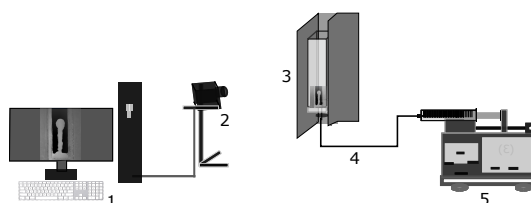


Figure 3: Flow-driven system for studying chemical garden (not to scale): 1. processing unit, 2. digital camera, 3. reactor of dimensions  $1 \times 1 \times 10\ \text{cm}^3$  and support jacket with dark background, 4. connector tube, and 5. injection pump.

### 3 New Scientific Results

- I. The rate of lithium phosphate precipitation in a well-stirred reactor is described by  $r = a'[\text{PO}_4^{3-}]_0^b$ , where  $b = 4.22 \pm 0.04$ . [3]

The induction time  $t_{ind}$ , which is inversely proportional to the nucleation rate  $r$ , is determined from the turbidity–time profile. The induction time varies with the  $[\text{PO}_4^{3-}]$  according to a power law of

$$\frac{1}{t_{ind}} = a[\text{PO}_4^{3-}]_0^b \quad (1)$$

as indicated in Fig. 4. The order  $b = 4.22 \pm 0.04$ , obtained from the fitting has a value consistent with that predicted by the law of mass action kinetics for this reaction with the proportionality constant of  $a = (3.5 \pm 0.3) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-b}$ .

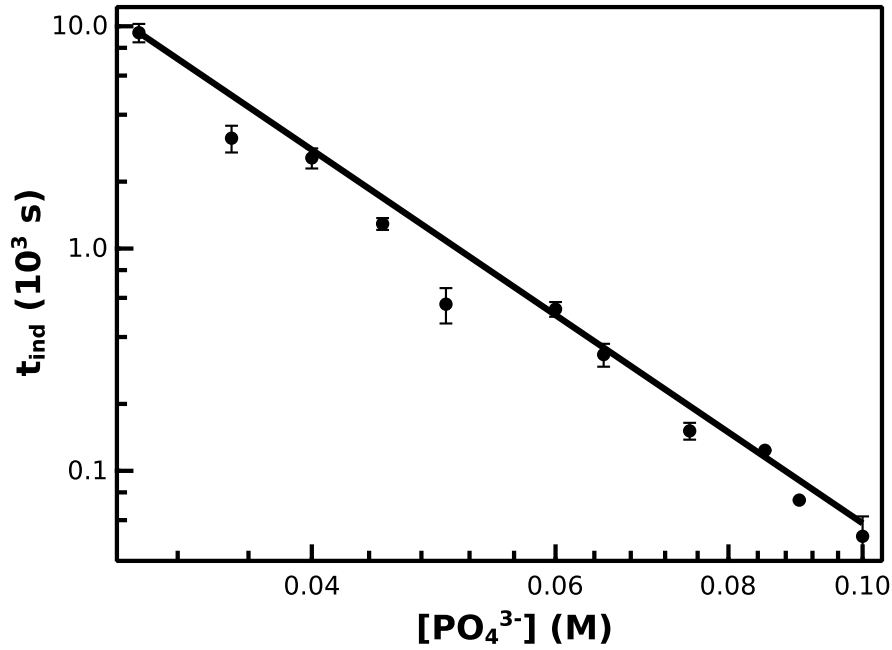


Figure 4: Induction time as a function of concentration at  $T = 25 \text{ }^\circ\text{C}$ . The solid line shows the fitting by Eqn. 1.

II. *The shape of the polycrystalline lithium phosphate formed in microchannels is a function of injection rates with higher flow rates inducing a symmetric deformation along the flow on the initially spherical structure. The obovate particles grow faster along the direction of flow than in the transverse direction.*[1]

Injection rate influences the circularity in the shape of the polycrystalline particle, such that at  $q_v \leq 0.4 \mu\text{L}/\text{min}$  and the reactant ratio  $R = [\text{Li}^+]/[\text{PO}_4^{3-}] = 10$ , with  $[\text{Li}^+] = 0.75 \text{ M}$  (Fig. 5(a)) the particles are circular in the horizontal plane. The shape transitions to an obovate under the same condition but at  $q_v > 0.4 \mu\text{L}/\text{min}$  (Fig. 5(b)). Analysis of the growth profiles along and transverse to flow gives a similar growth rate of  $(2.6 \pm 0.2) \times 10^{-2} \mu\text{m}/\text{s}$  in both directions for the lower injection rate (Fig. 5).

Particle growth profile when  $R = 6$ , reveals that along the direction of reactants flow, growth is faster and linear with average growth rate  $r_x = (3.2 \pm 0.3) \times 10^{-2} \mu\text{m}/\text{s}$ . Transverse to the flow, the growth is slower and scales to a power law  $d_y = r_y t^\alpha$  with exponents  $\alpha \geq 0.5$  characteristic of reactions between initially segregated reactants with only diffusional support.

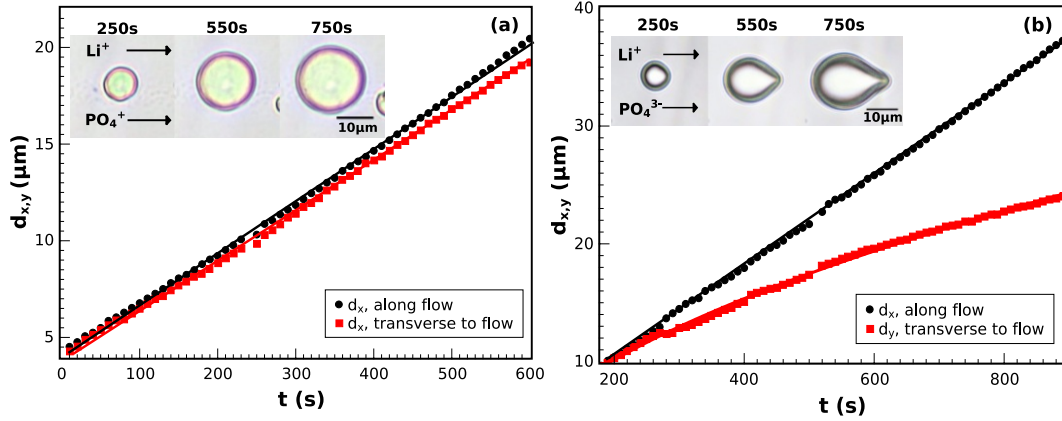


Figure 5: Typical growth profiles along  $d_x$  and transverse  $d_y$  to the direction of flow;  $q_v = 0.2 \mu\text{L}/\text{min}$  (a) and  $q_v = 3.0 \mu\text{L}/\text{min}$  (b), when  $R = 10$ . The inset shows the image sequence of lithium phosphate polycrystalline particle in the microchannel.

III. The growth rate expression for the particle formed in the microchannel is  $r_x = \kappa[\text{Li}^+]^2[\text{PO}_4^{3-}]$ , for a wide range of chemical composition and injection rate.

Investigations at  $R = 6$  for  $0.39 \text{ M} \leq [\text{Li}^+] \leq 0.75 \text{ M}$  and  $1 \mu\text{L}/\text{min} \leq q_v \leq 5 \mu\text{L}/\text{min}$  reveal that the growth rate along the direction of flow  $r_x$  is proportional to the product of the reactant concentrations (Fig. 6) where the slope of the linear fitting gives the growth rate constant for the growth of a lithium phosphate polycrystal in a microchannel as  $\kappa = 0.88 \pm 0.03 \mu\text{m M}^{-3} \text{ s}^{-1}$ . This consequently implies that in the microfluidic system, the fast formation of  $\text{Li}_2\text{PO}_4^-$  - complex takes place prior to the rate determining step in the growth. To affirm this finding a plot of the logarithm of growth rate as a function of logarithm of the phosphate ion concentration is a straight line with slope  $\eta$  being the growth order with a value of  $2.71 \pm 0.16$  confirming the rate law expression.

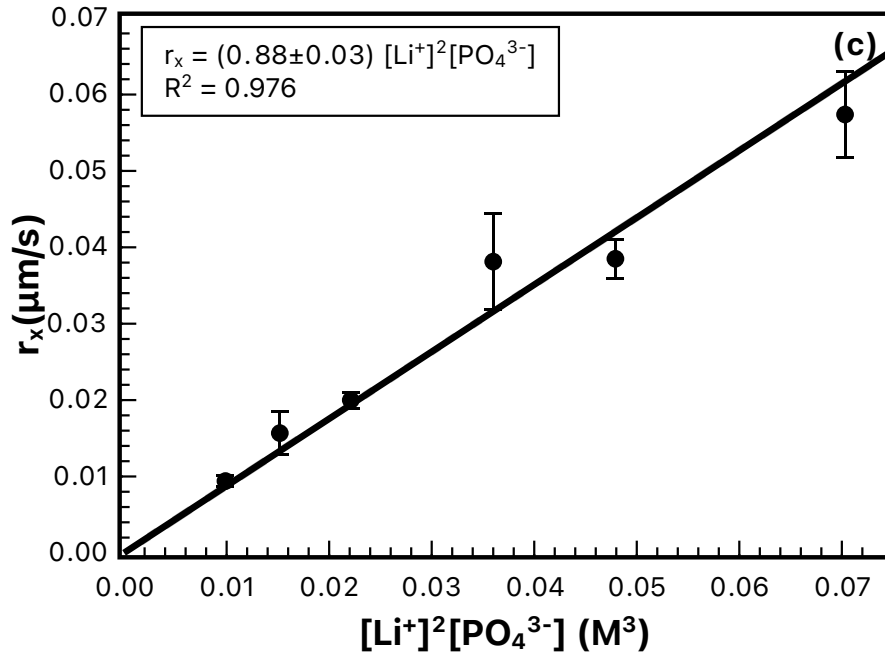


Figure 6: Linear dependence of the growth rate  $r_x$  on the product of the reactant concentrations.

IV. *The formation of lithium phosphate chemical gardens consists of two growth regimes with linear growth rates independent of the injection rates yielding a universal growth profile.*[2]

The height evolution of the chemical garden formed at different injection rates shows that the structure evolves first at a fast rate of  $u_1 = 74.0 \pm 0.6 \mu\text{m/s}$  which is significantly smaller than the fluid jet velocity that is in the range of 200–1000  $\mu\text{m/s}$ . Then the growth slows down drastically with  $u_2 = 2.86 \pm 0.33 \mu\text{m/s}$  after a maximum height is attained (Fig. 7). This considerable decrease in growth indicates a gradual diffusive change in the pH as the liquid jet advances. The growth rate is constant for the two regimes, independent of the injection rates.

Both the maximum height  $h_{\text{max}}$ , i.e., the utmost height achieved during the fast growth regime, and the time to reach this height  $t_{\text{max}}$  relate linearly with the injection rates. As a result, a universal growth profile can be constructed for all the measurements where height is scaled to  $h_{\text{max}}$  by the precipitate structure during the first stage. By plotting the dimensionless height, defined as  $H = h/h_{\text{max}}$ , as a function of the dimensionless time, with  $\tau = t/t_{\text{max}}$ , the data merges onto a single curve with

$$H = \begin{cases} \tau & \tau \leq 1 \\ 1 + \frac{u_2}{u_1}(\tau - 1) & \tau > 1 \end{cases} \quad (2)$$

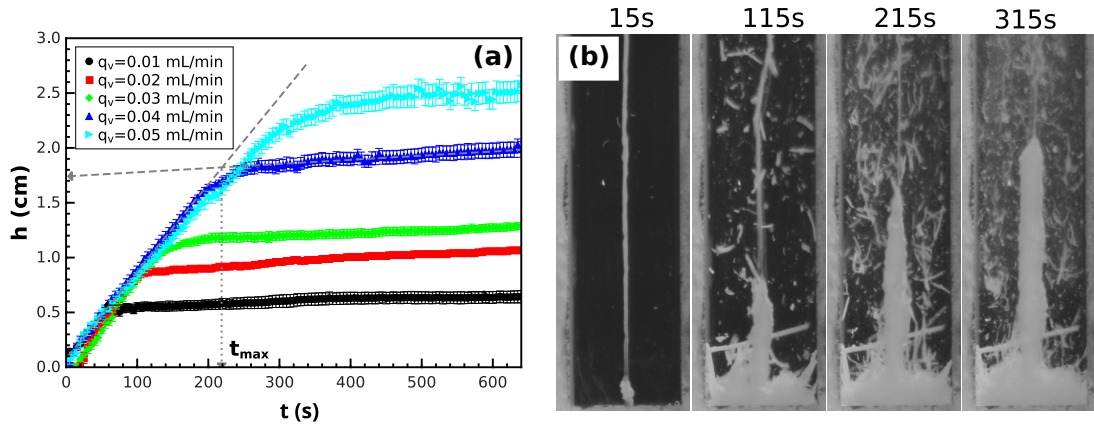


Figure 7: Growth profile of the precipitate structure at different injection rates (a), and image sequence showing the development of a 3–dimensional chemical garden–like precipitate structure of lithium phosphate (b).



- V. *The volume growth rate of lithium chemical gardens is the same for both growth regimes and it is consistently smaller than the injection rate.*[2]

The volume growth rate depends on the injection rate but in a single experiment it remains constant even when the growth characteristic changes at  $t = t_{max}$ . Even though the structure's extension in height follows two growth regimes, the volume of the entire material remains constant and increases linearly with time as shown in Fig. 8(a). Upon comparing it with the injection rate in Fig. 8(b), a linear relation is revealed with a slope of  $0.55 \pm 0.05$ . This implies that the precipitate tube does not form a closed structure; the injected solution can leak through the porous membrane into the external solution or through any opening, mostly at the tip of the tube.

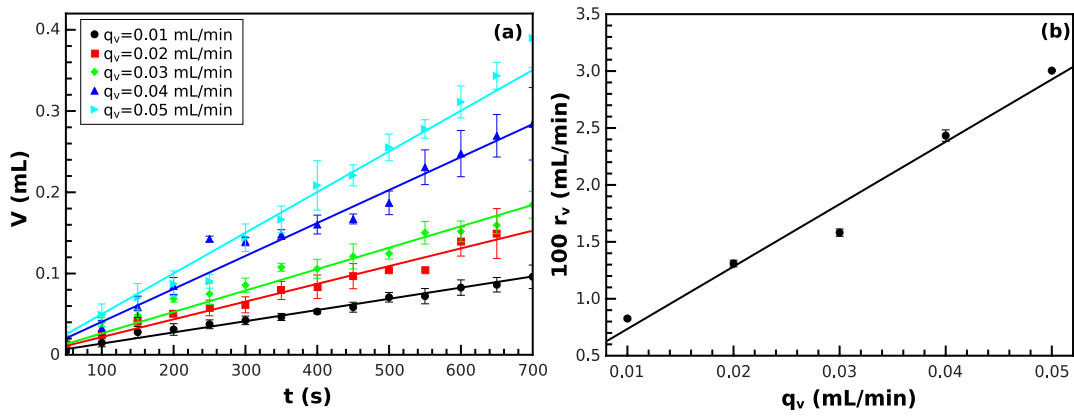


Figure 8: Temporal evolution of the precipitate volume for various injection rates (a), and the volume growth rate  $r_v$  obtained from the slopes of (a) as a function of the injection rate (b).

VI. *The expansion of the tip in the second growth regime follows a power law function with an exponent of  $\eta = 0.75 \pm 0.01$ . [2]*

When the maximum height is reached for a given injection rate, the diameter of the precipitate structure begins to increase mostly localized at the tip. This expansion follows a power law function of

$$\Delta d = (d - d_0) = k (t - t_0)^\eta \quad (3)$$

where  $d$  is the diameter at any time  $t$ ,  $d_0$  is the initial diameter at the time when vertical growth stopped  $t_0 = t_{max}$ ,  $k$  is a proportionality constant, and  $\eta$  is the growth order. By fitting the curves in Fig. 9 to Eqn. (3), we obtain  $\eta = 0.75 \pm 0.01$ , with  $k = (3.12 \pm 0.03) \times 10^{-3} \text{ cm/s}^\eta$ . Since the exponent is greater than 0.5, convection alongside diffusion plays a role in the structure formation.

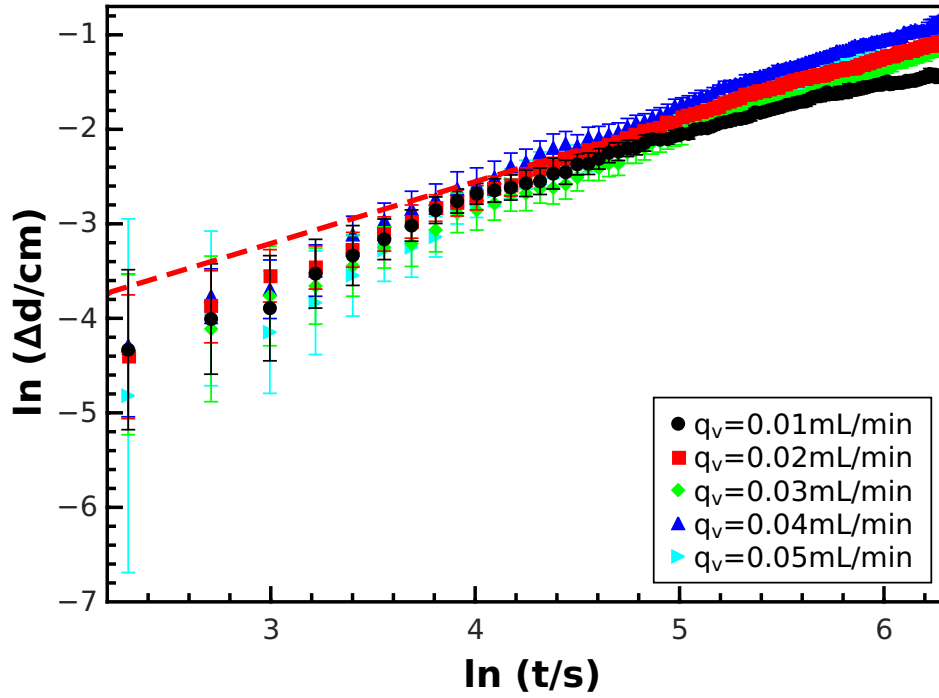


Figure 9: Temporal change in the tip diameter of the precipitate after maximum height was reached.

## 4 List of scientific publications related to the topic of the dissertation

1. M. Emmanuel, D. Horváth, Á. Tóth

*Flow-driven crystal growth of lithium phosphate in microchannels*

CrystEngComm., **22**, 4887–4893 (2020).

IF<sub>2020</sub> = 3.545

2. M. Emmanuel, E. Lantos, D. Horváth, Á. Tóth

*Formation and growth of lithium phosphate chemical garden*

Soft Matter, **18**, 1731–1736 (2022).

IF<sub>2020</sub> = 3.679

3. M. Emmanuel, P. Papp, G. Schusztar, Á. Imre-Deák, L. Janovák, Á. Tóth, D. Horváth,

*Nucleation kinetics of lithium phosphate precipitation*

CrystEngComm., (2022).

IF<sub>2020</sub> = 3.545

$\Sigma$ IF = **10.769**

## 5 Lectures Related to the Topic of the Dissertation

1. M. Emmanuel, D. Horváth, and Á. Tóth

*Flow-driven crystallization and precipitation kinetics in the lithium phosphate System*

XLII. Chemistry Lecture Days of the Hungarian Chemical Society–Group of Csongád County, Szeged, Hungary; October 28 – 30, 2019.

2. M. Emmanuel, D. Horváth, and Á. Tóth

*Flow-driven crystallization and precipitation kinetics in the lithium-phosphate system*

COST Action Chemobrionics Prague Meeting, Prague, Czech Republic; January 29–31, 2020.

3. M. Emmanuel, D. Horváth, and Á. Tóth

*Kinetics of lithium phosphate precipitation*

Reaction Kinetics and Photochemistry Working Committee Meeting of the Hungarian Academy of Sciences. Budapest, Hungary–online presentation; November 6th, 2020.

4. **M. Emmanuel**, D. Horváth, and Á. Tóth

*Formation and growth of lithium phosphate chemical gardens*

COST Action Chemobionics Third Annual Meeting, Ankara, Turkey; September 22–24, 2021.

5. **M. Emmanuel**, D. Horváth, and Á. Tóth

*Preliminary presentation of Ph.D. thesis work: Nucleation kinetics and flow-driven crystallization of lithium phosphate*

Reaction Kinetics and Photochemistry Working Committee Meeting of the Hungarian Academy of Sciences. Balatonvilágos, Hungary; May 19th-20th, 2022.

## 6 Poster presentations related to the topic of the dissertation

1. **M. Emmanuel**, G. Schuszter, Á. Tóth, and Dezső Horváth

*Flow-driven crystallization*

GRC on Crystal Growth and Assembly, Manchester, NH, USA; June 23–28, 2019.

2. **M. Emmanuel**, D. Horváth, Á. Tóth

*Nucleation and growth kinetics of lithium phosphate precipitation*

2<sup>nd</sup> International Conference on Reaction Kinetics, Mechanism and Catalysis Budapest, Hungary– Online; May 20–22, 2020.

3. **M. Emmanuel**, D. Horváth, Á. Tóth

*Flow-driven crystallization of lithium phosphate in microchannels*

21<sup>st</sup> International Symposium on Industrial Crystallization Online; August 30–September 2, 2021.

4. **M. Emmanuel**, G. Schuszter, Á. Tóth, and Dezső Horváth

*Kinetic characterization of flow-driven precipitation*

Faraday discussion on crystallization York, UK; March 28-30, 2022.

MTMT identification number: 10081544

## 7 Declarations

I, the undersigned, as the co-author of the (M. Emmanuel, *et al.*, Nucleation kinetics of lithium phosphate precipitation. CrystEngComm, 2022, DOI: 10.1039/D2CE00333C) publication associated with the doctoral dissertation of Michael Emmanuel, Ph.D. candidate entitled as *Nucleation kinetics and flow-driven crystallization of lithium phosphate*, hereby declare that the role of the candidate was decisive in achieving the scientific results related to this publication and the candidate's thesis point (I), therefore these results have not been used to obtain a Ph.D. degree so far, and I will not do so in the future.

---

Paszkál Papp

I, the undersigned, as the co-author of the (M. Emmanuel, *et al.*, Formation and growth of lithium phosphate chemical gardens. Soft Matter, 18:1731–1736, 2022.) publication associated with the doctoral dissertation of Michael Emmanuel, Ph.D. candidate entitled as *Nucleation kinetics and flow-driven crystallization of lithium phosphate*, hereby declare that the role of the candidate was decisive in achieving the scientific results related to this publication and the candidate's thesis points (IV–VI), therefore these results have not been used to obtain a Ph.D. degree so far, and I will not do so in the future.

---

Emese Lantos

We, the undersigned, as the supervisors of the Ph.D. candidate Michael Emmanuel in connection with the doctoral dissertation entitled as *Nucleation kinetics and flow-driven crystallization of lithium phosphate*, hereby declare regarding the ((1). M. Emmanuel, *et al.*, Flow-driven crystal growth of lithium phosphate in microchannels. CrystEngComm, 22:4887–4893, 2020., (2). M. Emmanuel, *et al.*, Formation and growth of lithium phosphate chemical gardens. Soft Matter, 18:1731–1736, 2022., and (3). M. Emmanuel, *et al.*, Nucleation kinetics of lithium phosphate precipitation. CrystEngComm, 2022, DOI: 10.1039/D2CE00333C) publications and the candidate's thesis point (I–VI) that the results used in this dissertation reflect the Ph.D. candidate's independent contribution.

---

Dr. Ágota Tóth

---

Dr. Dezső Horváth