

# Continuous Wet Chemical Synthesis of Molybdenum Carbide Precursors in the Microjet Reactor

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## Introduction

Continuous wet chemical synthesis applying a microjet reactor is a possibility for large scale production of well-defined (nano)particles. Under high pressure two reactant solution are passed to a chamber where the reaction occurs. High shear forces and enormous mixing rates will be generated, which allows the synthesis of homogenous particles with narrow size distribution.<sup>[1]</sup>

Here we present the application of the microjet approach for the formation of molybdenum carbide ( $\text{Mo}_2\text{C}$ ) as well as molybdenum oxycarbide ( $\text{MoOC}$ ). The resulting particles are suitable as materials for electrodes in energy storage applications. The commercial lithium-ion batteries (LIBs) use graphite as an anode revealing a quite low capacity of  $372 \text{ mA h g}^{-1}$ . Promising candidates with higher theoretical capacities are transition metal oxides, sulphides, and carbides.<sup>[2]</sup> Molybdenum oxides ( $1117 \text{ mA h g}^{-1}$  for  $\text{MoO}_3$  and  $837 \text{ mA h g}^{-1}$  for  $\text{MoO}_2$ ) represent good candidates due to their high electrochemical activity and theoretical capacity. Because of the high electrical conductivity and furthermore the excellent mechanical and chemical stability molybdenum carbides like  $\text{Mo}_2\text{C}$  and  $\text{MoC}$  shows favorable lithium storage properties. Hence,  $\text{MoOC}$ -based electrodes can merge the properties of the two worlds.<sup>[2]</sup>

The particles were prepared via a direct pyrolysis of  $\text{MoOx}/p$ -phenylenediamine<sup>[3]</sup> precursors. Based on this work we use various aromatic and non-aromatic diamines to compare their suitability as precursors. The diamines act as a carbon source during the pyrolysis. Parameters such as the structure of the diamine and the ratio between the ligand and the metal source were investigated. In addition we compared batch and microjet synthesis with each other. Variation of the pyrolysis temperature also allows the production of  $\text{MoOC}$  particles.

## Synthesis with the microjet reactor

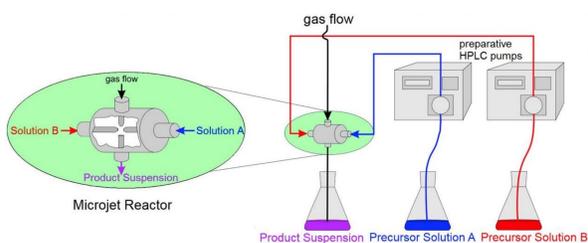
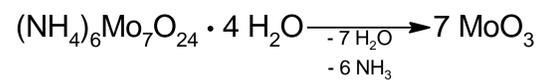


Fig. 1: Illustration of the microjet reactor.<sup>[4]</sup>

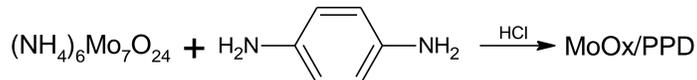
- Solutions are delivered under high pressure through a nozzle to a reaction chamber
  - At the collision point high shear forces are generated in short times, which results in complete mixing before the nucleation of the product starts<sup>[5]</sup>
  - Leads to separation of nucleation and growth
- **Benefit:** Synthesis of homogenous particles with narrow size distribution.<sup>[1,4]</sup>

## Mechanism of Pyrolysis



- Correlation between the amount of the carbon in the precursor and the product after the pyrolysis
- $\text{MoO}_3$  is reduced by CO to  $\text{Mo}_2\text{C}$ 
  - diamines acts as carbon source
  - amount of the diamines in the precursor important for the reduction
  - variation of ratio important<sup>[6,7]</sup>
- necessary to investigate the influence of the reaction temperature

## Synthesis of precursors



- Precursor solution A: ammonium heptamolybdate (AHM) and p-phenylenediamine (PPD) dissolved in water
- Precursor solution B: 0.05 M HCl solution
  - precursor was obtained through precipitation route
- Batch synthesis with various ratios of AHM and PPD; 1:1; 1:2; 1:5; 1:9; 1:10; 1:15; 1:18; 1:20; 1:25; 1:30
  - transfer to a continuous approach in the to microjet reactor
- Conditions of microjet reactor: 250 mL/min flow rate at 20°C

## Microjet Samples

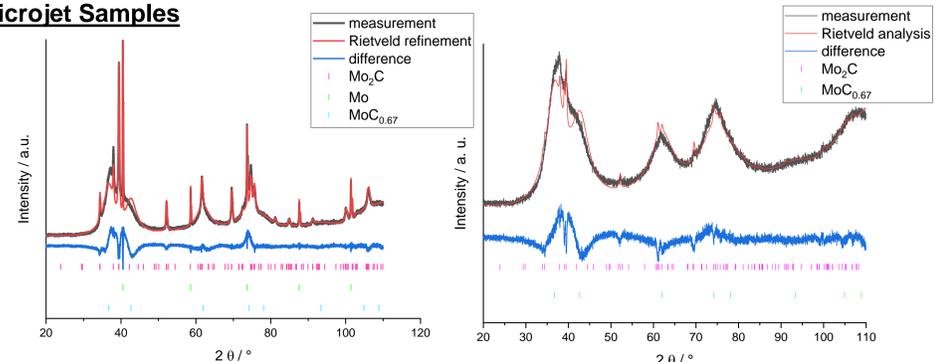


Fig. 5: Rietveld refinements of  $\text{MoOx}/\text{PPD}$  (1:5) after pyrolysis at 750 °C (left) and after pyrolysis at 600 °C (right).

## Batch Synthesis

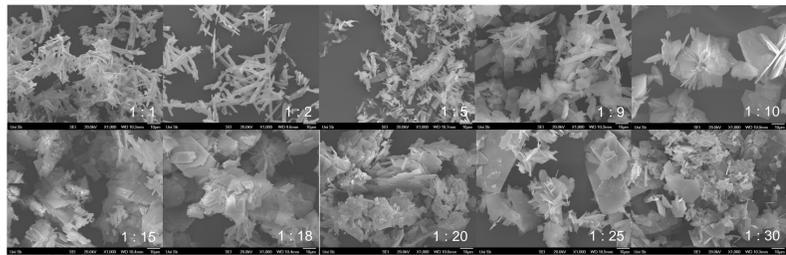


Fig. 2: SEM images of  $\text{MoOx}/\text{PPD}$  precursors from batch synthesis.

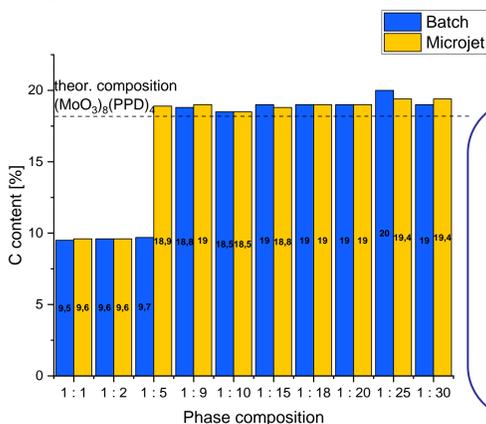


Fig. 3: C content (%) from  $\text{MoOx}/\text{PPD}$  precursors obtained via elemental analysis.

- Smaller amounts of PPD leads to highly anisotropic morphologies
  - another structure of precursor
- Larger amounts of PPD lead to sheet-like morphologies
- Correlation between elemental analysis and different morphologies
- Crystalline products were obtained in all cases, low PPD amounts lead to other products compared to high PPD amounts

## Microjet Synthesis

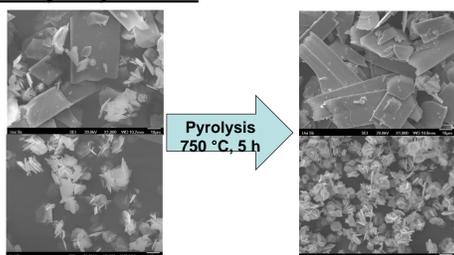


Fig. 4: SEM images above  $\text{MoOx}/\text{PPD}_{\text{RT}}$  and underneath  $\text{MoOx}/\text{PPD}_{50^\circ\text{C}}$ .

- Homogeneous particle morphologies are obtained
- Increased reaction temperature results in smaller particles
- Morphology is preserved after pyrolysis

- Phase  $\text{MoC}_{0.67}$  is isostructural to  $\text{Mo}_2\text{N}$  and  $\text{MoOC}$ 
  - Challenging in identifying the phase  $\text{MoC}_{0.67}$
  - $\text{MoC}_{0.67}$  cubic phase with a stacking error density
  - No satisfying Rietveld refinement
- Pyrolysed products shows high amount of carbon due to amorphous carbon in the sample (see Tab. 1)
- Presence of carbon is confirm by Raman spectroscopy, where characteristic D- and G-mode is observed (see Fig. 7)
  - The combination of molybdenum oxide/carbide and carbonaceous materials leads to an potential anode with high capacity and cycling stability

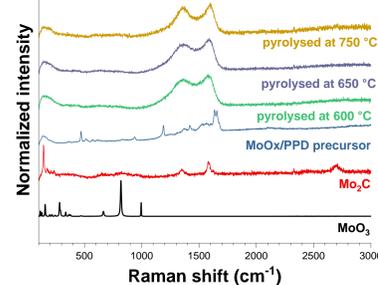


Fig. 7: Raman Spectra's measured with an excitation of 532 nm. In collaboration with Prof. Volker Presser Leibniz-Institute of New Materials (INM) Saarbrücken.

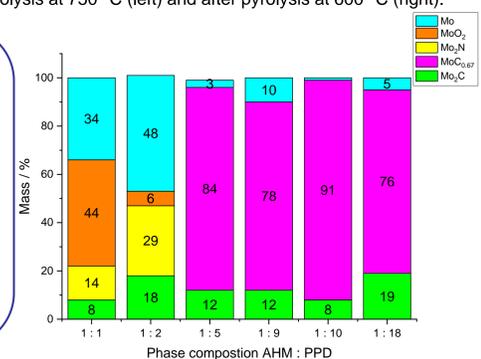
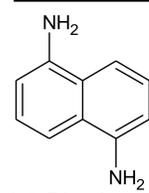


Fig. 6: Phase Composition determined via Rietveld Analysis.

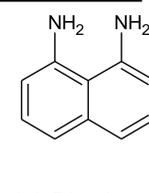
Tab. 1: Elemental analysis of  $\text{MoOx}/\text{PPD}$  precursors after the pyrolysis.

	C / %	H / %	N / %
Theor. $\text{Mo}_2\text{C}$	5.89	0	0
Theor. $\text{MoOC}$	9.69	0	0
$\text{MoOx}/\text{PPD}_t$ (t=750°C)	20.35	0	0.22
$\text{MoOx}/\text{PPD}_t$ (t=600°C)	21.44	0.31	0.71

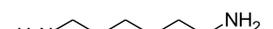
## Further studies with other diamines



1,5-Diaminonaphthalene (1,5-DAN)



1,8-Diaminonaphthalene (1,8-DAN)



Hexamethylenediamine (HMDA)

## Conclusion / Outlook

We successfully prepared the precursors  $\text{MoOx}/\text{PPD}$  with different ratios for the preparation of molybdenum carbide or oxycarbide via batch synthesis and microjet reactor. Pyrolysis of these precursors lead to the desired product  $\text{Mo}_2\text{C}$ . However, the synthesized products were not phase pure. Therefore, further optimization is necessary. SEM images show in the case of  $\text{MoOx}/\text{PPD}$  that the precursor morphology differs with the different ratios. Based on our results we can assume that two different precursors could be obtained by variation of the ratio between ligand and metal precursor. Rietveld analysis of the pyrolysed products reveals that only the precursors with higher diamine amounts lead to molybdenum carbides. Further amines will be investigated for the production of the pre-pyrolysis precursors and their influence on the formation of the desired phases will be studied.

## References

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