Challenges of Synthesizing Ni-rich 'Single Crystal' Layered Oxide Cathodes for Lithium Ion Batteries

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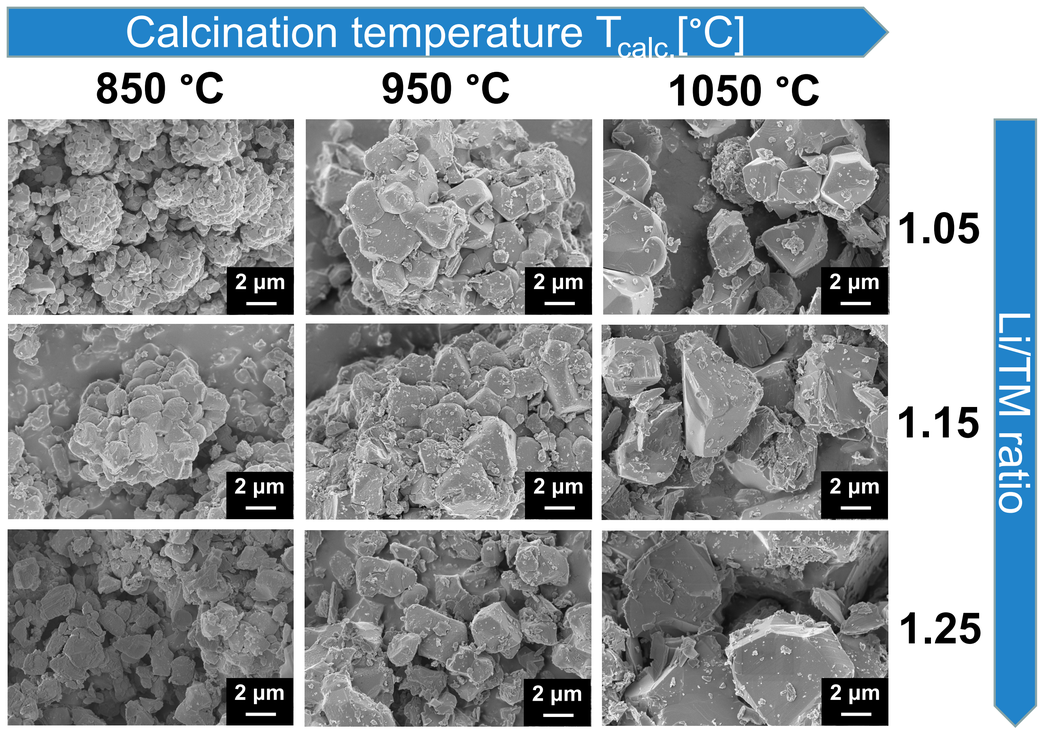
Introduction

Increasing the Ni-content of mixed transition metal layered oxide cathodes (LOCs) like $Li[Ni_xCo_yMn_z]O_2$ (NCM*xyz*) has been a viable strategy to increase energy output and reduce cost.[1] However, the drawback of these Ni-rich formulations ($x \geq 0.8$) is a loss of cycling stability. In this regard, secondary particle cracking has been identified as a major failure mechanism as it allows surface-related degradation phenomena such as ongoing electrolyte decomposition to continue on newly formed, highly reactive surface cycle after cycle.[2,3] As opposed to their polycrystalline (PC) counterparts, 'Single-crystal' (SC) NCMs are comprised of separated micron-sized primary particles and are therefore promising candidates to mitigate this issue. Despite this, the literature on the synthesis of Ni-rich SC-NCMs is still scarce, but could be relevant for more sustainabale rechargeable lithium ion bateries.[4] In this work, a systematic study on the high temperature synthesis of SC-NCM811 is carried out. Lithium-to-transition metal ratio (Li/TM) and calcination temperature ($T_{calc.}$) are investigated in terms of their impact on the crystal structure, particle morphology and electrochemical performance.

Synthesis Conditions

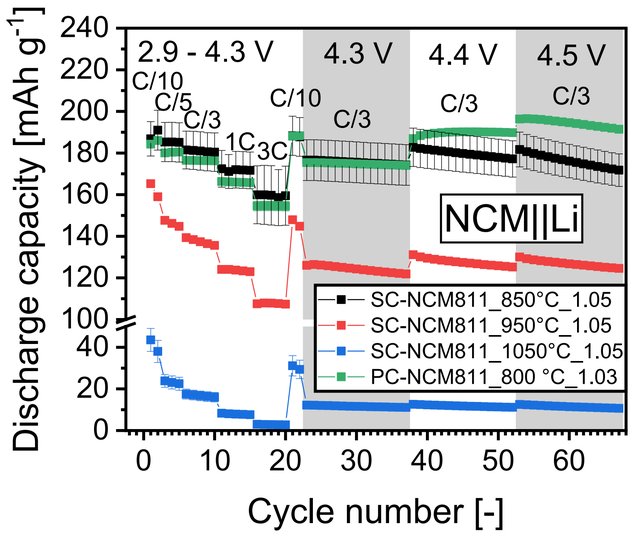
- $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor (Pre811) synthesized by coprecipitation using Couette-Taylor Flow Reactor (CTFR) as described elsewhere[5]
- Rotational speed 1300 rpm → small precursors, D_{50}(Pre811) ≈ 4 µm (typically used for high temperature single-crystal synthesis[6])
- Calcination: Muffle box furnace, $LiOH{\cdot}H_2O$; 3h@500 °C, then 12h@$T_{calc.}$; heating rate 2 °C/min; O_2 flow
- Li/TM ratio = 1.05, 1.15, 1.25 and $T_{calc.}$= 850 °C, 950 °C, 1050 °C
- PC-NCM811 reference: Li/TM ratio = 1.03, $T_{calc.}$ = 800 °C and D_{50}(Pre811) ≈ 8 µm

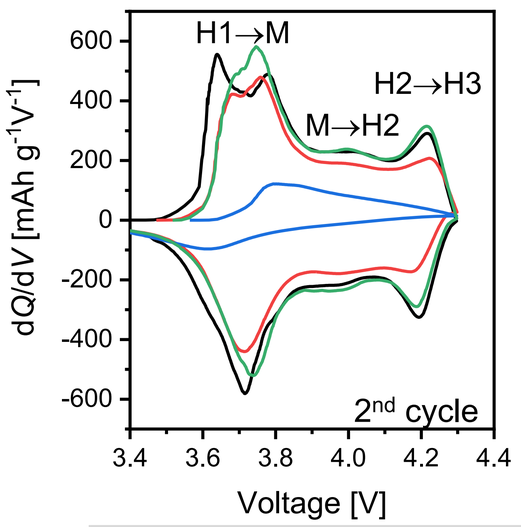
Particle Morphology



- Primary particle size increases with increasing temperature (strongly) and with increasing Li/TM ratio (slightly)
- At high temperatures and high Li/TM ratios primary particles begin to separate from each other
- General problem: strong particle agglomeration (beyond precursor size)

Electrochemical Investigations

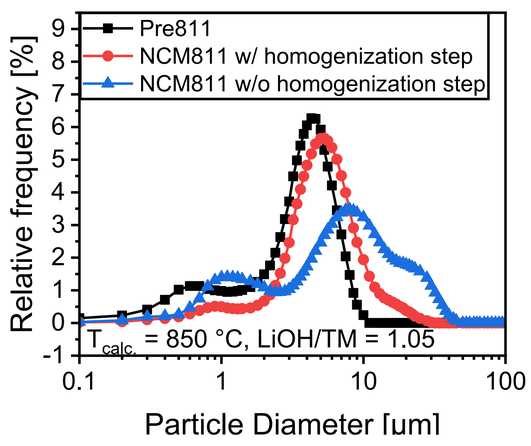


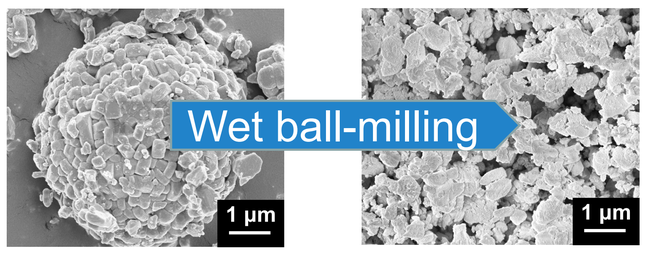


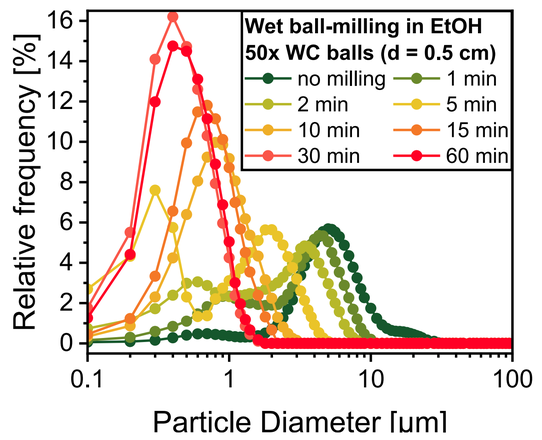
- SC-NCM811 calcined at > 850 °C show strongly reduced capacity and C-rate performance
- SC-NCM811_850°C_1.05 can compete with PC-NCM811 reference, but primary particle size is too small to be characterized as 'single-crystal'

Coin-type CR3202 NCM||Li
Cathode: 94/3/3 NCM/Carbon C65/PVdF
Anode: Li metal
2.9 – 4.3 V (4.4 V, 4.5 V), 1C = 190 mAh g^{-1}
Charge at C/5 to avoid Li plating
Data from 3 cells

Particle Separation

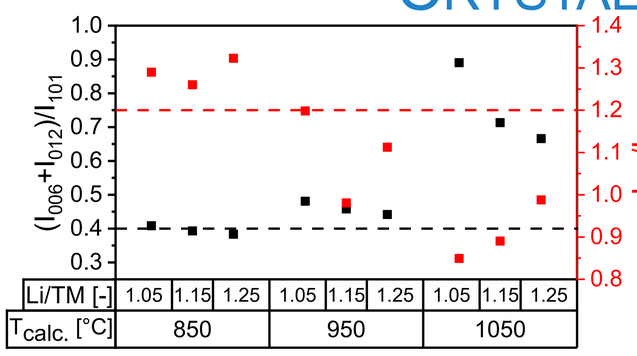






- Agglomeration can be avoided by homogenization step (2°C/min → 500 °C, hold 3h, let cool, grind again)
- Separation of primary particles is possible by wet ball-milling, but particle morphology and crystal structure will be damaged

Crystal Structure



$T_{calc.}$ [°C]	Li/TM [-]	*a* [Å]	*c*/*a* [-]	Ni@Li [%]	GoF
850	1.05	2.872726(8)	4.94382(3)	1.5(1)	2.0
950	1.05	2.87604(1)	4.94111(6)	3.2(1)	2.3
1050	1.05	2.8842(2)	4.9378(8)	-	-
850	1.05	2.872726(8)	4.94382(3)	1.5(1)	2.0
850	1.15	2.871077(9)	4.94540(4)	1.2(1)	1.9
850	1.25	2.87040(1)	4.94591(5)	0.9(1)	2.1

- Screening by ratio of integrated PXRD intensities: $(I_{006}+I_{012})/I_{101} \approx 0.4$, $I_{003}/I_{104} > 1.2$ → only $T_{calc.}$ = 850 °C promising → confirmation by Rietveld refinement
- Li/Ni disorder follows trend of $(I_{006}+I_{012})/I_{101}$ → $T_{calc.}$ > 950 °C not practically relevant
- For higher $T_{calc.}$: Lattice parameter *a* increases, while ratio *c*/*a* decreases
- For $T_{calc.}$ = 1050 °C: structure too distorted for proper Rietveld refinement

Conclusion

The synthesis of SC-NCM811 is challenging as the Ni-rich material hardly tolerates the high calcination temperatures necessary for sufficient crystal growth (> 1 µm). This is evident from the high Li/Ni disorder which is reflected in strongly reduced capacity. To make matters worse, the high Li excess and small precursor size can cause severe agglomeration and complicate the separation of primary particles. As opposed to NCMs with lower Ni-content, Ni-rich SC-NCMs seem to require more sophisticated synthesis approaches.[4,6]

Acknowledgments

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