# Investigation of the Influence of a $WO_3$ Coating on High-Ni NCM-Type Layered Oxide Cathode Materials

**Friederike Reissig[1], Aurora Gomez-Martin[2], Richard Schmuch[2], Tobias Placke[2], Martin Winter[1,2]**

[1] Helmholtz-Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149 Münster, Germany

[2] University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstr. 46, 48149 Münster, Germany

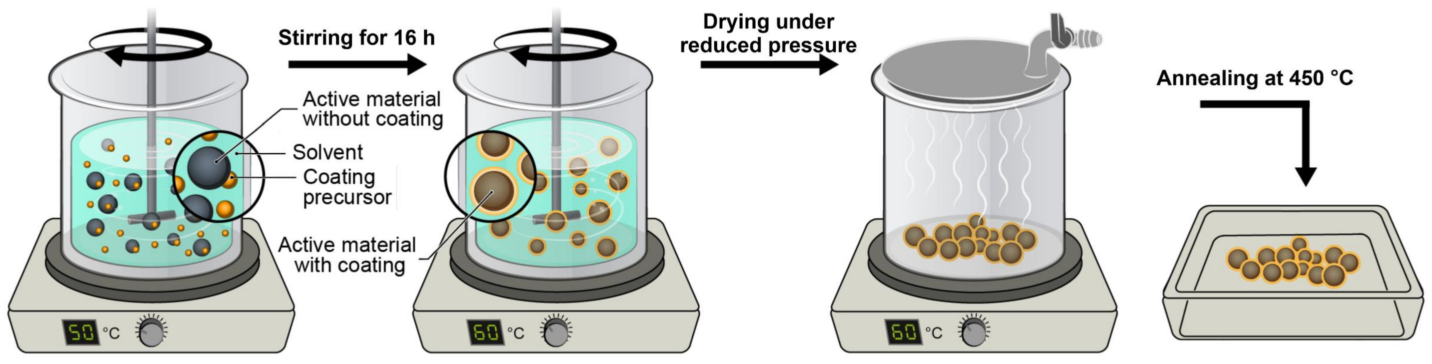
## Introduction

To achieve $CO_2$ neutral mobility, alternatives for fossil fuel such as hydrogen or green electricity are needed. In order to achieve a broader public acceptance longer driving ranges, lower cost, less critical raw materials[1] and higher safety are needed. A promising option for the first three challenges are Ni-rich NCM type layered oxide cathode materials in Li ion batteries. Despite the achieved higher specific discharge capacity, there are however major drawbacks in terms of life time and thermal stability which are crucial for customer acceptance. Those challenges can be addressed by e.g. particle design approaches, elemental substitutions in the bulk or surface coatings.

In the present study, we investigated the impact of surface modifications of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ (NCM90-05-05) layered oxide cathodes with $WO_3$[2-4] by a simple sol-gel coating process via synchrotron X-ray powder diffraction (XRD) investigations, low energy ion scattering (LEIS), scanning electron microscopy (SEM) investigations and electrochemical cycling.

## Modification Process and Material Characterization

- NCM90-05-05 was surface modified *via* a simple Sol-Gel process with a $(NH_4)_{10}H_2(W_2O_7)_6$ precursor: "$WO_3$ Coated"



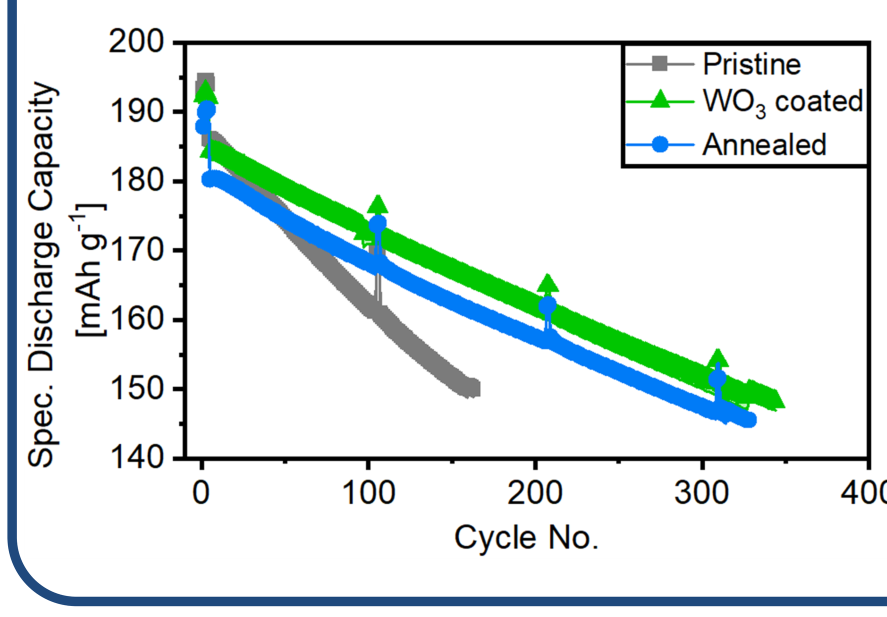

- Reference sample undergoing the same process without coating as comparison "Annealed"
- All samples (Pristine, $WO_3$ Coated and Annealed) exhibit a well defined layered structure
  - Annealing step increases the *c*/*a* lattice parameter ratio and decreases the Li-Ni mixing
  - Synchrotron XRD data revealed:
    - Up to 3 % impurities ($Li_2CO_3$ and $Li_2SO_4$)
    - $WO_3$ coated sample showed $Li_2W_2O_7$ and $Li_2WO_4$ hydrate impurities
- Low energy ion scattering (LEIS) indicates:
  - Pristine sample shows an unusually thick layer of surface impurities (due to moisture sensitivity/ exposure to dry air)
  - $WO_3$ coated sample only has 20 % surface coverage

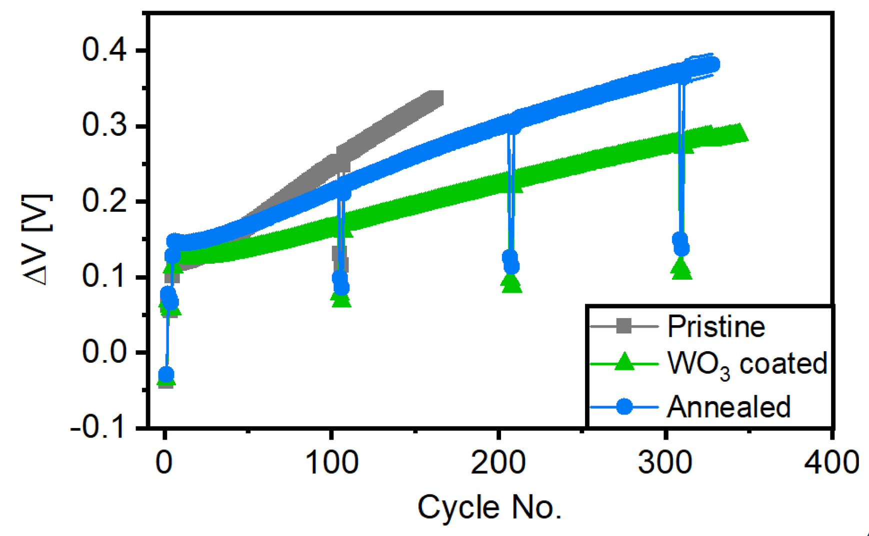
## Electrochemical Cycling

- Coated material shows:
  - High rate capability
  - High initial capacity
  - Improved cycling stability
  - Lower polarization growth

Coin cells (2032)
NCM90-05-05 *vs*. Graphite, 2.35 : 2.70 mAh/cm²

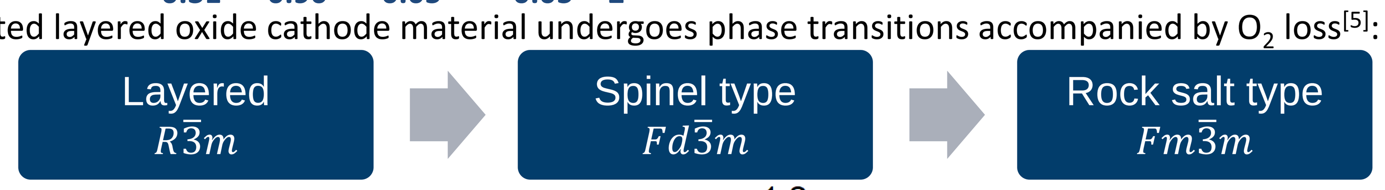
| | |
|---|---|
| Electrolyte | 35 µL 1 M $LiPF_6$ in 3:7 vol.% EC:EMC 3:7 + 2 wt% VC (Solvionic) |
| Separator | Celgard 2500 (1 layer) |
| Cell voltage window | 2.8 – 4.2V |
| CCCV | 4 × 0.1C & 100 × 0.33C & 2 x 0.1C … |
| C-Rate | 1C = 190 $mA \cdot g^{-1}$ |
| NCM/PVdF/Super C65 | 94 : 3 : 3 |



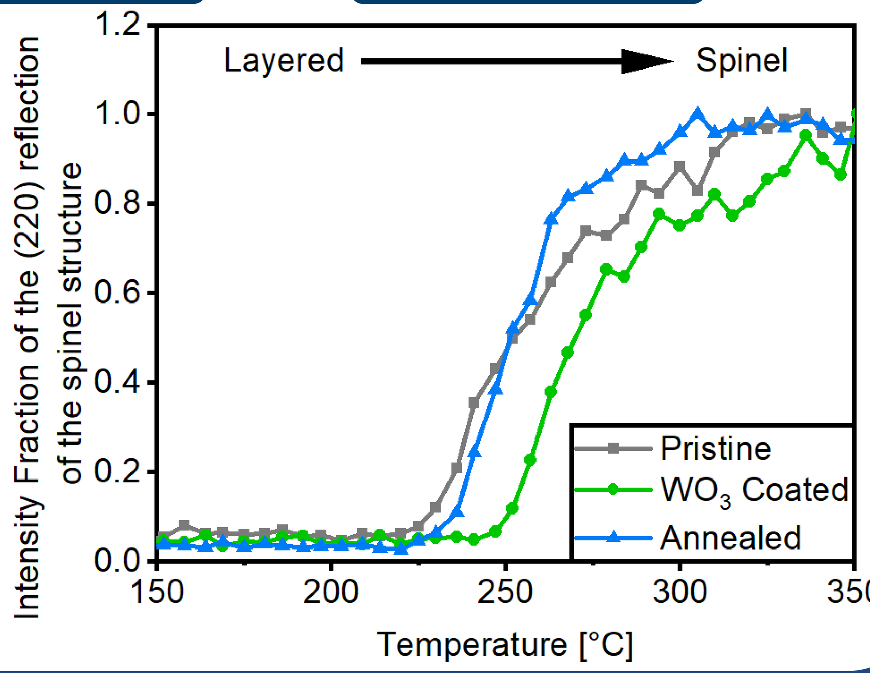




## High Temperature Synchrotron XRD Investigations of Cathode Materials delithiated to $Li_{0.31}Ni_{0.90}Co_{0.05}Mn_{0.05}O_2$

- Delithiated layered oxide cathode material undergoes phase transitions accompanied by $O_2$ loss[5]:




- Figure on the right shows the evolution of the (220) reflection of the spinel structure indicating the phase transition of the delithiated material
- Onset of the phase transition is shifted to higher temperatures for modified samples
  - + 5 °C for annealed sample
  - + 25 °C for coated sample
- Possible explanations:
  - Cleaning of the surface residues
  - Protection of the surface
  - Stabilization of the surface




## References

[1] R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, *Nat. Energy* **2018**, *3*, 267–278.

[2] D. Becker, M. Börner, R. Nölle, M. Diehl, S. Klein, U. Rodehorst, R. Schmuch, M. Winter, T. Placke, *ACS Appl. Mater. Interfaces* **2019**, *11*, 18404–18414.

[3] Z. Gan, G. Hu, Z. Peng, Y. Cao, H. Tong, K. Du, *Appl. Surf. Sci.* **2019**, *481*, 1228–1238.

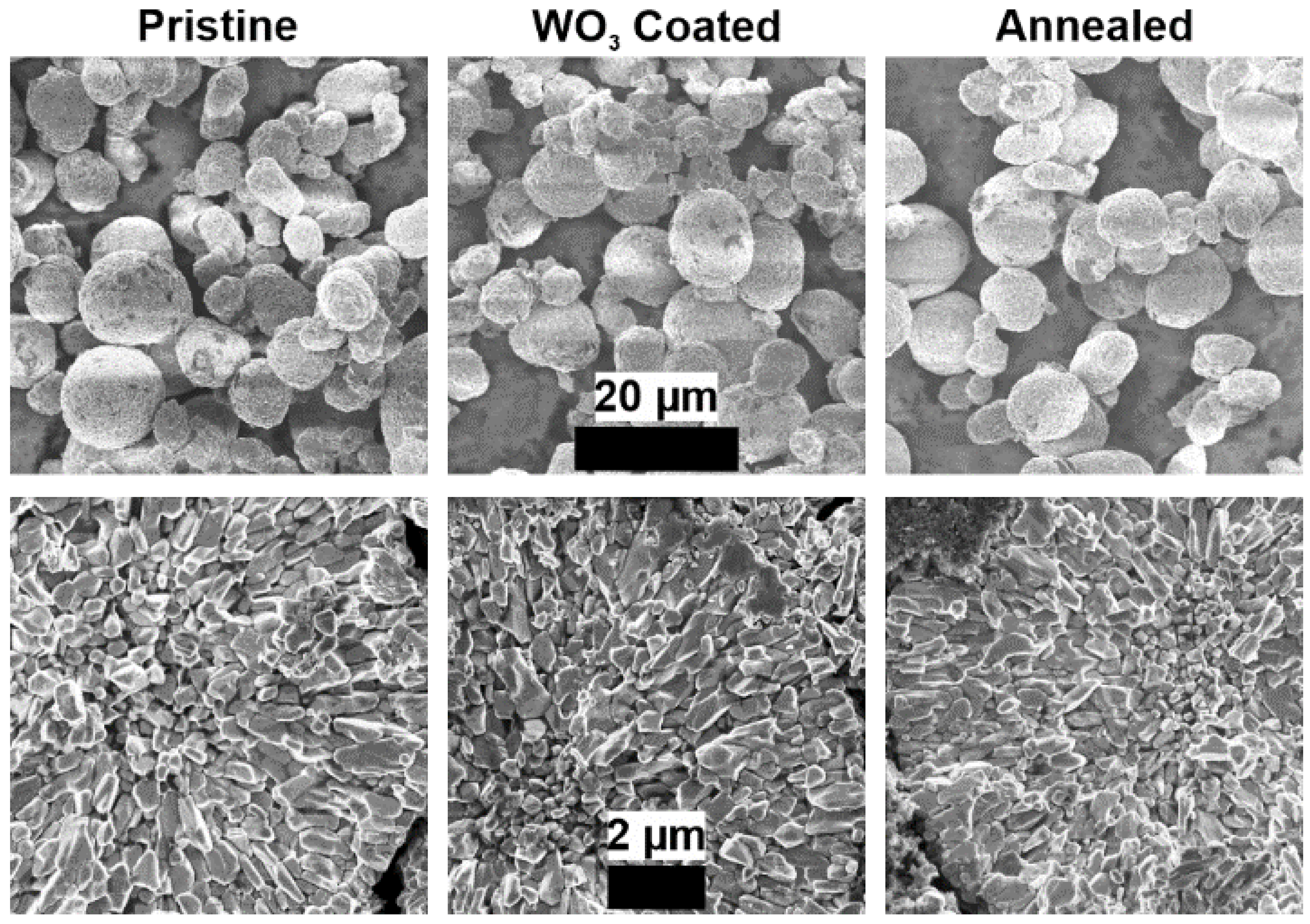
[4] F. Reissig, M. A. Lange, L. Haneke, T. Placke, W. G. Zeier, M. Winter, R. Schmuch, A. Gomez-Martin, *ChemSusChem* **2021**, DOI 10.1002/cssc.202102220.

[5] S.-M. Bak, E. Hu, Y. Zhou, X. Yu, S. D. Senanayake, S.-J. Cho, K.-B. Kim, K. Y. Chung, X.-Q. Yang, K.-W. Nam, *ACS Appl. Mater. Interfaces* **2014**, *6*, 22594–22601.

## SEM investigations

- No change in the primary particle morphology

**Pristine** | **$WO_3$ Coated** | **Annealed**



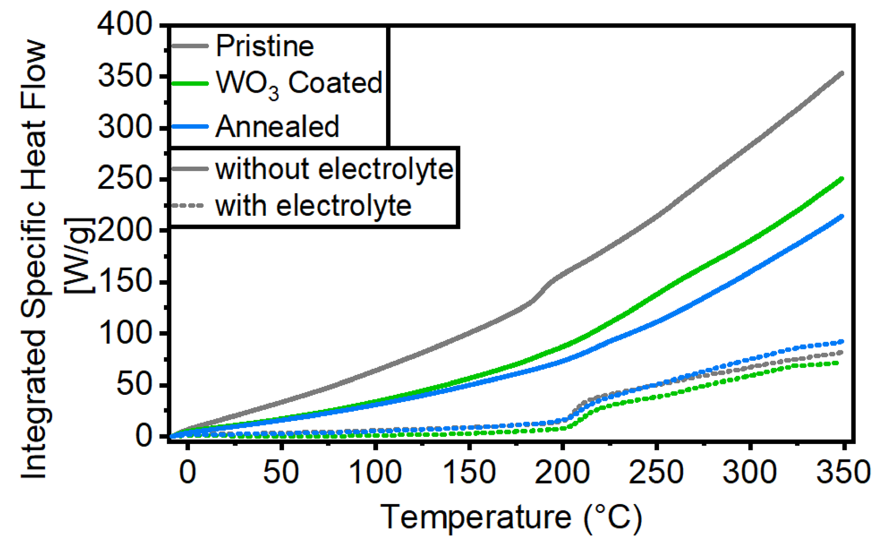

- Post cycling:
  - Thick layer of decomposition products on surface of electrodes of "Pristine" sample
  - Mitigation for coated and annealed samples

## Differential Scanning Calorimetry of Cathode Materials delithiated to $Li_{0.31}Ni_{0.90}Co_{0.05}Mn_{0.05}O_2$

- Differences for measurements with and without electrolyte
- Integrated heat flow:

| Integrated heat flow [W/g] | Without electrolyte | With electrolyte |
|---|---|---|
| Pristine | 353.5 | 81.8 |
| Coated | 250.9 | 72.0 |
| Annealed | 214.5 | 92.1 |

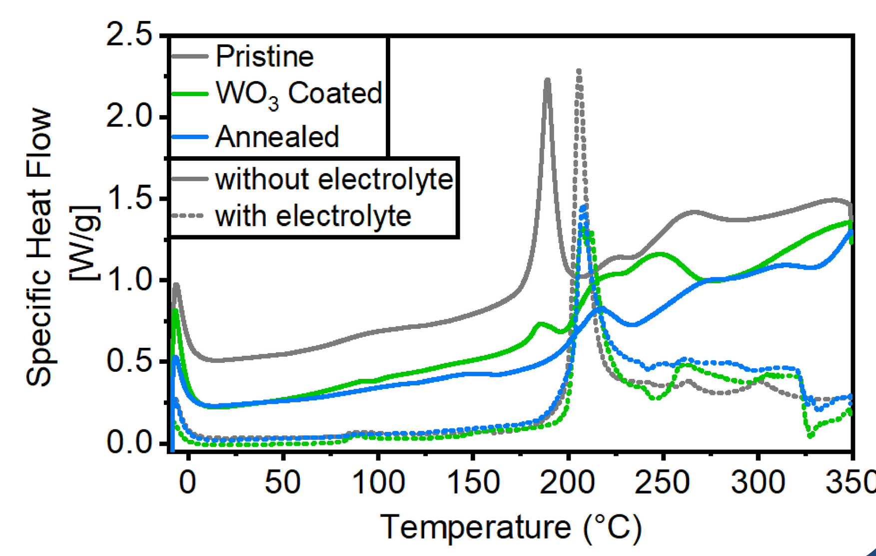
- Without electrolyte:
  Reduction by 30 - 40 % for surface treated samples
- With electrolyte:
  Reduction by 12 % for coated sample




- Onset Temperature and peak maxima

| Onset T [°C] | With electrolyte |
|---|---|
| Pristine | 192 |
| Coated | 199 |
| Annealed | 190 |

- Without electrolyte:
  Less pronounced peaks
- With electrolyte:
  Onset point is shifted to higher temperatures for coated sample




## Conclusion

Surface modification of $LiNi_{0.90}Co_{0.05}Mn_{0.05}O_2$ *via* a simple Sol-Gel process with an additional annealing step was performed to obtain a $WO_3$ surface coating. Various tungstates were identified via synchrotron XRD including $Li_2WO_4$ hydrate and $Li_2W_2O_7$. In addition a solvent and heat treated reference sample was prepared.

Coating and thermal treatment lead to an improved long term cycling stability. Furthermore, high temperature synchrotron XRD investigations showed a significantly improved thermal stability of the coated delithiated cathode material due to the suppression of structural changes.

## Acknowledgements

The authors thank the European Union for funding this work in the project "SeNSE": This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 875548. We thank Solvionic for supply of electrolyte. Synchrotron XRD experiments were performed at MSPD at ALBA Synchrotron with the collaboration of ALBA staff. Surface analysis via LEIS measurements was carried out by the tascon GmbH Münster.