Combustion of Lithium Particles in N2 – Reaction Rates

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Abstract

The combustion of single lithium particles ($d_p < 200\,\mu m$) with N_2 was investigated in a laminar flow reactor. A particle sampling probe was used to extract and quench particles at various residence times. Burnout of the extracted particles was analyzed using X-ray diffraction and CHN-analysis to determine the burnout constituents. The burnout consists mainly of Li_3N and Li as well as some impurities ($LiOH$, Li_2O, Li_2CO_3) due to the experimental and analytical procedures. The resulting trend of lithium conversion depending on the particle residence time was used to calculate reaction rates for the nitration reaction of lithium.

1 Introduction

Metal particle combustion has been studied for many years, as the high energy density of metals makes them attractive as additives of solid propellants, pyrotechnics and metalized explosives [1–3]. Furthermore, the increasing demand for carbon-neutral energy motivates the use of metal fuels for storing renewable energy for international energy trade and power generation [4–10] or the in-situ water splitting reaction to produce hydrogen gas on demand [4,6,11–15]. Lightweight metals show the best energetic-density performance for such applications, while abundant metals should have the lowest

costs. The fundamentals of metal combustion have been studied for a wide range of metals, including aluminum [16–18], magnesium [19–21], iron [22–24], boron [25,26] and lithium [7,27–29].

The exothermic reactions of lithium with gaseous species, e.g. O_2, CO_2, H_2O and, also, N_2 have been investigated in the past focusing on different issues like fire safety or propulsion of space craft [30,31]. Additionally, the use of lithium in energy processes has become of increasing interest during the past few years [7,8,28]. The main idea in these processes is to use lithium in an exothermic reaction with one of the gaseous species mentioned above. Specifically, the reaction with CO_2 has been investigated in detail, as the combustion temperature in the range of 1600 K is sufficiently high to use lithium as a fuel in thermal power plant processes [8].

Lithium is also able to react with nitrogen exothermically [30,31]:

$$6Li + 3N_2 \rightarrow 2Li_3N \ - 164.6 \ kJ/mol_{Li3N}$$

Equation 1

This process is not only exothermic, but could also be used to produce ammonia by the subsequent exothermal reaction $Li_3N + 3H_2O \rightarrow 3LiOH + NH_3 - 436.2$ kJ/mol_{Li3N}, providing a valuable by-product for economic benefit and additional heat.

The nitration reaction (Equation 1) has been investigated by several groups using lithium blocks or pools [32,33] or utilizing lithium powder [34–36], but as reactions were reported to start with significant rate above lithium's melting temperature (180 °C), it is supposed that the powdery structure of the samples had changed during the experiments due to melting.

The reaction of single lithium particles in nitrogen is investigated in the present work. As complete chemical conversion is of major importance in chemical processes, lithium particles with a diameter below 200 µm were chosen. The nitration reaction was carried out in a drop tube reactor and the solid residues were collected and analyzed for their chemical composition to determine the reaction progress and reaction rate parameters for the nitration reaction of single "burning" lithium particles or droplets. Similar experiments were carried out previously in CO_2 [8] and N_2/CO_2 mixtures [27,29]. In the latter experiments, where N_2 concentrations up to 90 %$_{mol}$ were applied, only products of the reaction of

lithium with CO_2 were found, thus the reaction with nitrogen had to be investigated in pure N_2 atmospheres.

2 Experimental Setup

As the reactor setup has been described in detail in [8], only a short description is given here. The reactor is shown in Figure 1. An electrical gas heater is used to preheat 70 slpm of N_2 to a temperature of approx. 800 K. A steady laminar flow of heated nitrogen is established in the quartz tube (d= 65 mm), which supports the determination of time-dependent variables like reaction kinetics parameters. The lithium particles, which were produced as described in [7] from lithium rods (purity 99.9%, <1500 ppm trace metals), were injected into the reaction atmosphere through a water-cooled injector from the top, following the gas flow in a linear streak. The particle feed rate was kept at 1-2 grams per hour to avoid particle-particle interactions. The initial particle size distribution of the particle sample is given in Figure 2, showing a volumetric d_{50} of 130 µm (d_{10}= 92 µm, d_{90}= 158 µm). From the feed rate and d_{50}, a rate of ~900 particles/s results, meaning that the particle-particle separation is above 1 mm assuming that the particles are travelling in-line. As the particle streak has a diameter of approx. 3-4 mm, the real particle-particle distance is slightly larger. A water-cooled sampling probe, described in detail previously [8], was used to extract solid samples of (partially) reacted lithium particles from the reactor for composition determination with varying residence times to cover the burn-out history of the particles for kinetics calculations. The particles were quenched by the cooled probe walls and an additional argon co-flow, which was used to cool down and dilute the reaction atmosphere by a factor of approx. 5 (~8 slpm Ar feed and 2 slpm N_2 from the reactor).

After sampling, the particles were analyzed by X-ray diffraction (PANalytical X'Pert Pro diffractometer) to determine the mineral phase composition and CHN analysis (Leco TrueSpec Micro) was carried out for further quantification of the chemical composition.

Particle velocities were measured to calculate residence times of the particles at different sampling positions. A high speed camera system was used to measure the velocity of single particles by shadow imaging and double exposure [37].

The gas temperature profile was measured using a Pt/PtRh10 thermo-couple made from 30 µm wires. Radiation correction was applied as described in [38].

Figure 1: Schematic of the drop tube reactor with gas heater, mass flow controller and sampling probe.

Figure 2: Volumetric particle size distribution of the used lithium sample.

3   Experimental Results

Particle velocities were measured at five positions along the particle trajectory, as the results indicate (Figure 3) the particle velocity is nearly constant at $1.22\ \mathrm{ms^{-1}}$. The standard deviation for all measurements is approx. 0.1 m/s. This is attributed to the shadow imaging procedure. Note, that the same camera system was used to determine the temperature of lithium particles burning in CO_2 and CO_2/N_2 mixtures [8,29], but lithium particles burning in nitrogen did not emit a sufficient amount of radiation for this system to detect particle radiation directly.

Figure 3: Gas temperature and particle velocity of lithium particles in the drop tube reactor, error bars represent 1σ uncertainty in particle velocity.

The gas temperature measurement (pure gas phase without addition of particles) shows the lowest temperature of 730 K directly below the particle inlet, where the Ar carrier gas flow leads to a cooling effect (Figure 3). Mixing with the preheated N_2 flow leads to a significant increase to a gas temperature above 780 K with a slight increase to T_{gas}= 820 K, this means a change in gas temperature of approx. 5%. As the feed-rate of lithium particles was kept low, no significant change in gas temperature was assumed. As the volumetric concentration of argon is 0.5% related to the total gas flow, and the first measurement was taken more than 100 mm downstream of the particle inlet, complete mixing was assumed and the small dilution of the nitrogen by argon was neglected.

In contrast to experiments in CO_2 containing atmospheres [7,8,29], no optical diagnostics were applied in these experiments. The visual impression of the combustion process implied very little thermal radiation, as only weak radiation emission was visible for the naked eye, which is in clear contrast to the CO_2 findings, where, especially during the initial gas-phase combustion step, particle burning is accompanied by intensive radiation emission. Furthermore, no aerosol formation was visible, which is another clear difference compared to the experiments in CO_2. Considering the thermo-physical properties of lithium and Li_3N, the missing aerosol formation becomes plausible, as the formation of lithium nitride is limited to temperatures below 1235 K. FactSage [39] calculations show, that at this temperature Li_3N completely decomposes into its constituents, giving an upper temperature limit for

the chemical reaction in this case (Figure 4). However, in this temperature region the vapor pressure of lithium is 0.03 bars (Figure 5), which limits the vaporization rate and reduces the tendency for gas phase combustion accompanied by aerosol formation. Thus, the overall findings indicate a surface reaction

Figure 4: Chemical equilibrium calculations for 3Li+1/2 N_2→Li_3N (FactSage).

Figure 5: Vapor pressure of lithium [40]

process, which has been found to be typical for lithium combustion in other gases like CO_2/N_2 mixtures with low CO_2 content [29] and the final stages for lithium particle combustion in pure CO_2 atmospheres [8].

The particle velocities depicted in Figure 3 were used to calculate the residence times for different sampling probe positions. At these positions, particle samples were extracted from the reactor and analyzed for their chemical and elemental composition. These experiments were repeated at least once to check the reproducibility. The qualitative XRD analysis showed that all samples consisted of mainly of Li and Li_3N (as expected), additional traces of LiOH, Li_2O and Li_2CO_3 are attributed to the sample handling, which could not be done under inert atmosphere due to the XRD setup. As quantitative XRD maps are not available for all species included in the analysis, further analysis regarding the CHN content was carried out to investigate the chemical composition of the samples.

Two exemplary XRD spectra are shown in Figure 6. The spectrum taken from a sample extracted after 0.164 s shows dominating peaks of Li_3N, but additional peaks from Li, Li_2O, LiOH and traces of Li_2CO_3 appear. In contrast, the final data point, taken after 0.246 s shows very few peaks except those related to Li_3N. This already indicates a high degree of conversion. As there are no quantitative maps available for Li and LiOH, only the relative proportion of the three remaining components was determined by XRD. Additional measurements of the C, H and N content were used to calculate the amount of all constituents, in molar concentrations the resulting formulas are:

$$X_{Li_2CO_3} = \frac{\bar{\mu}}{\mu_C} Y_C$$

Equation 2

$$X_{Li_3N} = \frac{\bar{\mu}}{\mu_N} Y_N$$

Equation 3

$$X_{LiOH} = \frac{\bar{\mu}}{\mu_H} Y_H$$

Equation 4

The molar fraction of Li_2O was derived from the mass ratio of Li_2O and Li_3N. The relative mass fraction of both materials is a direct result from the XRD analysis, which only measures the products but not the

lithium content, thus the mass fraction $Y_i = m_i/(m_{LiOH} + m_{Li_3N} + m_{Li_2O} + m_{Li_2CO_3})$ cannot be converted into a molar fraction directly. Instead, the molar fraction of Li_3N determined from Equation 3 has to be used to calculate X_{Li_2O}:

$$X_{Li_2O} = X_{Li_3N} \frac{\mu_{Li_3N}}{\mu_{Li_2O}} \frac{Y_{Li_2O}}{Y_{Li_3N}}$$

Equation 5

The average molar concentration was calculated using the mass fractions Y_i and molar masses μ_i of the sample constituents, $\bar{\mu} = (\sum Y_i/\mu_i)^{-1}$. As there were no other constituents detected during the XRD measurements, the lithium content was determined as the difference between unity and the molar fractions of the previous four constituents.

Figure 6: XRD spectra after 0.164 s (top) and 0.246 s (bottom).

The measured mole fractions for the investigated residence times are given in Figure 7. The relative concentrations in this figure are given related to the amount of lithium bound in the particular compound, as the following calculation of reaction kinetics parameters is related to the converted amount of lithium. The error bars are calculated using Gaussian error propagation as described in [8]. The uncertainty in the XRD data was set to 25% relative error, as XRD is known to have large uncertainties for quantitative measurements, and the error of the CHN analysis was set to 15% relative uncertainty.

Figure 7: Sample constitution in relative lithium content per compound.

As the results show, the lithium content significantly decreases between 0.082 s and 0.246 s. At the final data point, the sample contains more than 85% of lithium bound in Li_3N. If the measurement uncertainty is considered, it is possible that complete lithium conversion to Li_3N has occurred. The error in lithium content is largest of all calculated errors, contributing to ±23% for the final data point, where 7% lithium were found in the sample. This is caused by the calculation of lithium as the difference between sample

mass and all remaining constituents, such that the errors of each of the single constituents compound. The amount of the oxygen containing compounds, which are assumed to be caused by sample handling, indicates that less than 5% of lithium is bound in these constituents.

3.1   Apparent kinetics calculation

The experimental data described above was used to calculate rate parameters for the nitration reaction. The model applied uses apparent kinetics. As is reported in literature, the nitration reaction leads to the formation of product layers on the sample [32], which cause a transport limitation, e.g. described by a shrinking core model [41], as the reacted product on the surface hinders the diffusion of gaseous reactants to the surface of the non-reacted material. Figure 8 illustrates such a situation. The particle surface is covered with Li_3N, which represents a diffusion resistance for both lithium vapor moving outwards and nitrogen flowing to the surface. The reaction takes place in this porous product layer. Note, that the gradients of both N_2 and Li vapor do not necessarily have to begin at the surface of the lithium core and the outer surface of the product layer. It is also possible that the reaction front is a thinner layer within the product layer, and its exact position is determined by the transport properties of both gaseous educts. As the particle is small, leading to a low Biot number ($Bi = 2\,\lambda_{N2}/\lambda_{Li} < 1$ for suspended particles), the temperature is assumed to be equal to the decomposition temperature in the entire particle, in the boundary layer ($d > d_p$) the temperature drops to gas temperature.

Figure 8: Sketch of concentrations of Li, and temperature profiles assumed in the current model.

The description of transport phenomena needs a detailed knowledge of the product layer properties, e.g. porosity and pore diameter [42]. Examples of the importance of surface or product layer related transport processes are available for carbonaceous fuels [41,43,44], metal particles [16,18,45,46] or lime stone [47] or other processes [48,49]. Another good example is classical Thiele analysis [44,50]. However, the porosity and thickness of the product layer are sometimes neglected, instead the chemical and pore diffusion related resistances are combined into one effective reaction rate constant [51–53]:

$$k_{eff} = \left(\frac{1}{k_{chem}} + \frac{1}{k_{pore}}\right) = A * exp\left(-\frac{E_a}{RT_p}\right)$$

Equation 6

The conversion curve for lithium over time is very monotonic, so the simple approach of a one-step Arrhenius expression was chosen to describe the conversion rate in $mol_{Li}/(m^2 s)$:

Equation 7

$$\dot{n}''_{Li} = A * exp\left(-\frac{E_a}{RT_p}\right) p_{N_2,s}$$

The conversion rate of lithium depends upon the frequency factor A, the activation energy E_a, the universal gas constant R and the particle temperature T_p. It has to be noted, that the absence of aerosol formation and visible lithium gas phase combustion leads to the conclusion that the reaction occurs solely at the particle surface or in the porous boundary layer, so the particle temperature was assumed to be the relevant temperature for the reaction. To consider the previously mentioned characteristics of Li_3N to decompose at elevated temperature, the maximum temperature limit for T_p was set to 1235 K for the presented calculations. Furthermore, no gaseous reaction products are expected (Equation 1), thus the nitrogen pressure at the particle surface $p_{N2,s}$ was set to 1 atm, the pressure in the free gas stream.

The determination of burning rate parameters was carried out using an iterative routine. Along its trajectory, a lithium particle undergoes inert heating, melting, and finally combustion. Therefore, the surface-related energy balance was solved:

$$\dot{q}_{react} = \frac{Nu \cdot \lambda}{d_p} \cdot (T_p - T_{gas}) + \sigma\varepsilon(T_p^4 - T_w^4) + \frac{d_p \rho_p c_p}{6} \cdot \frac{dT_p}{dt} \quad \left[\frac{W}{m^2}\right]$$

Equation 8

From left to right, the considered contributions are the heat from chemical reaction $\dot{q}_{react} = \dot{n}''_{Li}\Delta H_{Li\rightarrow Li_3N}$ (for the reaction enthalpy see [54]), convective heat transfer between particle and gas, radiative heat transfer between particle and wall and heating of the particle. As the particles are small and the density of lithium is relatively low (~530 kg/m³), particles can be assumed to be at rest in the gas, resulting in Nu=2. The thermal conductivity λ of N_2 was taken from [55]. The gas temperature profile (T_{gas}) was fitted to the temperature curve given in Figure 3. Next, the radiative heat exchange between particle and wall is considered, where the wall temperature was set to 400 K, but due to the T^4

dependency this is of minor relevance. The emissivity of lithium was set to ε=0.2 [56]. The heating of the particle takes place as long as the particle has not reached the upper temperature limit, which is the decomposition temperature of Li_3N (Figure 4). The decomposition temperature is a suitable assumption for the upper flame temperature limit of metal gas phase combustion reaction, as previously has been reported [8,57]. From the current point of view and the experimental findings for lithium burning in CO_2 [8], there is no reason which allows temperatures significantly higher than the decomposition temperature for surface combustion. Note that prior to ignition $\dot{q}_{react} = 0$ is used to calculate the inert heating of the particle. When the melting temperature is reached, the particle is assumed to rest at this temperature until all lithium is molten, than the exothermic reaction starts.

As the particle size distribution ranges over a certain span, particle diameters from 10-210 µm are considered in 10 µm steps for the fitting procedure of the best-fit A/E_a values. The fitting routine works as follows:

For each particle diameter, the temperature history is derived by calculating *T*(*t*) from Equation 8 using an actual pair A/E_a. In this step, the temperature dependent reaction rate (Equation 7) is calculated. The total relative conversion, $X_{Li,react}(t)$, is summed for each time step:

$$X_{Li,react}(t, d_p) = 1 - \frac{\sum_{\Delta t} \Delta t \, \frac{\pi}{4} d_p^2 \, \dot{n}_{Li}''(t)}{\rho_{Li} \, \frac{\pi}{6} \, d_p^3 \Big/ \mu_{Li}}$$

<div align="right">**Equation 9**</div>

The denominator represents the initial molar lithium content of the particle. The relative conversion for each particle size is than weighted with the volumetric particle size distribution,

$$X_{Li,react}(t) = \frac{V(d_p)}{V_{total}} X_{Li,react}(t, d_p),$$

<div align="right">**Equation 10**</div>

which is summed up for all particle bins to calculate the total conversion of the sample. The volume fraction of a given particle diameter follows directly from the data in Figure 2.

The calculated average composition from Equation 10 is compared to the measured composition for the residence times which were used for particle sampling (Figure 7). To obtain suitable A/E_a values, a grid search routine was applied varying A and E_a to find the minimum residuum

$$r_{fit} = \left(\sum_{i=1}^{5} \left(X_{Li,react}(t_i) - X_{Li,meas}(t_i) \right)^2 \right).$$

Equation 11

The fit procedure found an pre-exponential factor A= 165 kmol$_{Li}$/(m^{2}s) and an apparent activation energy E_a= 75.1 kJ/mol.

3.2 Comparison to literature data

In the literature, activation energies for reaction of lithium and N_2 according to Equation 1 are given by several authors. Table 1 summarizes some of the data available and covers the range of available activation energies, more detailed discussions on available data are given in the corresponding references.All these measurements were carried out using lithium samples of several grams, and typically the N_2 pressure was lower than in the presented experiments. Lithium temperature was measured with thermo-couples in the lithium bath and not at the reacting surface, which might lead to

miss-estimated reaction temperatures [58]. However, some of the values are in the same range as the free fit activation energy presented in section 3.1.

Table 1: List of activation energies and parameter ranges for the reaction of molten lithium with nitrogen, sample mass is related to single particles for the given experiment.

Additional to the free fit approach, activation energies from [58] (45.2 kJ/mol), [59] (65.3 kJ/mol) and [32] (96.3 kJ/mol) were used to determine the best fit pre-exponential factor. For all activation energies the best-fit values are summarized in Table 2. As expected from the Arrhenius approach, the pre-exponential factor shows a strong increase with increasing activation energy.

Table 2: Comparison of best-fit results for different activation energies

In Figure 9, the resulting conversion curves for all parameter sets from Table 2 are compared to the measured lithium content. As it shows, the different parameters represent the measured data with different, but acceptable accuracy. The lowest activation energy [58] shows slower conversion with

Figure 9: Conversion curves for the fit parameters from Table 2**.**

decreasing lithium content, while the highest activation energy [32] leads to low conversion rates at the beginning and faster conversion with decreasing lithium content.

In Figure 10, time-dependent conversion for particles of 80, 120 and 160 µm is depicted together with the resulting temperature curves. The selection of particle sizes covers the relevant particle size distribution (Figure 2). The conversion curves show the influence of varying E_a and resulting A in detail,

Figure 10: Conversion and temperature history for particles with diameters 80 µm, 120 µm and 160 µm. Conversion is marked with black decreasing lines, temperature trends are red increasing lines.

supported by the temperature curves. The particle temperature rises continuously until T_{decomp} is reached, but smaller activation energy leads to a more rapid temperature increase, as smaller reaction rates supply enough energy to exceed the activation barrier. Regardless of d_p and E_a, significant conversion begins when the particle temperature is close to the upper limit. As a consequence, lower activation energies lead to earlier conversion, but a lower conversion rate for a given particle diameter. For the lowest activation energy (E_a= 45.2 kJ/mol), the conversion curves of 80 µm and 120 µm particles show a certain overlap, as the smaller particle carries still some lithium when the larger particle has reached its final temperature and shows significant conversion. The comparison between 120 µm and 160 µm particles shows the same tendency. Increasing activation energy not only leads to a delayed increase in temperature, but also shifts the onset of conversion to later times, which reduces the overlap between different particle sizes until the three considered particle sizes in Figure 10 are burning completely separated in time. Thus, although all A/E_a combinations listed in Table 2 represent the integral conversion measurement relatively well, the effect on different particle sizes is clearly visible.

Depending on the chosen activation energy different fractions of the particle size distribution contribute to the conversion curve at different time steps.

4 Discussion

The measured particle composition presented in Figure 7 shows uncertainties in the composition of the lithium mass fraction, which directly affects the accuracy of the reaction rate parameters. A simple variation was tested to identify the impact of the variance in lithium content on the resulting rate parameters. As the final sample temperature is limited in the given experiment due to decomposition, the uncertainty was assigned to the pre-exponential factor solely. Counting the five measurements with increasing time, the lithium content was varied as $X_{Li,var,i} = X_{Li,meas,i} \pm \frac{3-i}{2}\sigma_{Li}$, where i denotes the time step, the plus sign leads to the conversion curve with the maximum slope and the minus flattens the conversion to a minimum. The resulting pre-exponential factors are $A_+ = 189.8$ kJ/mol and $A_-= 136.5$ kJ/mol. The maximum relative error is thus +15% and -18%.

Although the current results give first reaction rate parameters for the reaction of lithium with nitrogen for particles in the size range around 100 µm, the results also show that some further investigation will help to improve the given parameters and to limit the uncertainty in useful A/E_a combinations. The following points would support such measurements:

- Particle temperature measurements: In absence of temperature measurements, the maximum particle temperature and ignition temperature were taken from literature and thermo-physical calculations (Figure 4). Measured temperatures would help to improve the understanding of lithium combustion in nitrogen, as this was previously done for lithium burning in carbon dioxide [8,9]. Fitting activation energies would further be improved by experimental conditions where the particles do not necessarily reach a constant final temperature. According to Equation 8, a possible setup should allow for lithium particle combustion with gas and wall temperatures at different levels to balance particle temperature by heat loss. One could also suggest TGA or DSC measurements to get reaction rates at varying temperature, which are typical for the determination of activation energies for chemically controlled reactions. However, as lithium

would have to be placed in crucibles, the experiments would show some similarities already mentioned in [32,33,58,60,59]. These experiments were carried out using heated pools measuring the pressure drop of nitrogen in a closed vessel, keeping the reactor temperature constant. However, none of these experiments could guarantee a specific sample temperature. Furthermore, the formation of a solid product layer was reported for some of these experiments. The properties of this product layer need to be considered when TGA is used, as the thermal changes during the experiment could cause changes in the physical structure of this product layer. Additionally a comparison between the product layers on pool samples and on sub-mm lithium particles is necessary to provide comparability between the different experiments.

- As Table 1 summarizes, the experimental determination of activation energies in literature was carried out under relatively low lithium temperatures for large lithium samples, the nitrogen pressure typically being low compared to the present experiment. The sample temperature in these cases was measured in the lithium bath. The temperature of the reaction zone, which could have been located either in a porous product layer or in a diffusion flame above the sample, was not reported. In contrast, the current approach uses the decomposition temperature of Li_3N to provide an upper temperature limit justified by FactSage calculations for equilibrium compositions (Figure 4, [39]), and the fit results show that the particles easily reach this temperature level.

- Due to the still relatively wide particle size fraction, overlap effects in the conversion curves of single particle sizes participate in the kinetics determination routine. Measurements with narrower particle size distributions or at least particle size measurements which differentiate between non-ignited, burning and burned-out particles at different positions in the reactor would help to reduce these effects. However, already the production of lithium particles in the used particle size distribution is of enormous effort, a further reduction in width seems not reasonable with available techniques. Measurement of size (and temperature) would require an optical measurement device, which could be an option for later work.

As Li_3N only exists in solid form, the formation of a product layer as indicated in Figure 8 is likely. The formation of such product layers has been identified for other metal fuels, e.g. aluminum. As already

mentioned, this product layer builds a resistance for both metal vapor and gaseous reactant. This effect has been discussed in literature on metal fuels [16,18,61,62], and one solution is the description of this phenomenon as shrinking core process [5,45,46,63], For magnesium particles, the final stage has been found to be a spherical hollow particle [64] with a significant void inside, which is a similar phenomenon requiring consideration in conversion and kinetics calculations. However, modelling the combustion process including the restricting effects of product layers on the surface requires more detailed knowledge, which is a possible step for further investigations.

As there is still few literature available on the reaction of separated small lithium particles, the only comparable work was published by Fischer at al. [8,9,27,29], where lithium particles with an average diameter of ~85µm were burned in pure CO_2 [8] and modelled using computational fluid dynamics [9]. Mixtures of CO_2 and N_2 were used to investigate the temperature and composition of burning lithium particles in a similar size range in [27,29]. The particle temperature, measured by ratio pyrometry, in all experiments was higher than the decomposition temperature of Li_3N when CO_2 was present. The solid sample results in all works show, that the particle are free from Li_3N, only consisting of the products of the Li/CO_2 reaction. This supports the assumption of the current work that the decomposition temperature of Li_3N is the limit temperature for the nitration reaction.

5 Summary and Outlook

Experiments on the combustion of lithium particles in the 100 µm size range were carried out in nitrogen atmospheres. Particles were fed to a drop tube reactor, where the solid reaction product was investigated by solid sampling and subsequent XRD and CHN analysis. The experiments show that the formation of Li_3N was nearly complete in the time frame investigated in the experiment.

The measured conversion was used to derive the first set of apparent reaction kinetics parameters for the combustion of lithium particles. A best-fit decomposition temperature in agreement with thermo-physical calculations was found. The influence of the ignition temperature is rather small. A parameter set for the reaction of lithium with nitrogen was calculated. It represents the experimentally determined sample conversion properly.

The influence of particle size, particle temperature and partial pressure of nitrogen on the reaction kinetics parameters is not completely resolved in the current work. Further experiments are needed to add this information. The kinetics parameters presented relate to apparent kinetics, thus they do not resolve the possible formation of a product layer on the particle surface which reduces the transport of gaseous components at the particle surface. Instead, these effects are included in the given kinetics parameters.

6 Acknowledgements

7 Symbols used

A	mol/(m²s)	pre-exponential factor
c_p	J/(kg*K)	heat capacity, calculated for the mass fraction of Li and Li$_3$N
d	m	diameter
d_p	m	particle diameter
$d_{10/50/90}$	m	characteristic diameters (10/50/90% quantil)
E_a	kJ/mol	activation energy
k_{eff}	mol/(m²s)	effective reaction rate constant
k_{chem}	mol/(m²s)	chemical reaction rate constant
k_{por}	mol/(m²s)	pore diffusion reaction rate constant
$\dot{n}''_{Li}$	mole$_{Li}$/(m^{2}s atm)	conversion rate
Nu	[-]	Nusselt number
p	bar	pressure
$\dot{q}$	W/m²	heat flux
r_{fit}	[-]	Fit residual
R	J/(mol*K)	universial gas constant
t	s	time
t_{ign}	s	ignition time
T_{decomp}	K	decomposition temperature
T_{gas}	K	gas temperature

T_{ign}	K	ignition temperature
T_p	K	particle surface temperature
T_w	K	wall temperature
$V(d_p)$	[-]	Particle volume correlated to particle size d_p
X	mol/mol	mole fraction
$X_{Li,react}(t)$	mol/mol	reacted fraction of lithium by calculation
$X_{Li,meas}(t)$	mol/mol	measured fraction of lithium
Y	[kg/kg]	mass fraction
ε	[-]	emissivity
λ	W/(m*K)	thermal conductivity
μ	kg/mol	molar mass
ρ_p	kg/m³	particle density
σ	$5.67*10^{-8}$ W/(m²K⁴)	Stefan-Boltzmann constant

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