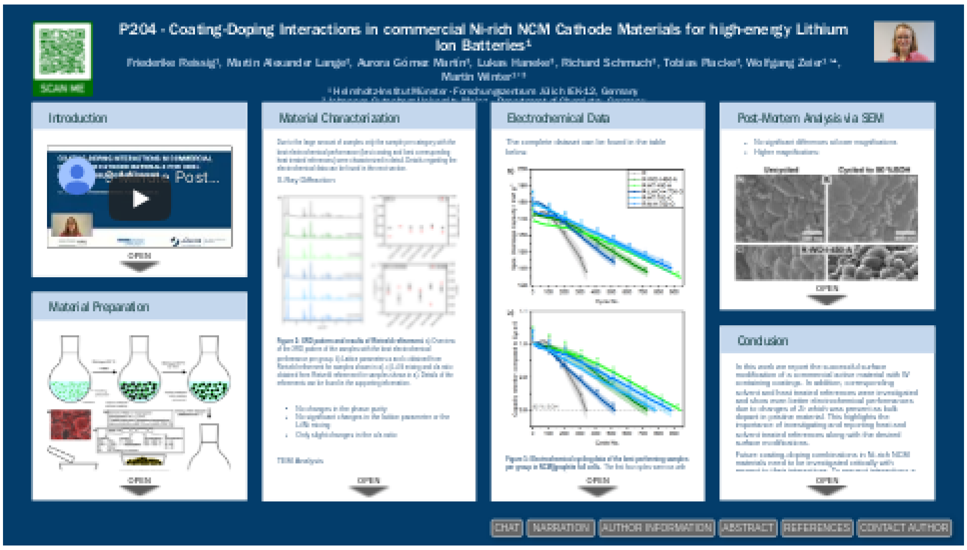
P204 - Coating-Doping Interactions in commercial Ni-rich NCM Cathode Materials for high-energy Lithium Ion Batteries[1]



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INTRODUCTION

[VIDEO] https://www.youtube.com/embed/J1rWKozd00Y?rel=0&fs=1&modestbranding=1&rel=0&showinfo=0

Coming from the global picture of climate change and the crucial need to reduce greenhouse gases there is a huge demand for renewable energies. Innovations in different fields are necessary to account for the increased demand in generation, storage and distribution that evokes. The storage of green electricity is one example with the challenge that every application has different requirements in cost, lifetime, gravimetric and volumetric energy density. In the sector of individual mobility, a user will expect a comparable cost, safety and driving range of an electric car as the one that can be obtained from a combustion engine.[7] Therefore, the future generations of battery systems in electric vehicles (EV) need to become cheaper and at the same time gain energy density.

Ni-rich NCM-type layered oxide materials are promising candidates to satisfy those needs. The main advantages of increasing the Ni content lies on an increased energy density at the material level and the reduction of cobalt as critical raw material.[2] There are however mayor drawbacks in terms of instability issues and cycling stability. Several mitigation strategies are often applied in literature such as doping to mitigate strong lattice parameter variations, coatings to protect the surface in contact with the electrolyte or core shell/gradient concentration design approaches. Although it is well-known that each of these approaches separately benefits the cycling stability of Ni-rich cathode materials, there are however no systematic reports investigating the simultaneous combination of two of the approaches.[3] However a combination of coating and doping will be needed to overcome the instability issues for NCM materials with Ni contents above 90 %.

In this work, the combination of Zr as frequently used dopant in commercial materials with a W-coatings[4,5] is thoroughly investigated with a special focus on the impact of different processing conditions and post-processing temperatures. Beside material characterization via XRD, SEM, TEM and XPS also the electrochemical performance in Lithium ion batteries (LIBs) is reported. It sheds light onto the importance to not only investigate the effect of individual dopants or coatings but also the interactions between both.

MATERIAL PREPARATION

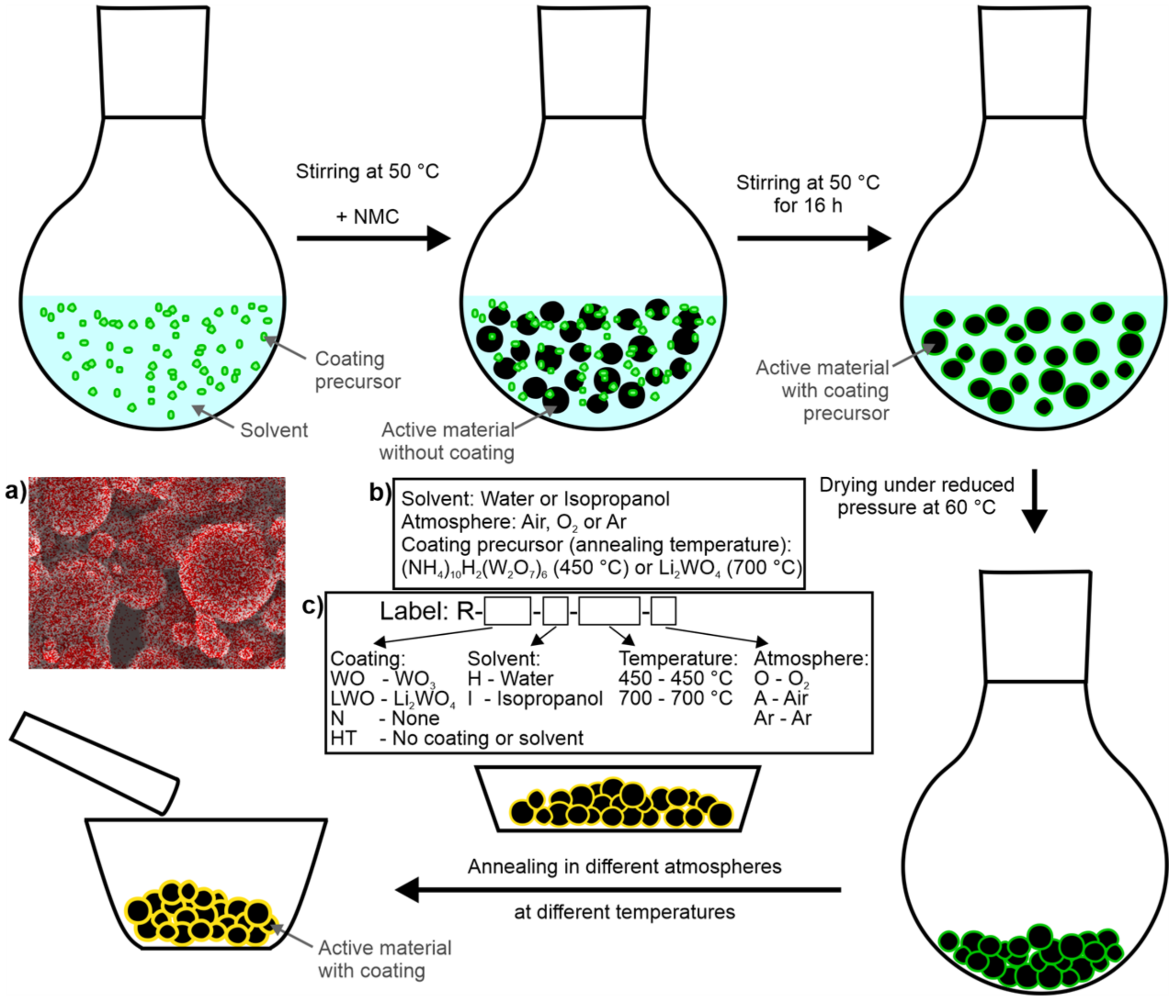


Figure 1: Synthesis procedure and labelling of the samples. The process shows the dispersion of the coating precursor (1 wt% of the active material) in the respective solvent and subsequent addition of the active material (Ni-rich NCM, commercial material "Ronbay S85EL-1st sintering"). The resulting dispersion has a solid content of ~40 %. After moderate stirring for 16 hours at 50 °C the solvent is evaporated at 60 °C under reduced pressure. The active material now coated with the precursor is then annealed at the desired temperature in different atmospheres. a) SEM-EDX mapping for W after the synthesis. b) List of different solvents and annealing atmospheres and temperatures. c) Labelling of the samples with the abbreviation in the labels followed by the corresponding meaning.

- Simple sol-gel/ co-precipitation process for WO_3 and Li_2WO_4 coatings
- Systematic screening of reaction parameters:
    - 2 coatings with corresponding temperatures, 2 solvents and 3 annealing atmospheres (see Figure 1)
- To investigate the effect of the additional annealing step a heat treated reference was prepared only carrying out the same annealing step at different temperatures and in different atmospheres without other modifications
- To investigate the effect of the solvent treatment two samples were prepared that went through the co-precipitation and annealing process but without a coating being added
- Literature studies often don’t analyze suitable reference materials (heat- or solvent-treated) or use Ar as expensive annealing gas[4,5,8,9]

MATERIAL CHARACTERIZATION

Due to the large amount of samples only the sample per category with the best electrochemical performance (best coating and best corresponding heat treated references) were characterized in detail. Details regarding the electrochemical data can be found in the next section.

X-Ray Diffraction

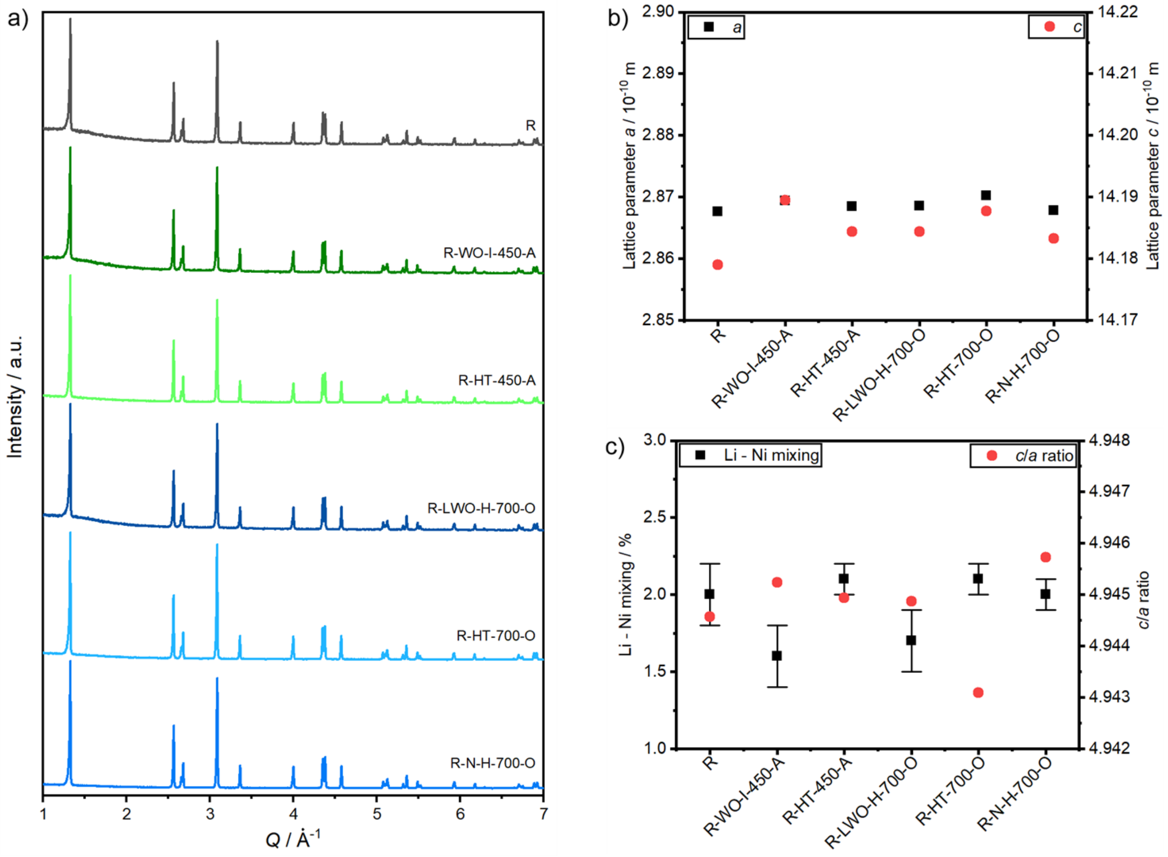


Figure 2: XRD pattern and results of Rietveld refinement. a) Overview of the XRD pattern of the samples with the best electrochemical performance per group. b) Lattice parameters a and c obtained from Rietveld refinement for samples shown in a). c) Li-Ni mixing and c/a ratio obtained from Rietveld refinement for samples shown in a). Details of the refinements can be found in the supporting information.

- No changes in the phase purity
- No significant changes in the lattice parameter or the Li/Ni mixing
- Only slight changes in the c/a ratio

TEM Analysis

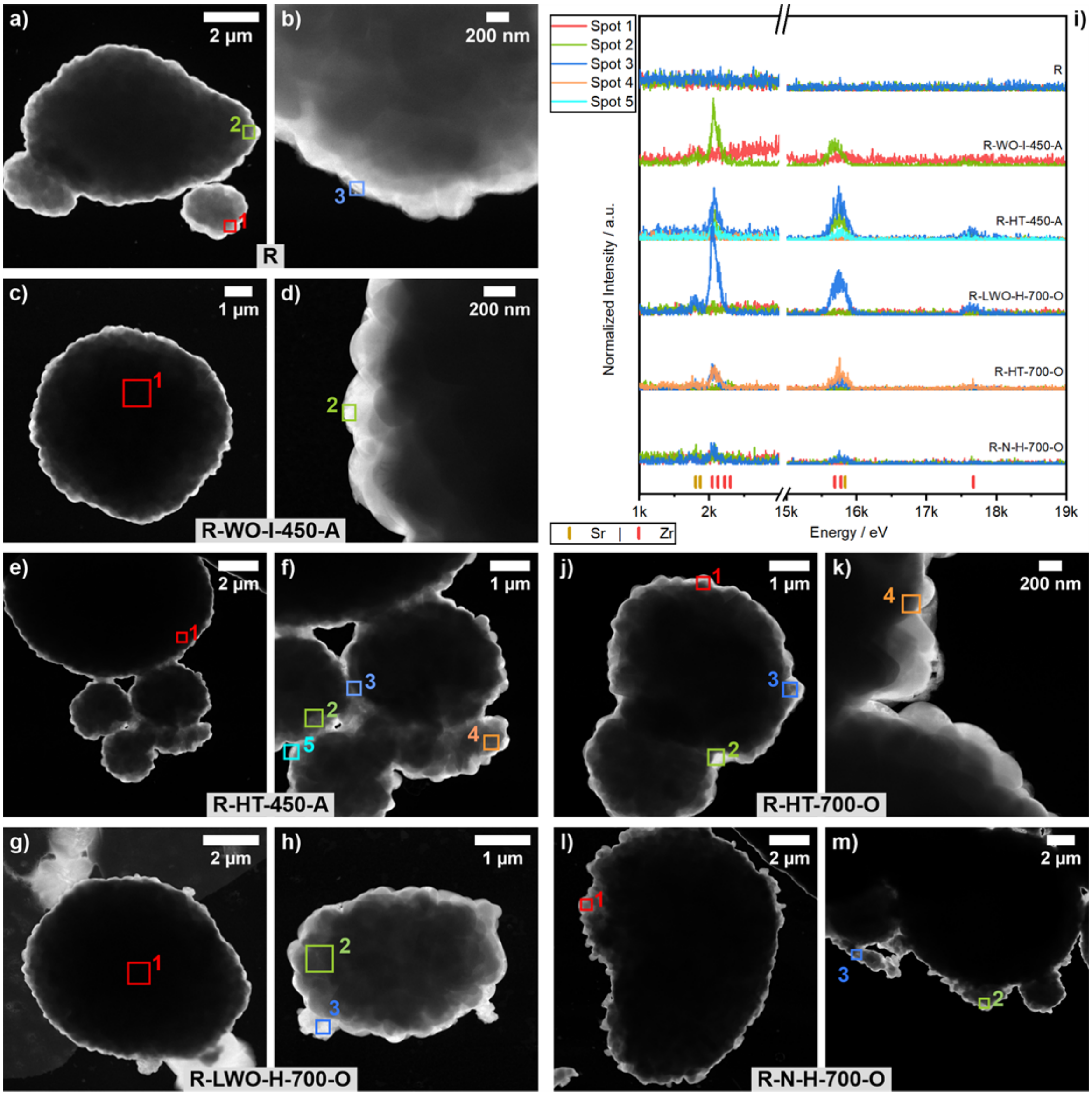


Figure 3: TEM images and TEM EDX results. a) - h) and j) - m) TEM images of the secondary particles of the active material. Color coded and numbered are the spots where EDX was measured. i) EDX spectra corresponding to the spots marked in the TEM images with the same color code. Energy regions of Sr and Zr are show and the peak positions are marked in yellow and red.

- The pristine material (R) and samples R-WO-I-450-A, R-HT-450-A and R-HT-700-O have a smooth particle surface.
- The combination of solvent treatment plus the annealing step at 700 °C lead to agglomerations on the particle surface.
  - Without a coating (R-N-H-700-O): Small, distributed agglomerates
  - With a coating (R-LWO-H-700-O): Very large agglomerates
- EDX results:
  - Never show Zr in the bulk measurements
  - Zr detectable on the particle surface for all heat treated samples but not for the pristine
  - Report in literature that Zr can diffuse to the surface during annealing[10]

XPS Analysis

Table 1: XPS results of the samples with the best electrochemical performance per group. The values were obtained from fitting the core spectra with CasaXPS Version 2.3.22PR1.0. For some elements absolute values in % atomic concentration are given. In other cases ratios are given for better comparability. The sample labels correspond to the ones given in Figure 1.

All numbers are a ratio or in %At concentration	R	R-WO-I-450-A	R-HT-450-A	R-LWO-H-700-O	R-HT-700-O	R-N-H-700-O
Zr 3d	0.17 ± 0.01	0.15 ± 0.02	0.217 ± 0.005	0.043 ± 0.009	0.123 ± 0.005	0.16 ± 0.01
Zr 3d / Ni 3p	0.040 ± 0.004	0.032 ± 0.004	0.039 ± 0.001	0.02 ± 0.005	0.039 ± 0.003	0.039 ± 0.004
C (CO_3^{2-})	6.86 ± 0.09	5.5 ± 0.3	5.5 ± 0.2	10 ± 0.2	8.99 ± 0.08	7.1 ± 0.3
Li(CO_3^{2-}) / Li(NMC)	4 ± 2	2.3 ± 0.8	2.9 ± 0.8	13 ± 7	5.8 ± 0.4	2.1 ± 0.5
Li 1s / Ni 3p	3.7 ± 0.1	3.0 ± 0.1	2.4 ± 0.1	8.0 ± 0.4	5.5 ± 0.4	3.7 ± 0.2
W 4f		0.763 ± 0.005		0.320 ± 0.008		

- Higher carbonate amounts for Pristine and 700 °C samples
- More W on the surface with WO_3-Coating (R-WO-I-450-A)
- Lowest Zr-amount detected for R-LWO-H-700-O: Large agglomerations = Less exposed area
- For all treated samples better electrochemical performance correlates with:
  - Higher (Zr concentration and) Zr 3d/ Ni 3p ratio
  - Lower surface carbonate concentration and Li(CO_3^{2-}) / Li(NMC) ratio
  - Lower Li 1s / Ni 3p ratios

ELECTROCHEMICAL DATA

The complete dataset can be found in the table below.

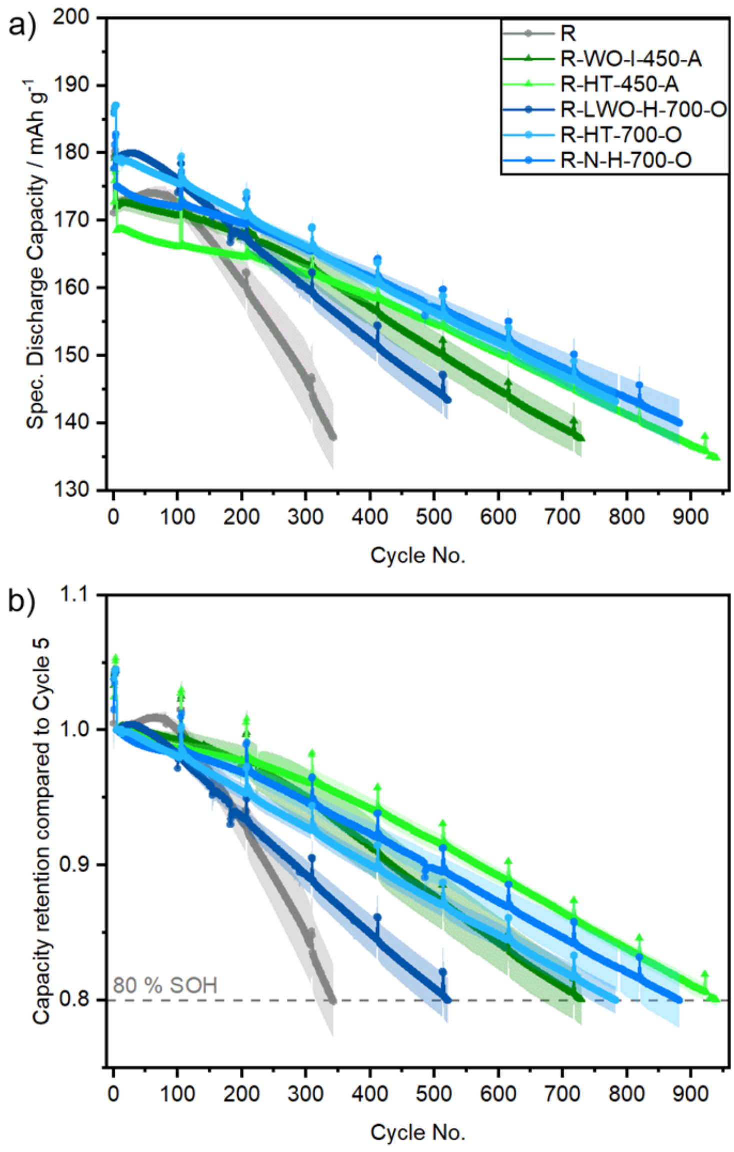
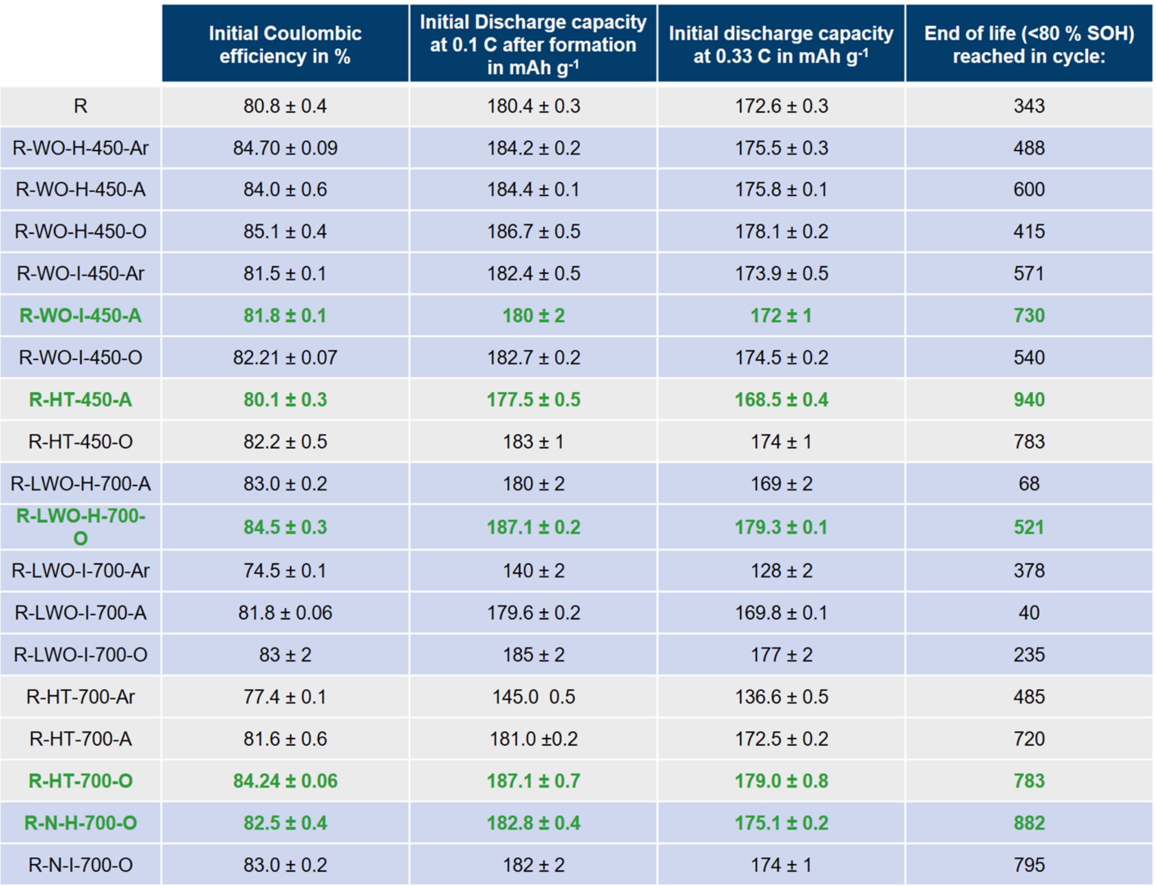


Figure 5: Electrochemical cycling data of the best performing samples per group in NCM||graphite full cells. The first four cycles were run with 0.1 C (1 C = 190 mAh g^{-1}), while the following long term cycling took place at 0.33 C. The voltage window was 2.8 - 4.2 V. a) Shows the specific discharge capacities while b) the capacity retention compared to the first cycle at 0.33C displays. Initial discharge capacity, end of life cycle and initial Coulombic efficiency are also shown in Table 2. The Coulombic efficiencies during cycling for the pristine material R is 99.75 % for all other samples it is above 99.9 %.

- Coated samples perform better than the pristine material, BUT heat and solvent treated references show an even better long term stability
- After cycle 500 the heat and solvent treated references all have similar capacities
    - Differences in capacity retention can partially result from different initial capacities

Full data set:

Table 2: Initial Coulombic efficiency, discharge capacity at 0.1 C after formation, initial discharge capacity at 0.33 C and end of life of all samples. Data of best sample per group is marked in bold. The Coulombic efficiencies during cycling for the pristine material R is 99.75 %, for samples reaching the end of life in less than 100 cycles it is above 99.5% and for all other samples it is above 99.9 %.



	Initial Coulombic efficiency in %	Initial Discharge capacity at 0.1 C after formation in mAh g^{-1}	Initial discharge capacity at 0.33 C in mAh g^{-1}	End of life (<80 % SOH) reached in cycle:
R	80.8 ± 0.4	180.4 ± 0.3	172.6 ± 0.3	343
R-WO-H-450-Ar	84.70 ± 0.09	184.2 ± 0.2	175.5 ± 0.3	488
R-WO-H-450-A	84.0 ± 0.6	184.4 ± 0.1	175.8 ± 0.1	600
R-WO-H-450-O	85.1 ± 0.4	186.7 ± 0.5	178.1 ± 0.2	415
R-WO-I-450-Ar	81.5 ± 0.1	182.4 ± 0.5	173.9 ± 0.5	571
R-WO-I-450-A	**81.8 ± 0.1**	**180 ± 2**	**172 ± 1**	**730**
R-WO-I-450-O	82.21 ± 0.07	182.7 ± 0.2	174.5 ± 0.2	540
R-HT-450-A	**80.1 ± 0.3**	**177.5 ± 0.5**	**168.5 ± 0.4**	**940**
R-HT-450-O	82.2 ± 0.5	183 ± 1	174 ± 1	783
R-LWO-H-700-A	83.0 ± 0.2	180 ± 2	169 ± 2	68
R-LWO-H-700-O	**84.5 ± 0.3**	**187.1 ± 0.2**	**179.3 ± 0.1**	**521**
R-LWO-I-700-Ar	74.5 ± 0.1	140 ± 2	128 ± 2	378
R-LWO-I-700-A	81.8 ± 0.06	179.6 ± 0.2	169.8 ± 0.1	40
R-LWO-I-700-O	83 ± 2	185 ± 2	177 ± 2	235
R-HT-700-Ar	77.4 ± 0.1	145.0 0.5	136.6 ± 0.5	485
R-HT-700-A	81.6 ± 0.6	181.0 ±0.2	172.5 ± 0.2	720
R-HT-700-O	**84.24 ± 0.06**	**187.1 ± 0.7**	**179.0 ± 0.8**	**783**
R-N-H-700-O	**82.5 ± 0.4**	**182.8 ± 0.4**	**175.1 ± 0.2**	**882**
R-N-I-700-O	83.0 ± 0.2	182 ± 2	174 ± 1	795

POST-MORTEM ANALYSIS VIA SEM

- No significant differences at lower magnifications
- Higher magnifications:

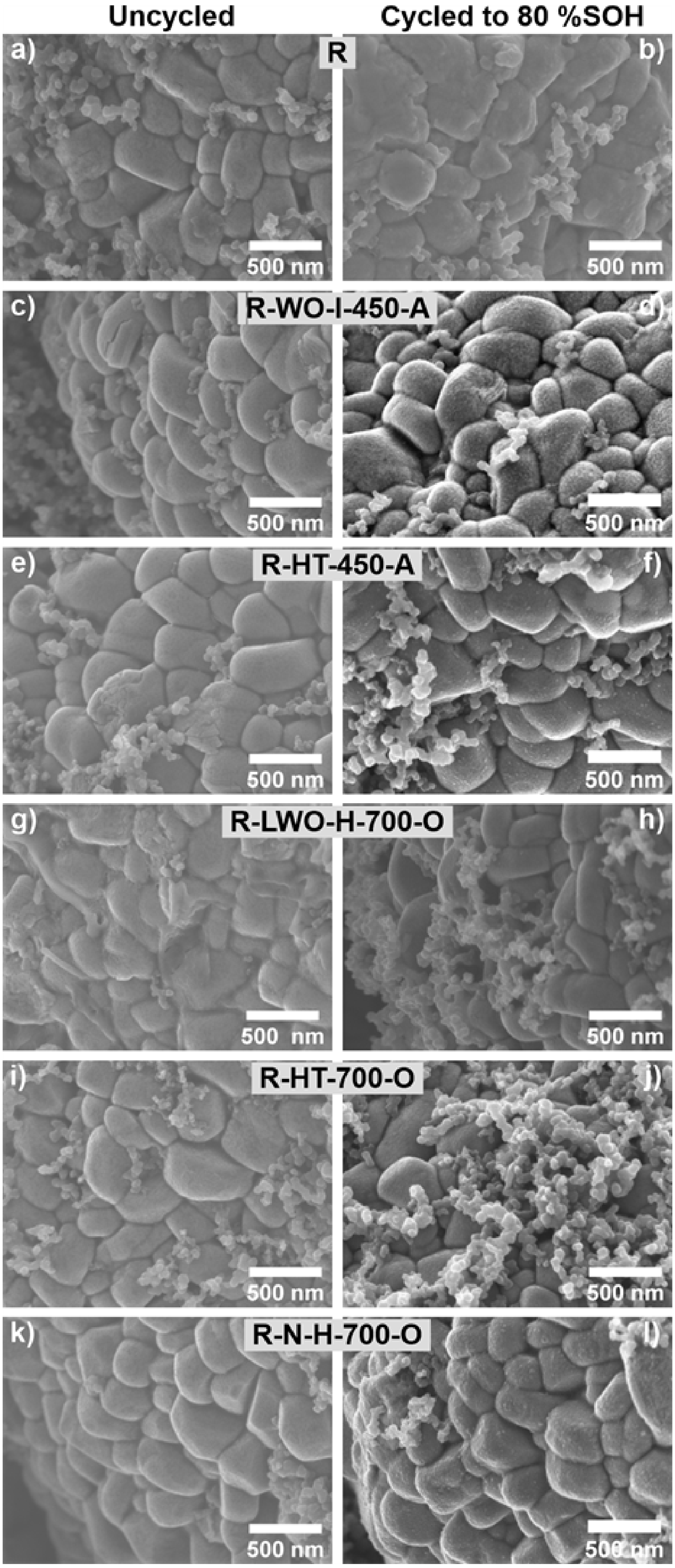


Figure 6: SEM images of the 6 samples with the best electrochemical performance before and after cycling until 80 % SOH are reached. The images were recorded with a magnification of 50k.

- Before cycling: Most particle surfaces look “clean”
    - Uncoated reference shows small amount of residues
    - Li_2WO_4 coated sample shows large amounts of inhomogeneous depositions on the surface
- After cycling:
    - Only uncoated reference shows depositions on the particle surface
    - Surface of Li_2WO_4 coated sample seems to be “cleaned” during cycling
        - Decomposition products might lead to the capacity fading

CONCLUSION

In this work we report the successful surface modification of a commercial active material with W containing coatings. In addition, corresponding solvent and heat treated references were investigated and show even better electrochemical performances due to changes of Zr which was present as bulk dopant in pristine material. This highlights the importance of investigating and reporting heat and solvent treated references along with the desired surface modifications.

Future coating-doping combinations in Ni-rich NCM materials need to be investigated critically with respect to their interactions. To prevent interactions a dopant should remain stable incorporated in the bulk upon additional annealing steps and only negligible amounts of the coating should diffuse into the bulk.

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SCAN ME

ABSTRACT

Ni-rich NCM-type layered oxide materials are promising candidates to satisfy the increasing energy demand for batteries for automotive applications. The main advantages of increasing the Ni content lies on an increased energy density at the material level and the reduction of cobalt as critical raw material.[2] There are however mayor drawbacks in terms of instability issues and cycling stability. Several mitigation strategies are often applied in literature such as doping to mitigate strong lattice parameter variations, coatings to protect the surface in contact with the electrolyte or core shell/gradient concentration design approaches. Although it is well-known that each of these approaches separately benefits the cycling stability of Ni-rich cathode materials, there are however no systematic reports investigating the simultaneous combination of two of the approaches.[3]

In this work, the combination of Zr as frequently used dopant in commercial materials with a WO_3[4+5] coating is thoroughly investigated with a special focus on the impact of different processing conditions and post-processing temperatures.[6] A combination of doping and coating, which will be needed for Ni contents above 90 % to overcome instability issues, however show significant challenges that might be difficult to overcome. The Zr dopant initially introduced in the bulk of the commercial material diffused to the surface during the post-process of the coating, leading to interactions between coating and dopant that negatively impact the electrochemical performance. This work sheds light onto the importance to not only investigate the effect of individual dopants or coatings but also the interactions between both. This is particularly challenging due to the small scale and concentrations that are investigated and the large differences for each doping-coating combination.

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