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Control of Flame Spray Pyrolysis synthesis of $Li_4Ti_5O_{12}$: Experimental and Computational study

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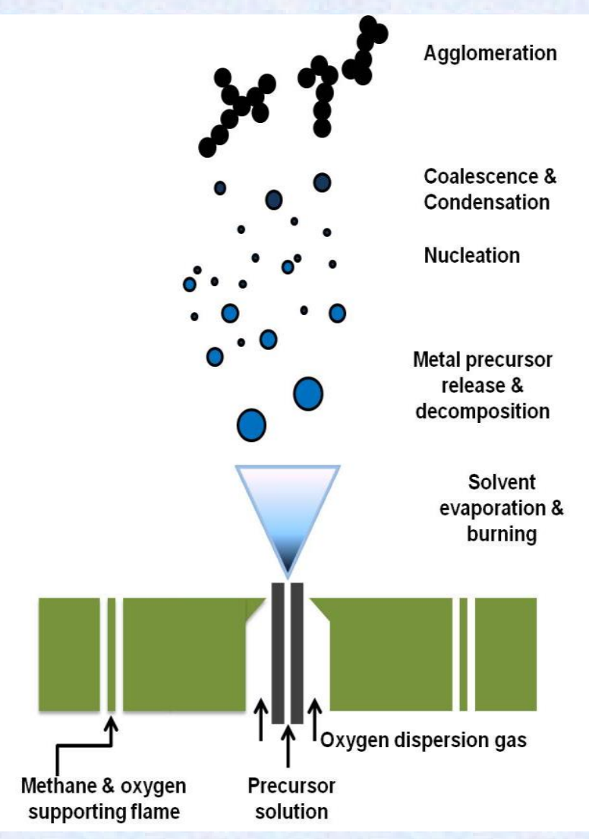
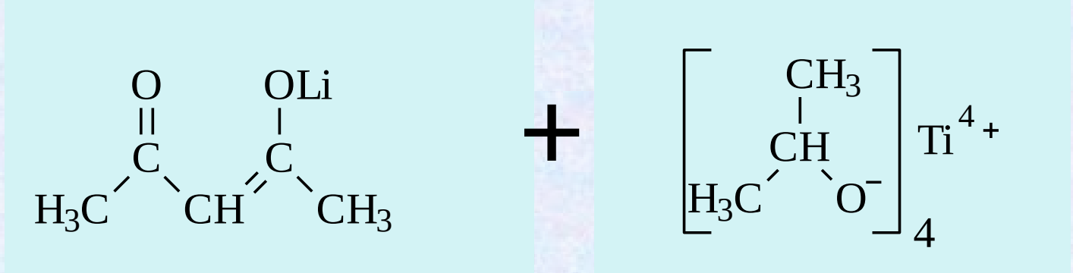
Abstract: Lithium titanate ($Li_4Ti_5O_{12}$, LTO) is a promising anode material for the next generation of lithium ion batteries. Its physical properties and morphology (which consequently affect its electrochemical performance) highly depend on its synthesis method. Flame spray pyrolysis (FSP) is an attractive process for the controlled one-step synthesis of functional multicomponent oxides from low cost precursors. The main aim of this study is to control the growth process of LTO by FSP in order to maintain the desired particle properties. LTO nanoparticles of different sizes are synthesized by variation of the FSP processing conditions and characterized accordingly. Numerical simulations based on Population Balance Models are also implemented in order to investigate the evolution of primary and agglomerate particle growth.

Oxide Nanoparticles' Synthesis by Flame Spray Pyrolysis



Nanoparticles' formation from solution droplets by FSP.

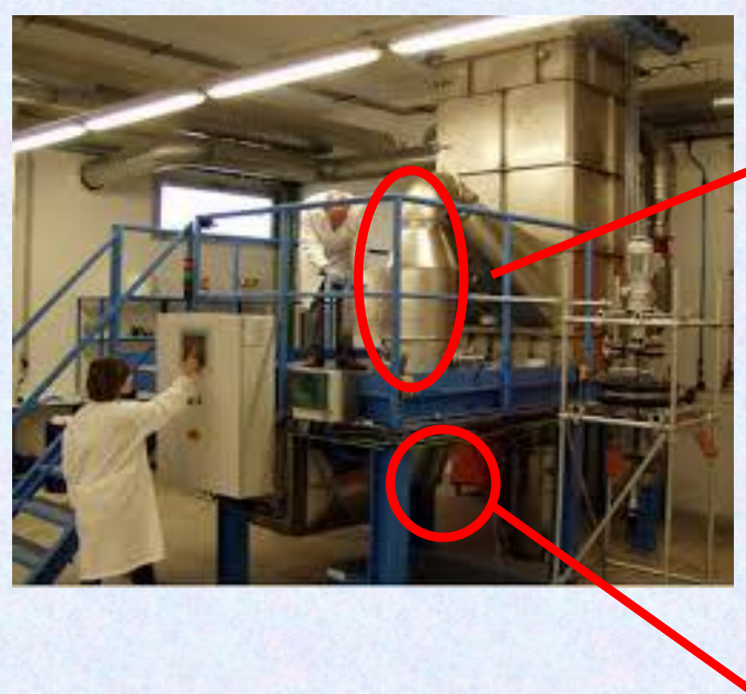
Lithium acetylacetonate + **titanium (IV) isopropoxide**



Isopropanol / 2-ethylhexanoic acid

FSP

Lithium titanate ($Li_4Ti_5O_{12}$)

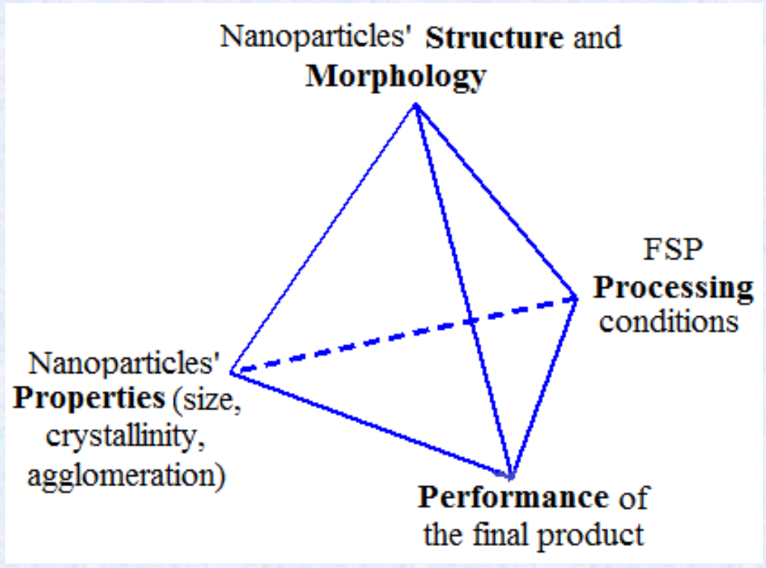


FSP apparatus in Technological Centre LUREDERRA.

FSP reactor chamber and filters.

Collection of nanoparticles.

Lithium Titanate ($Li_4Ti_5O_{12}$, LTO)
- ☺ Zero strain material.
- ☺ Intercalation of lithium at high potential.
- ☺ Flat voltage during charge/discharge.
- ☺ No reactions with electrolyte.
- ☹ Low conductivity.



Control of growth process ↔ Characterization ↔ Modeling

Population Balance Modeling of flame synthesis of LTO

General Dynamics Equation

$$\frac{dn(v_p,t)}{dt}=\underbrace{\frac{1}{2}\int_0^{v_p}\beta(v_p-v,v)n(v_p-v;t)\,n(v;t)dv\text{-}n(v_p;t)\int_0^{\infty}\beta(v_p,v)n(v;t)dv}_{\text{Coagulation terms}}+\underbrace{S(v_p,t)\cdot\delta(v_p-v_m)}_{\text{Nucleation term}}+\underbrace{\frac{d}{dv_p}\Big(\big(I(v_p,t)\cdot n(v_p,t)\big)\Big)}_{\text{Condensation term}}$$

Integrodifferential equation lacking analytical solution

<u>Assumptions</u>

Precursors react quickly to yield high particle concentration. As a result, Brownian coagulation is dominant, rather than nucleation and condensation

Monodisperse Model

$$\frac{dN}{dt}=-\frac{1}{2}\beta N^2$$

Assuming that all particles have the same size during coagulation.

Model accounting of polydispersity

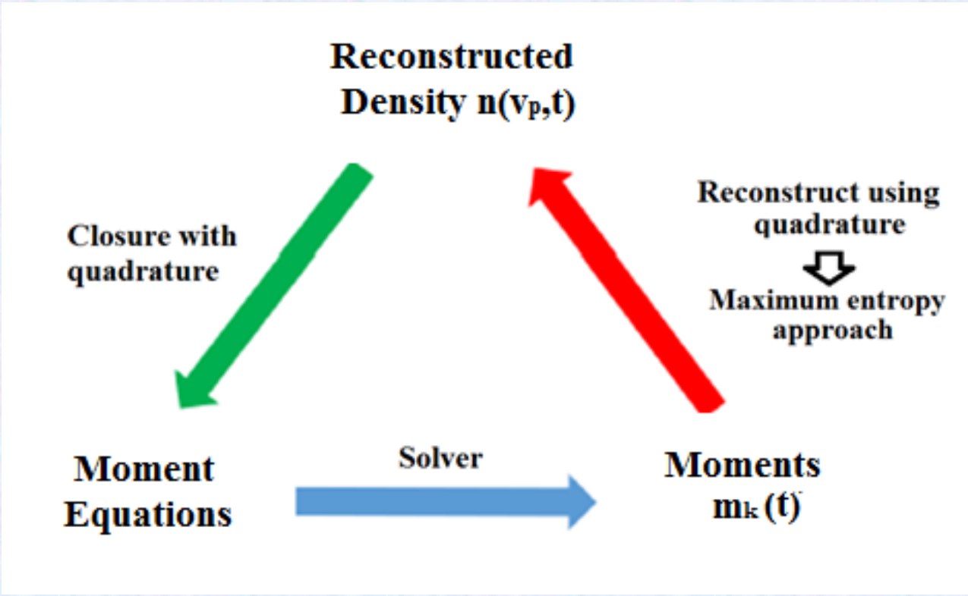
$$\frac{dn(v_p,t)}{dt}=\frac{1}{2}\int_0^{v_p}\beta(v_p-v,v)n(v_p-v;t)\,n(v;t)dv\text{-}n(v_p;t)\int_0^{\infty}\beta(v_p,v)n(v;t)dv$$

Method of moments

$$m_k(t)=\int_0^{\infty}n(v_p;t)\,{v_p}^k dv_p$$

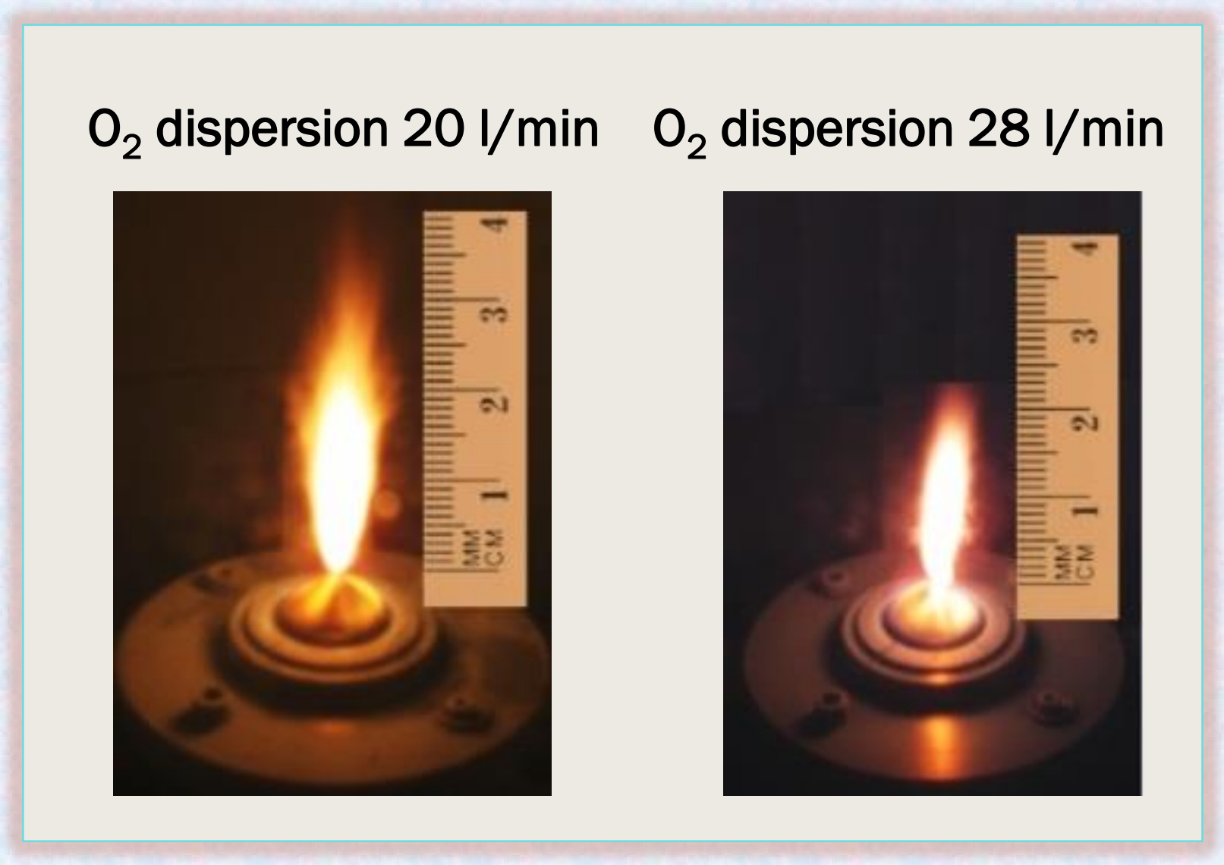
Quadrature method of Moments (QMOM)

$$m_k=\sum_{i=1}^{N}w_i{L_i}^k$$



Advantages of QMOM: QMOM permits calculation of the evolution of moments directly without a priori assumptions about the form of the evolving distribution. It is a robust and computational efficient method to track the evolution of the first six moments.

Experimental Results



O_2 dispersion 20 l/min O_2 dispersion 28 l/min

Fig. 1. Spray flames for different O_2 dispersion gas flow rates.

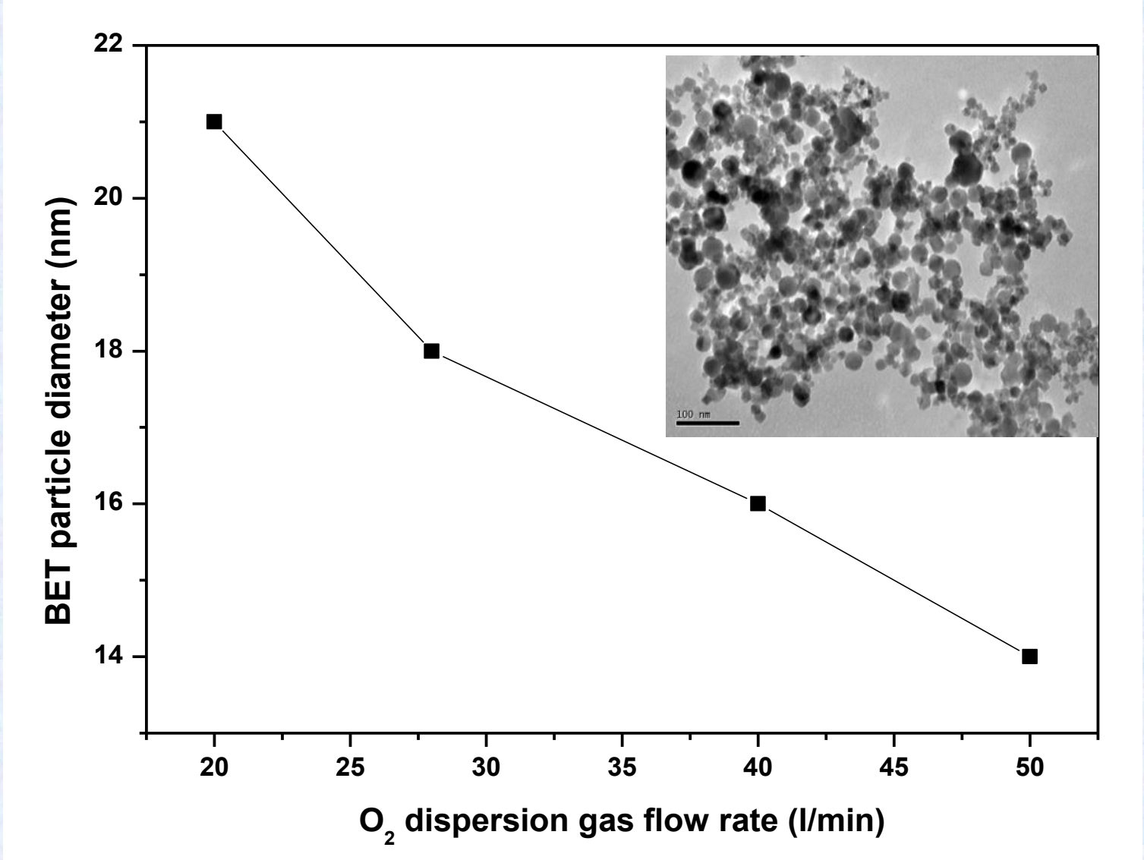


Fig. 2. BET particle diameter of the powder as a function of the O_2 dispersion gas flow rate.

An increase in O_2 dispersion gas flow rate intensifies mixing and accelerates combustion and in this way, the height of the flame is reduced.

LTO nanoparticles' size decreases from 21 to 14 nm with the increase of O_2 gas dispersion flow rate due to decrease of droplet concentration in the flame.

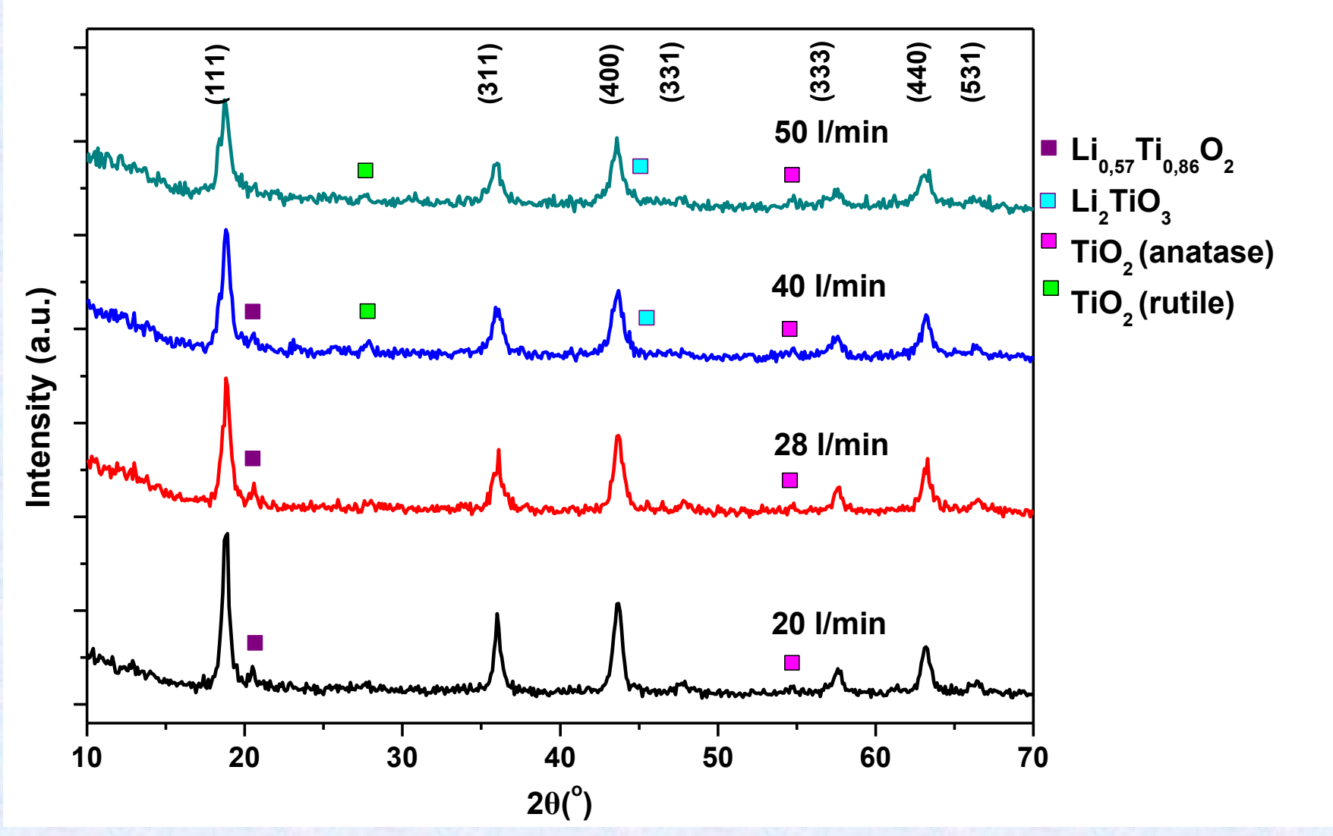


Fig. 3. XRD of LTO for different O_2 dispersion gas flow rates.

The stoichiometry of the material corresponds to the spinel form $Li_4Ti_5O_{12}$. Second phases also exist, which may be attributed to kinetics: i.e. insufficient time at high temperature, as FSP is a very rapid process.

Simulation Results

Monodisperse Model

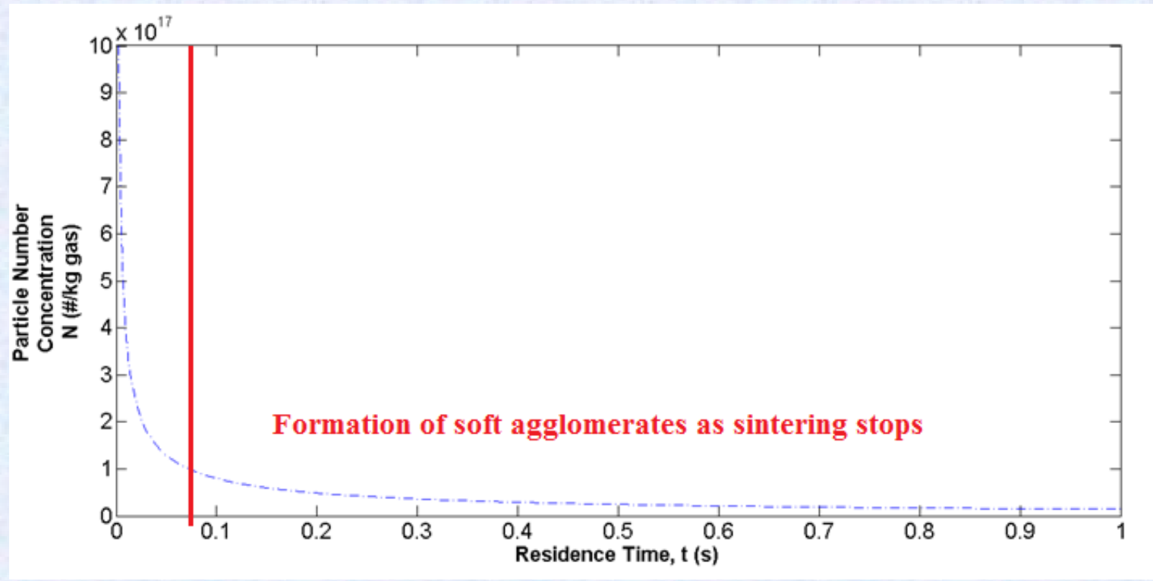


Fig. 4. Evolution of LTO total particle number concentration.

Decrease of particle number concentration by the dominance of coagulation.

Hard and Soft agglomerates formation.

Quadrature Method of Moments

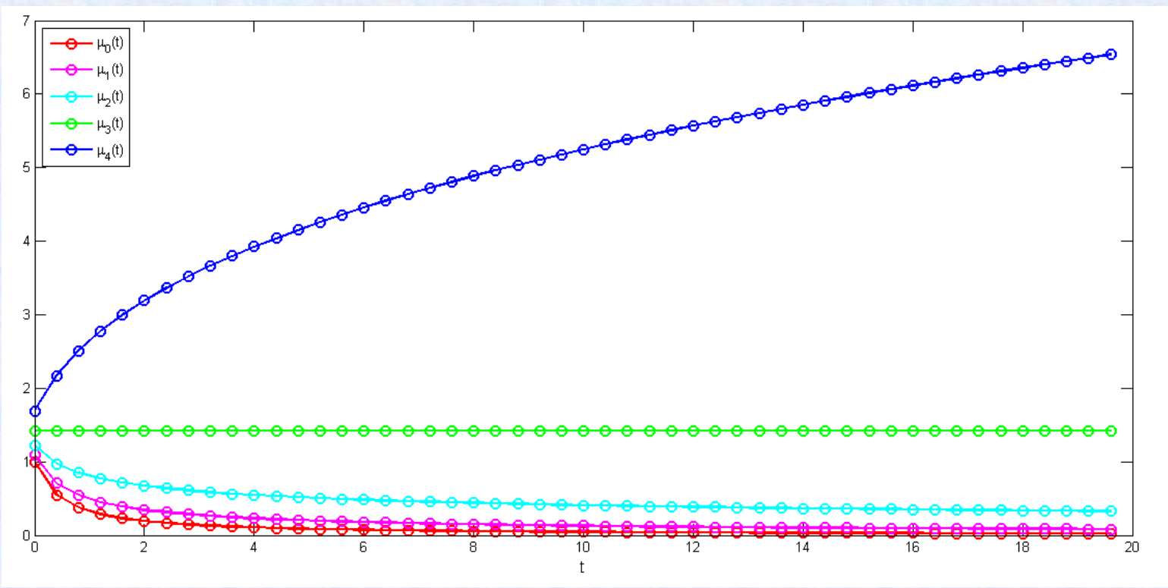


Fig. 5. Evolution of length based moments obtained by QMOM.

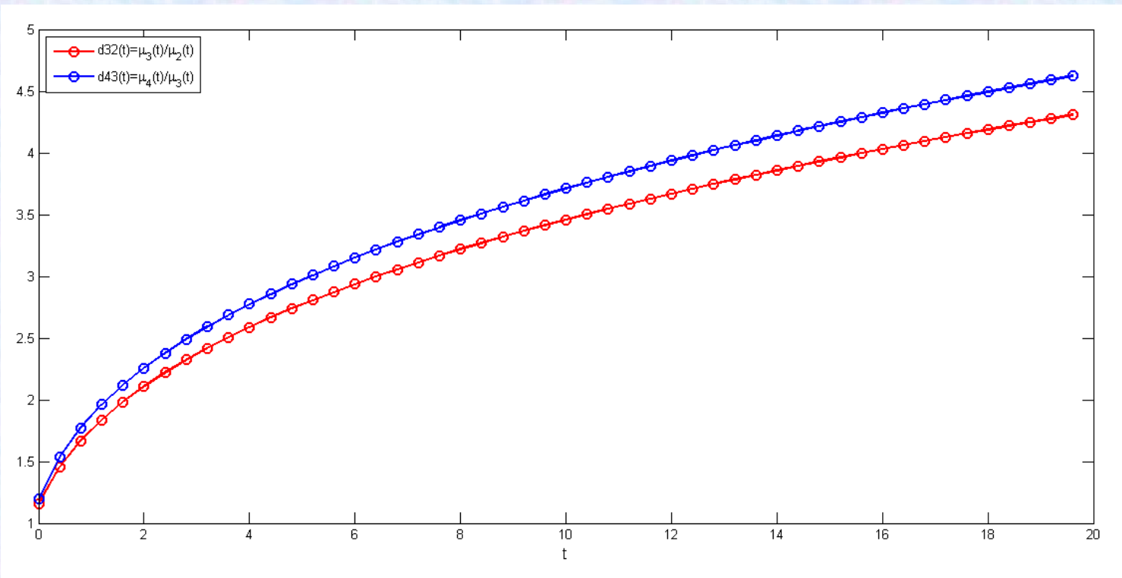


Fig. 6. d_{32} (Sauter mean diameter) and d_{45} calculated by the moments obtained by QMOM.

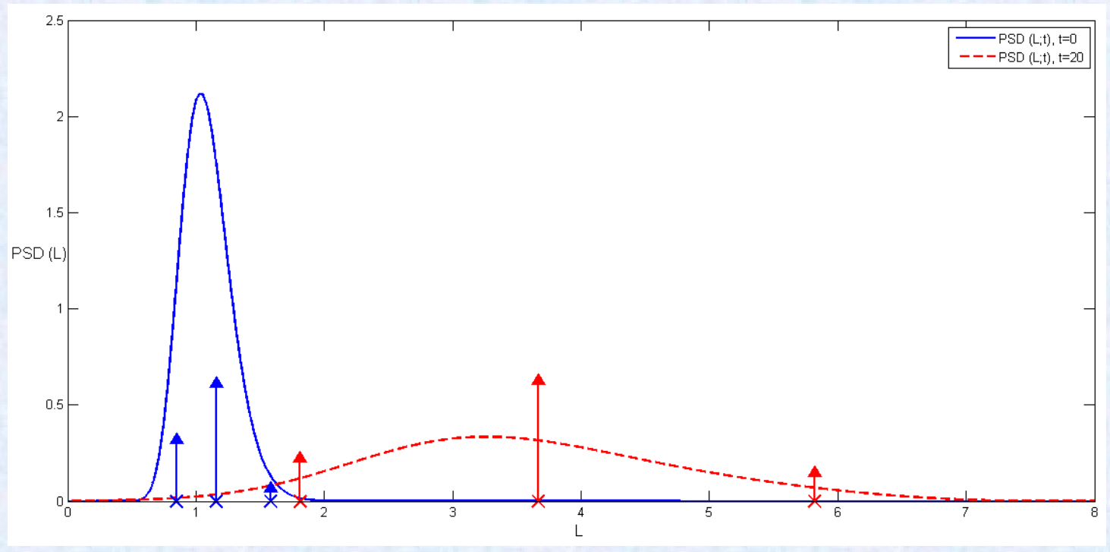


Fig. 7 Initial and Final PSD using Maximum Entropy approach. Values of weights, w_i, calculated by QMOM, are shown.

Physical Interpretation of moments	
m_0	Total number concentration
m_1	Related to number average particle diameter
m_2	Proportional to particles' surface area
m_3	Proportional to total particles' volume
m_4	Proportional to the total projected area
m_5	Proportional to mass flux of the material

Conclusions

- LTO nanoparticles have been synthesized by FSP. By varying the FSP operating conditions we can control the process and obtain LTO nanoparticles with optimized properties.
- Population balance modeling of LTO synthesis is performed by monodisperse model and QMOM model taking into consideration polydispersity. Promising results are presented for controlling the particle size distribution.

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