

„Die Synthese des Verbundwerkstoffes Lithiumeisenphosphat-Kohlenstoff durch Ultraschallsprühpyrolyse“

Von der Fakultät für Georessourcen und Materialtechnik der
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Albrecht Schwinger

aus Freiberg (Sachsen)

Berichter: Univ.-Prof. Dr.-Ing. Dr.h.c. (UA) Karl Bernhard Friedrich
PD Dr.-Ing. Srecko Stopic
Prof. Dr. rer. nat. Michael Binnewies

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Albrecht Schwingen

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Albrecht Schwinger, Werne, den 25.01.2016

Abstract

Abstract

This thesis presents the results of the investigation of the synthesis of the compound material Lithium-iron-phosphate-carbon (LiFePO_4/C) as a core shell material in the ultrasonic spray pyrolysis (USP).

LiFePO_4/C is a promising cathode material for Li-ion-batteries, because of its thermochemical stability, high energy density, cell voltage and cycle stability. The conductivity of LiFePO_4/C is with $10^{-9} \text{ S cm}^{-1}$ a restrictive parameter. It is possible to lift it up to $10^{-3} \text{ S cm}^{-1}$ with the help of carbon.

The motivation of this thesis is to synthesize core shell particles with LiFePO_4 in the core and C in the shell in one process step in the USP. Ultrasound forms the precursor to a spray. After this the spray transforms to LiFePO_4/C in a wall heated reactor tube. The purity of the product powder is proved with the help of X-ray-diffraction (XRD). The Differential Thermal Analysis and the thermogravimetry (DTA/TG) makes the steps of the pyrolysis process visible. Furthermore, investigations to the thermal transfer and the residence time are performed. The analysis of the droplet size and the particle size are investigated with laser diffraction. The morphology is investigated with TEM and EDX. These results answers the question of the influences of the different parameters contributing to the core shell synthesis.

A successful synthesis of defined core shell particles is done by employing optimized process parameters. For the evaluation of the core shell quality a CS-factor is developed.

$\text{Li}(\text{NiMnCo})_{0.33}\text{O}_2$ is synthesized to show the applicability of the USP for different cathode materials.

Kurzzusammenfassung

In dieser Dissertation wird die Forschungsarbeit zur Synthese des Verbundwerkstoffes Lithiumeisenphosphat(LiFePO₄)-Kohlenstoff als Core-Shell-Material durch Ultraschallsprühpyrolyse (USP) vorgestellt. LiFePO₄ ist ein vielversprechender Kathodenwerkstoff für Li-Ionen-Akkus, der thermochemisch stabil ist, eine hohe Energiedichte, Zellspannung und Zyklenstabilität hat. Die Leitfähigkeit von LiFePO₄ von 10⁻⁹ S cm⁻¹ ist eine einschränkende Größe. Sie kann aber durch Kohlenstoffzugabe bis auf 10⁻³ S cm⁻¹ verbessert werden kann.

Die Motivation zu dieser Arbeit besteht darin, mit der Ultraschallsprühpyrolyse in einem einstufigen Verfahren sphärische Partikel mit LiFePO₄ im Kern und Kohlenstoff in der Hülle herzustellen. Es werden Versuche durchgeführt bei denen ein Precursor mittels Ultraschallwellen zu einem Aerosol umgesetzt wird. Dieses wird in einem wandbeheizten Rohreaktor zu LiFePO₄/C umgesetzt. Mit Hilfe der Röntgenbeugungsanalyse wird die Reinheit des Pulvers untersucht. Mittels Differentieller Thermoanalyse und Thermogravimetrie (DTA/TG) wird der Ablauf der Zersetzungreaktionen untersucht. Weiterhin werden Aussagen über die Wärmeübertragung und eine sinnvolle Verweilzeit getroffen. Weiterführende Untersuchungen bilden die Analyse der Tropfengröße mittels Laserbeugung und der Partikelgröße mittels Laserstreuung. Die Morphologie der synthetisierten Partikel wird hinsichtlich der Trennschärfe von Kohlenstoff und LiFePO₄ mittels Transmissionselektronmikroskopie (TEM) und Energiedispersiver Röntgenstrahlung (EDX) untersucht. Somit werden die Einflussfaktoren auf die Core-Shell-Bildung identifiziert.

Es ist gelungen, mittels gezielter Anpassungen der Prozessparameter definierte Core-Shell-Partikel herzustellen. Für die Beurteilung der Trennschärfe zwischen Kern und Schale des Partikels und somit für die Qualität des Prozesses wurde der sogenannte CS-Faktor entwickelt.

Um die Eignung des Verfahrens der Ultraschallsprühpyrolyse für die Synthese anderer Kathodenwerkstoffe zu überprüfen, wird die Synthese von Li(NiMnCo)_{0,33}O₂ durchgeführt.

Extended Abstract

Within the „LiVe“ (Lithiumbatterie - Verbundstrukturen) network, all research focused on a fundamental question: which materials in which architecture of electrodes are promising for a better performance of lithium ion batteries? This thesis shows how to produce homogeneous, crystalline LiFePO₄/C particles with a core-shell-structure in a single-step process. The mechanisms involved in the synthesis are examined and the influence of characteristic parameters like droplet size, concentration of the reactants in the precursor and reaction time is examined.

There are about 11 alternative methods for the synthesis of LiFePO₄. The most important are the solid state reaction and the precipitation from aqueous solution with subsequent carbon coating. The thesis focuses on the development of the ultrasonic spray pyrolysis (USP) for the synthesis of LiFePO₄/C particles.

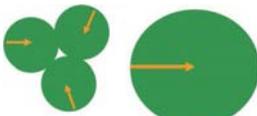
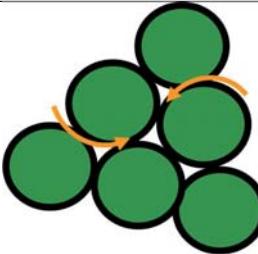
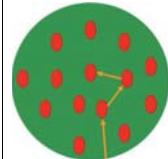
LiFePO₄/C is a promising cathode material for lithium ion batteries, because of the high energy density, thermochemical safety and low material cost. For a comparison of the properties of the common electrode material LiCoO₂ and LiFePO₄ see Table 1.

Table 1: Comparison of the properties of LiCoO₂ and LiFePO₄

Properties	LiCoO ₂	LiFePO ₄
Structure	layer structure	orthorombic
Redox couple	Co4+/Co3+	Fe3+/Fe2+
Cell voltage [V]	3,6	3,5
Theoretical capacity [mAh/g]	274	170
Real capacity [mAh/g]	145	155
Density [g/cm ³]	5,1	3,6
Energy density [Wh/kg]	520	540
Environmental safety	poor	good
Cost	€€€	€
Availability	+	+++
Safety	sufficient	high

But the conductivity of LiFePO₄ (10^{-9} S cm⁻¹) is a restrictive parameter. It is possible to increase it up to 10^{-3} S cm⁻¹. Basically, there are three options to increase the conductivity, as shown in Table 2.

Table 2: Strategies to rise conductivity of LiFePO₄. Yellow arrows indicate the shortest distance of the intercalation of the Li⁺ ion within the LiFePO₄.

1) Decrease the particle diameter	2) Coat with carbon	3) Contaminate with ions of super conductivity
		

The Li⁺-Ions have a shorter way into the center of the particle.

The Li⁺-Ions have a "highway" of a higher conductivity around the particles.

In the particles are islands of a higher conductivity.

The core shell synthesis of LiFePO₄

The USP is divided into three steps:

1. Production of an Aerosol out of the precursor
2. Pyrolysis in the reactor tube
3. Deposition of the nanoparticles at the electro static precipitation

The ultrasonic spray pyrolysis (USP) produces aerosol droplets out of a precursor by ultrasound. In the furnace tube, the pyrolysis of the educts and the formation of the spherical nanoparticles as the product with defined chemical composition takes place. The electro static precipitation manages to collect the nanoparticles out of the off gas. Therefore, the USP is a suitable method to produce LiFePO₄/C as a nanopowder.

Aerosol production

The first step, the production of droplets, is schematically shown in Figure 1. It is based on the constriction of capillary waves.

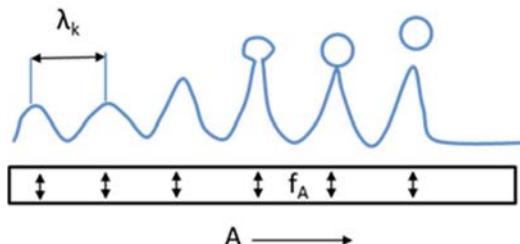


Figure 1: Schematic representation of the droplet production by constriction of capillary waves.

Equation 1 shows how the diameter of the droplet is influenced. The most important factor is the frequency of the generator. Because the precursor is an aqueous solution, the variance of surface tension and density are neglectable.

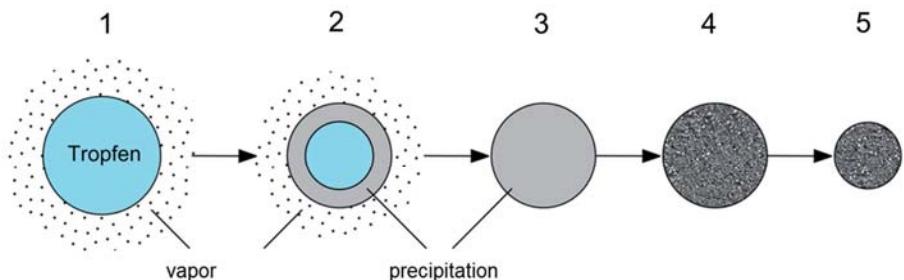
$$d = 0,34 \left(\frac{8 \cdot \pi \cdot \gamma}{\rho \cdot f^2} \right)^{1/3} \quad 1$$

d: diameter of the droplet [m]; γ : surface tension [kg/s^2]; ρ : density [g/cm^3]; f: frequency [s^{-1}]

Transformation from the droplet to the particle

The carrier gas transports the droplets to the reactor tube, where the transformation from the droplet to the particle takes place. As shown in Figure 2 the main steps are:

1. Evaporation
2. Crystallisation
3. Drying
4. Pyrolysis
5. Sintering



1: evaporation; 2: crystallisation; 3: drying; 4: pyrolysis; 5: sintering

Figure 2: Transformation from the droplet to the particle.

The five steps of the evaporation include:

1. Evaporation of the water from the surface of the droplet
2. Diffusion of the water vapor away from the droplet
3. Shrinking of the droplet
4. Temperature increase
5. Diffusion of the dissolved reactants

The pyrolysis works, because the products are thermochemical most stable at high temperatures. Equation 2 shows the reaction for the synthesis of LiFePO₄:



2

Thus, the particle size depends on the droplet size and the concentration of the reactants, as shown in equation 3:

$$D_p = D_0 \left(\frac{C_0 \cdot \rho_p \cdot W}{C_s \cdot \rho_o} \right)^{1/3} \quad 3$$

D_p: diameter of the dried particle; D₀: diameter of the droplet; C₀: precursor concentration before the evaporation of the solvent; ρ_p: density of the precursor; W: oxide ratio in the precursor; C_s: concentration of saturation; ρ_o: density of the oxide

Particle precipitation from the off gas

Because of the small size of the nanoparticles the electrostatic precipitation has a higher efficiency than an off gas filter. The principle of the ESP is based on the charging of the particles by corona and after this an interaction with the electric field. The steps are described in Figure 3.

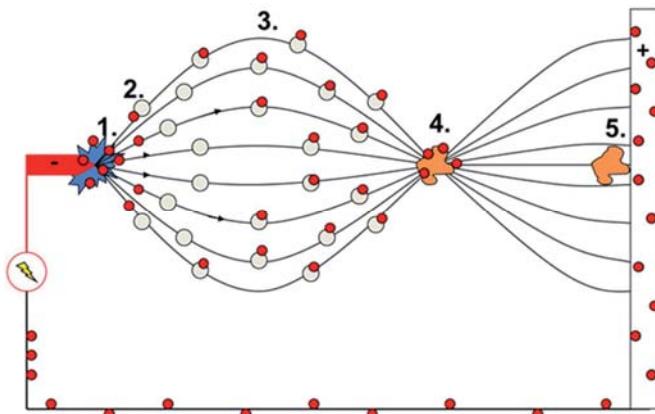


Figure 3: Steps of the electro static precipitation: 1. Emission of the electrons out of the cathode, 2. Charging the gas molecules, 3. Migration along the field lines to the

particle, 4. Charging the particle by discharging the gas molecule (Corona effect), 5. Precipitation and discharging of the particle at the collecting electrode.

Equipment

The ultrasonic spray pyrolysis is based on three steps, as shown. Every step takes place in a certain part of the equipment, see Table 3.

Table 3: Equipment for the process steps of the USP.

Process step	Equipment
Aerosol production	Ultrasonic generator
Pyrolysis	Tube furnace
Particle precipitation	ESP / wash bottle

In the laboratory, there are two different types of equipment. A vertical and a horizontal type, see Figure 5 and Figure 4. The ultrasonic generator (2) of the transformer (1) induces a piezo ceramic swinging. This forms an aerosol out of the solution. Nitrogen is the carrier gas, injected by a manometer (3). It carries the aerosol through the elbow (4) into the furnace tube (5) of the two furnaces (6) with the Al_2O_3 muffle (7). There evaporation, drying and pyrolysis take place. Afterwards, the wash bottles (8) collect the produced powder out of the off gas stream. An off gas tube (9) sucks the off gas out of the lab.

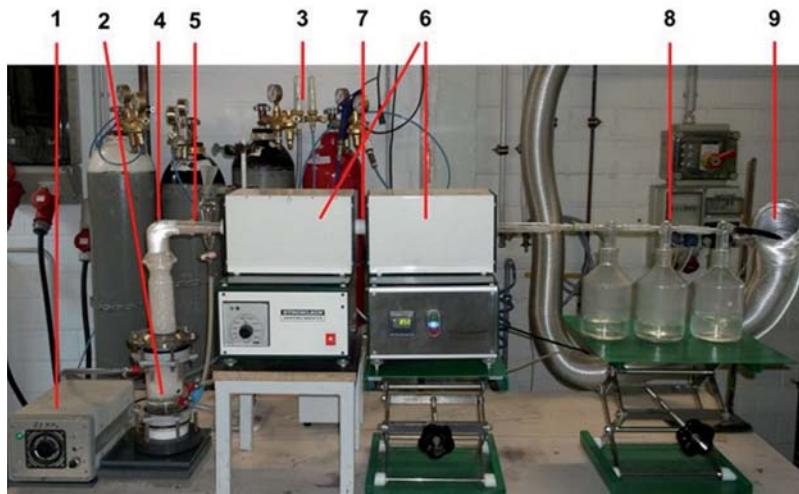


Figure 4: Horizontal equipment: (1) transformer (2) ultrasonic generator; (3) manometer; (4) rising pipe with glass elbow; (5) furnace tube; (6) resistance heated furnace; (7) Al_2O_3 -muffle; (8) wash bottles; (9) off gas tube.

The vertical equipment is encased. So there is a schematic representation added.

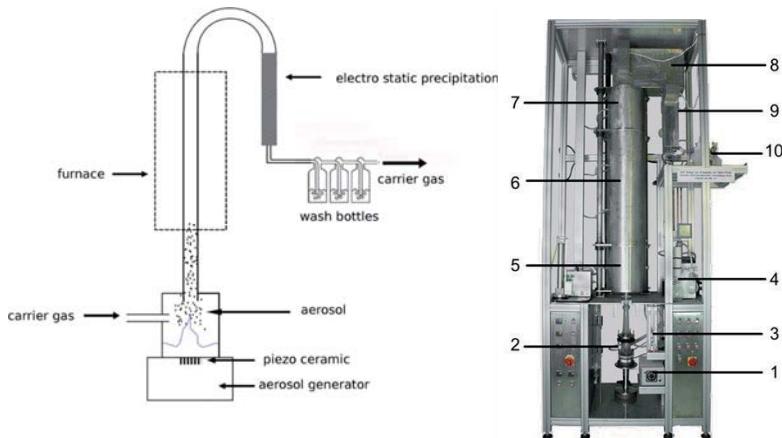


Figure 5: Schematic representation and photo of the vertical USP: (1) transformer (2) ultrasonic generator; (3) manometer; (4) vacuum pump; (5) first heating zone; (6) second heating zone; (7) third heating zone; (8) elbow; (9) electro static precipitation; (10) wash bottles.

Influence of the synthesis parameters

To show the influence of the educts and the synthesis parameters on the chemical purity and the crystallinity diverse salts and acid are tested. The experiments V2 and V3 result into a pure and crystalline LiFePO₄. Table 4 shows the condition of the experiment V2. Table 5 shows the possible educts.

Table 4: Reaction conditions of the experiment V2.

Carrier gas	Volume flow	Reactor temperature	Molarity of the precursor	Ultrasonic frequency
Nitrogen	0,5 l/min	800°C	0,05 M	2,5 MHz

Table 5: Possible educts for the successful synthesis of LFP.

Experiment	Lithium source	Phosphate source	Iron source
V2	LiCl	H ₃ PO ₄	FeCl ₂
V3	LiH ₂ PO ₄		FeCl ₂

Employing the conditions and educts presented in Table 4 and Table 5, the synthesis of pure and crystalline LiFePO₄ is possible as shown in Figure 6.

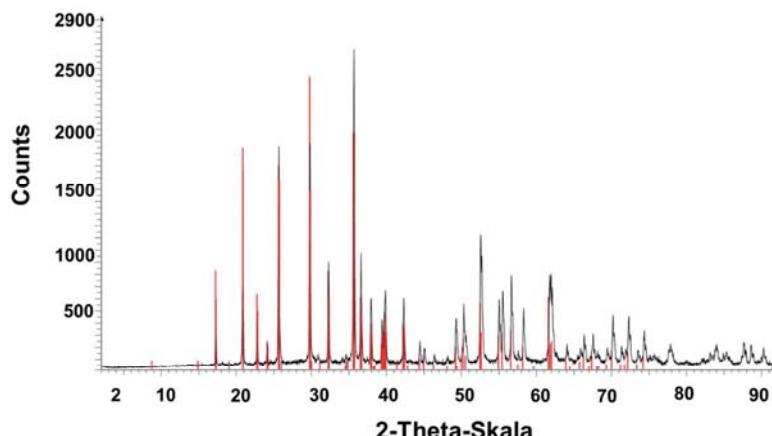


Figure 6: Diffractogram V2; homogeneous, crystalline LiFePO₄.

For the carbon shell, a carbohydrate source is essential in the precursor. But if the carbohydrate is present in the precursor, the diffractogram shows an amorphous fraction, as shown in Figure 7. This means the residence time is not long enough to synthesize graphite.

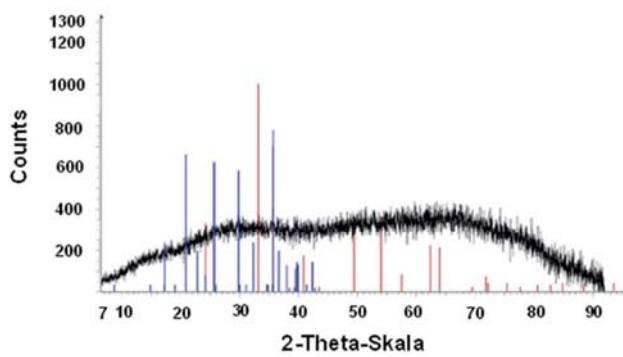


Figure 7: Diffractogram V4; homogeneous, crystalline LiFePO₄ with amorphous carbon.

Droplet size

As shown in equation 1, the droplet size depends on the density and the surface tension of the precursor and the frequency of the ultrasonic generator. According to this, in some experiments with laser diffraction the droplet size is measured. The salt molarity is changed to influence the precursor density. A varying ethanol content influences the surface tension and the frequency is modified by different generators. Results are presented below in Figure 8 and Figure 9.

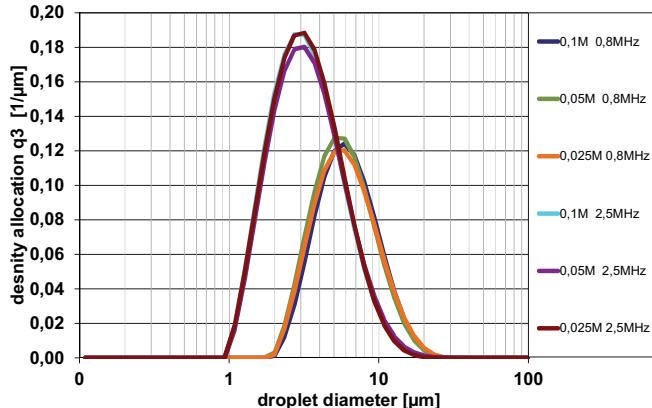


Figure 8: Density allocation of the droplet size depending from the frequency and the salt concentration.

For the experiments with the following results, the salt molarity is fixed to 0,05 M.

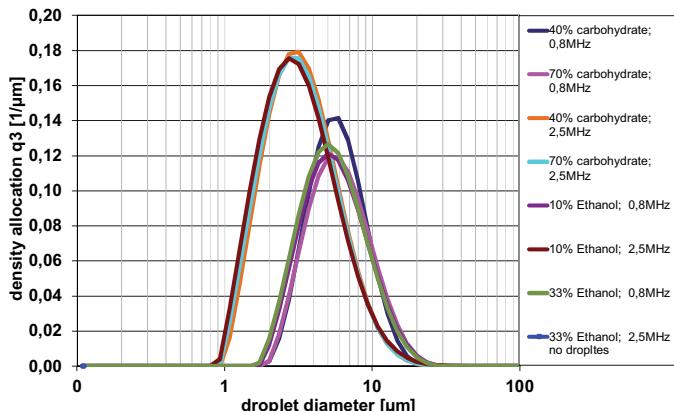


Figure 9: Density allocation of the droplet size depending on the frequency, the ethanol concentration and the carbohydrate concentration.

Particle size

Figure 10 shows the results of the particle size measurement at the zetasizer. It is measured by laser scattering. Therefore, the powder is dispersed in distilled water. So the particles swim in water and get an acceleration in an electric field. The four particle size distributions presented below are the results of the four different molarities in the precursor varying from 0,1 M to 0,0125 M.

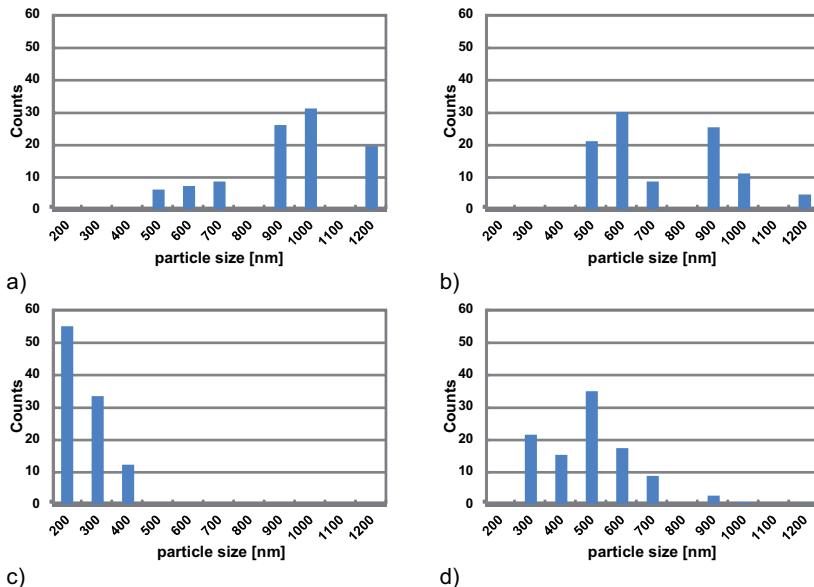


Figure 10: Distribution of the particle size depending on the molarity of the precursor:
a) 0,1 M; b) 0,05 M; c) 0,025 M; d) 0,0125 M.

Accessibility of the Core-Shell-Structure at the LiFePO₄-C-System

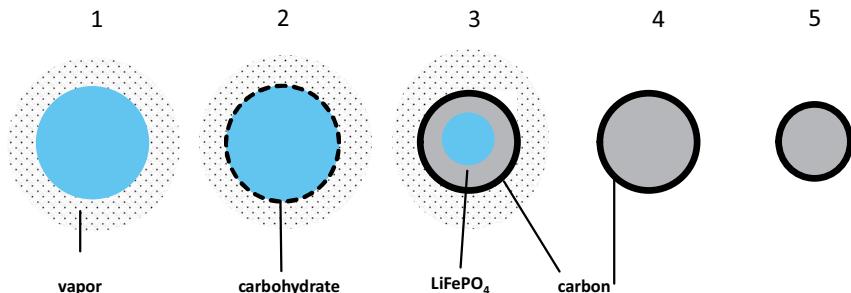
The production of core-shell-particles with LiFePO₄ in the core and C in the shell needs a decomposition of the carbohydrate from the rest of the reactants. Some experiments show the result of the modification of the following parameters to the CS-synthesis:

- salt molarity
- carbon concentration
- carbon source
- furnace temperature
- residence time

Two theories to explain the mechanism of core-shell formation are developed:

Proposal 1

Proposal 1 states that the shell forms at the beginning. That is because the carbohydrate crystallizes first. The front of crystallisation goes into the centre of the particle because with the continuous evaporation of water the solubility of the reactants is undercut: first carbohydrate, second the educts for LiFePO₄. So after the pyrolysis of all educts, the LiFePO₄ core is present in the carbon shell, as shown in Figure 11. In the moment of drying and pyrolysis, steam is set free. That means, the shell has to be permeable. Otherwise, the particles might explode.

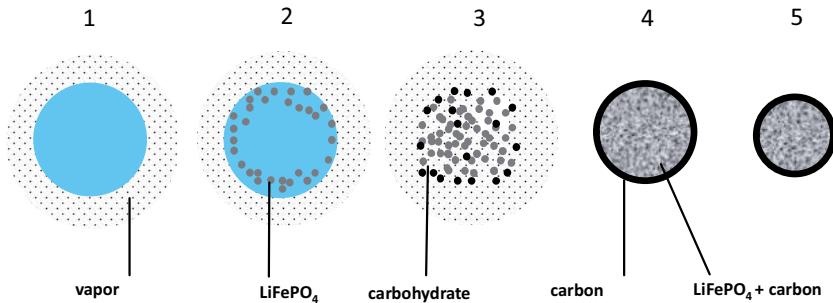


1: evaporation; 2: crystallisation; 3: drying; 4: pyrolysis; 5: sintering

Figure 11: Schematic representation of the core-shell-synthesis according to proposal 1.

Proposal 2

Proposal 2 states that the core-shell formation is initiated by the LiFePO₄ crystallization. The soluted carbohydrate outwards flows with the water vapor through the permeable core. The evaporation starts in the core yet. So the crystallization of the carbohydrate also starts in the LiFePO₄ core. Therefore, the decomposition is not so defined. In Figure 12 in process step 2 and 3, it is shown, how LiFePO₄ crystallizes first and afterwards the carbohydrate. The grey-black shaded core shall represent a higher carbon content than the core in proposal 1.



1: evaporation; 2: crystallisation; 3: drying; 4: pyrolysis; 5: sintering

Figure 12: Schematic representation of the core-shell-synthesis according to proposal 2.

The validation of the two proposals is evaluated in 19 experiments. In Table 6 the experimental conditions of experiment V3 and V8 are listed. V3 is an example for a failed synthesis. V8 marks a successful result of the core-shell-synthesis. Figure 13 and Figure 14 show the results of experiments V3 and V8. On the left side of the figure is a picture of the reviewed particle. On the right side, there is the diagram which states the results of line scan via edx.

Table 6: Conditions of the experiments V3 and V8.

number of experiment	molarity educts	temper-ature	carbon source	carbon concen-tration	residence time
V3	0,1	700°C	Saccharose	12 g/l	16 s
V8	0,05	700°C	Laktose	12 g/l	16 s

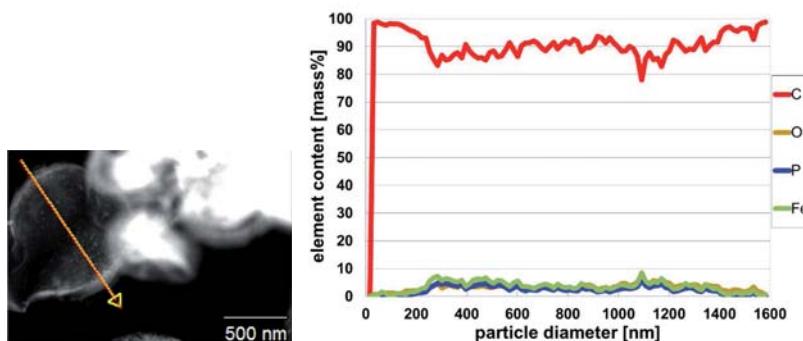


Figure 13: Experiment V3, TEM picture and result of line scan.

The result in Figure 13 pictures an excessive carbon content and the decomposition of LiFePO₄ and C is missing.

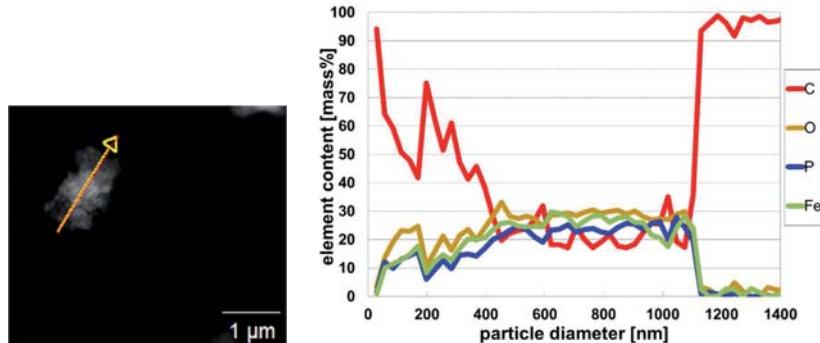


Figure 14: Experiment V8, TEM picture and result of line scan.

In Figure 14, a successful decomposition of LiFePO₄ and C is presented and a core-shell-morphology is visible.

Results of the core – shell - experiments

The evaluation of the experiments shows the dependence of the different parameters as described further down. For the quantitative evaluation of the results, a core shell factor was established. It helps to discuss the quality of the decomposition. The concentration of Fe and C in core and shell is based. The factor is defined as:

$$CS = \frac{c_{\text{außen}}^C / c_{\text{innen}}^C}{c_{\text{innen}}^{\text{Fe}} / c_{\text{außen}}^{\text{Fe}}} \quad 4$$

The higher the CS-factor is the better the decomposition works and the better the CS-morphology is.

Salt molarity in the precursor

The CS-factor is plotted versus the salt molarity of the precursor in Figure 15. The grey trend line shows an optimum of the salt molarity at 0,025-0,05 M. So the core-shell-synthesis works most suitable in this area. The experiments with 0,1 M are successful to 57%. The experiments with 0,0125 M show no useful results. This might be due to a nano effect, because the particles are smaller than 200 nm, as mentioned above.

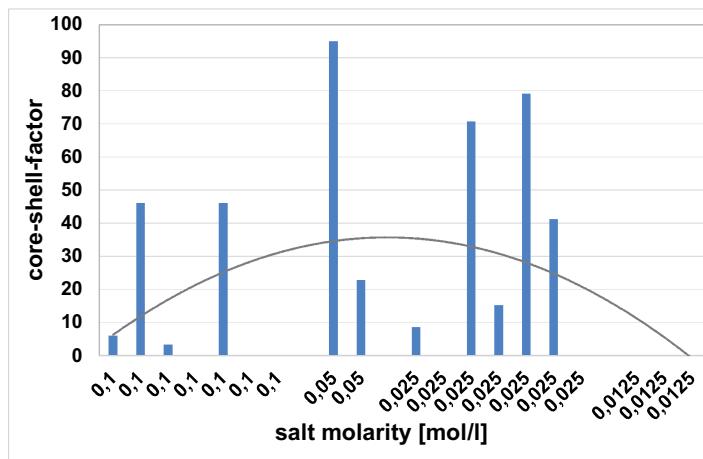


Figure 15: CS – factor plotted versus the salt molarity

Result: For the concentration of the educts, there is an optimum between 0,025 M - 0,05 M.

Carbon concentration

In Figure 16, the CS – factor is plotted versus the ratio Carbon / salt in the precursor. This figure shows an increasing CS-factor with a decreasing carbon / salt ratio in the precursor. Experiment 8 is an exception. 50 % of the experiments with a CS-morphology have a carbon / salt ratio of 10% or less. A higher carbon / salt ratio results in a higher carbon content in the core.

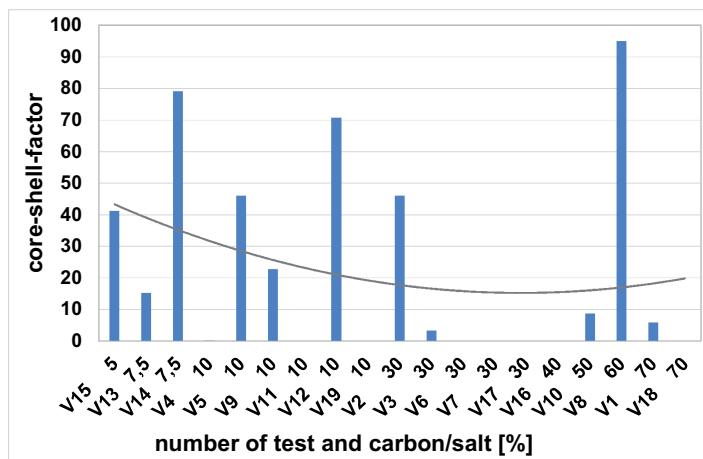


Figure 16: CS-factor plotted versus the carbon / salt ratio in the precursor.

Results: The lower the ratio carbon / salt is, the better the decomposition works.

Furthermore the parameters carbon source, furnace temperature and residence time influence the process:

- As a carbon source lactose is suitable, because due to its low solubility it guarantees a core-shell-morphology with carbon in the shell and with a clear decomposition of LiFePO₄ and C.
- The furnace temperature has an optimum at 750°C. At lower temperatures, the pyrolysis is not complete. At higher temperatures, the Fe₃C-synthesis takes place.
- A long residence time supports the steps of the synthesis which are influenced by diffusion. The residence time results from the reactor size employed and is 16 s for the large reactor and 4 s for the smaller one. Thus, the decomposition is improved using the large reactor.

Summary and outlook

The synthesis of LiFePO₄/C as a core-shell-material using the process of ultrasonic spray pyrolysis is possible. According to the results of the 19 experiments, the following table shows the influencing parameter and how to optimize them.

Table 7: Optimization of the parameters for the core-shell-synthesis.

Parameter	Adjustment
Molarity of salt in the precursor	0,025-0,05mol/l
Carbon concentration in the precursor	5-10%
Carbon source	Lactose
Furnace temperature	700°C
Residence time	16 s

The synthesis of Li(NiMnCo)_{0,33}O₂ is also possible. So the USP is a flexible process technology for the synthesis of cathode powder materials. The adjustment of the particle morphology and the particle size is well understood. This thesis helps to understand the process steps from the droplet with the dissolved educts to a core-shell-particle.

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