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*Embedding smart functionalities into battery cells (embedding sensing and self-healing functionalities to monitor and self-repair battery cells)
(Batteries Partnership)*



PHOENIX

Building more reliable and performant batteries by embedding sensors and self-healing functionalities to detect degradation and repair damage via advanced Battery Management System

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SHORT ABSTRACT FOR DISSEMINATION PURPOSES

Abstract

The target of this deliverable is to give the description of synthesis route and process parameters for the obtainment of core/shell structured NMC cathode powders. To optimize the morphological and compositional characteristics, three rounds of experiments have been conducted: i) individual synthesis of NMC90 core and NMC622 shell particles; ii) synthesis of WO₃-coated NMC90 particles; iii) combined synthesis of NMC core/shell structures with and without WO₃ layer. SEM, EDX and XRD techniques have been employed to investigate the effect of heat treatment temperature and Li content and to study the structural relations within the core/shell particles. The electrochemical performance of as synthesized NMC core/shell structures with and without WO₃ layer as cathode materials are evaluated using galvanostatic charge-discharge (GCD) in NEWARE battery tester by preparing CR2032 type half-coin cells.



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ABBREVIATIONS

Acronym	Description
AC	Activated carbon
EC	Ethylene carbonate
EDX	Energy-dispersive X-ray spectroscopy
DMC	Dimethyl carbonate
GCD	Galvanostatic charge-discharge
GF	Glass fiber
NMC	Lithium N ickel M anganese C obalt oxide
NMP	N-Methyl-2-pyrrolidone
SEM	Scanning electron microscopy
PVDF	Polyvinylidene fluoride
XRD	X-ray diffraction analysis



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EXECUTIVE SUMMARY

The aim of this deliverable is to describe the development of synthesis route of novel NMC based nanoparticles through a double step co-precipitation method yielding Ni-rich NMC cores and Mn-rich shells.

The document is divided into 3 main sections:

- Section 1 provides the main objectives and motivation for the development of core/shell structured NMC cathode powders.
- Section 2 describes the synthesis route to obtain NMC core/shell structured particles and illustrates the effect of process parameters (calcination temperature, Li content, WO_3 content) on morphological and compositional characteristics of the obtained powders.
- Section 3 presents results of electrochemical tests of NMC core/shell powders with and without WO_3 layer.



1. INTRODUCTION

NMC ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$) cathode materials with a nickel content exceeding 80%, exhibit a remarkable discharge capacity of 200 mAh/g at 4.3 V [1]. However, increasing Ni content can involve rapid capacity fading, short cycle life, and poor thermal/structural stability. These drawbacks stem from the increased reactivity of Ni with surface oxygen during charge-discharge cycles, as well as larger Li/Ni cationic mixing, which can deteriorate the electrochemical performance. In order to overcome these issues, different approaches to develop NMC materials with controlled core/shell structured morphology have been proposed [2]. For instance, high Ni content ensures high specific capacity, while Mn-rich shell provides the improved structural and thermal stability (Figure 1).

In this work, NMC core/shell particles have been synthesized via easy process-controlled oxalate-assisted co-precipitation method (Section 2.1). To achieve the formation of core and shell with different compositions, two-staged synthesis approach has been employed. To prevent interdiffusion between the core and shell, a thin WO_3 layer has been applied to the surface of the Ni-rich core particles [3].

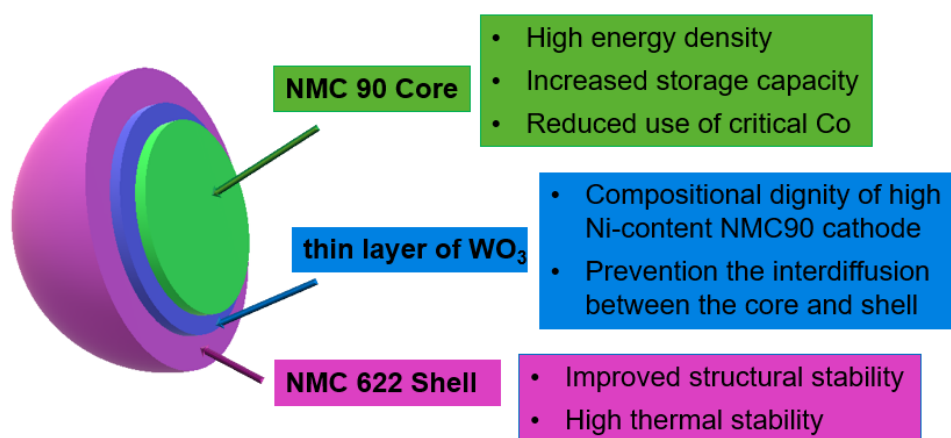


Figure 1 – Core/shell structured NMC powder as promising cathode material for Li-ion batteries

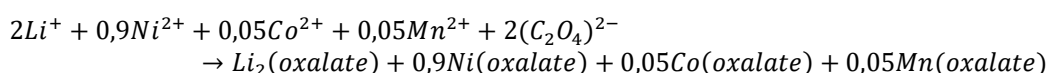


2. SYNTHESIS AND CHARACTERIZATION OF CORE/SHELL STRUCTURED NMC POWDERS

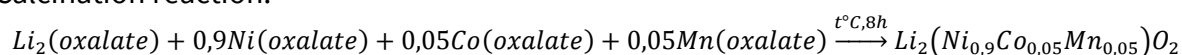
2.1 Two-staged oxalate assisted co-precipitation synthesis route

To obtain NMC90 core powder, $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ were dissolved separately in solvent (water) and then mixed in the ratio Ni:Co:Mn = 9:0.5:0.5. Simultaneously, $\text{Li}(\text{CH}_3\text{CO}_2)$ solution was prepared and then added to the Ni, Co, Mn mixed solution. The oxalic acid solution was poured slowly into the mixed metal solution under heating at 65°C with continuous stirring, and the reaction mixture was then stirred for 1 hour at 65°C. Afterwards the temperature was increased to 80°C to vaporize the solvent. The obtained slightly bluish precipitate was dried to remove absorbed water at 80°C overnight and then calcined at the required heat treatment conditions (Figure 2).

Precipitation reaction with oxalic acid:



Calcination reaction:



Two synthesis techniques were tested to produce WO_3 -coated NMC90 core particles. In the first approach, NMC90 powder was dispersed in ammonium tungstate in isopropanol solution under constant stirring and heating at 70°C. Afterwards the solvent was evaporated and the obtained precipitate was calcined at the required temperature. In the second approach, WO_3 was dissolved in a 25% ammonia solution with continuous stirring under heating at 90°C. Once the WO_3 was completely dissolved, the NMC90 powder was added and the stirring continued. Subsequently, the solvent was completely evaporated, followed by one-step calcination at the required temperature (in the range of 650-950 °C) and heating rate of 3°/min.

To obtain NMC core/shell structures, $\text{Li}(\text{CH}_3\text{CO}_2)$ solution was added to the Ni, Co, Mn mixed solution with ratio Ni:Co:Mn = 6:2:2. Afterwards WO_3 -coated NMC90 core particles were then suspended in the mixed metallic solution and oxalic acid was slowly poured in it, and all further steps were repeated as described above for the NMC90 core synthesis.



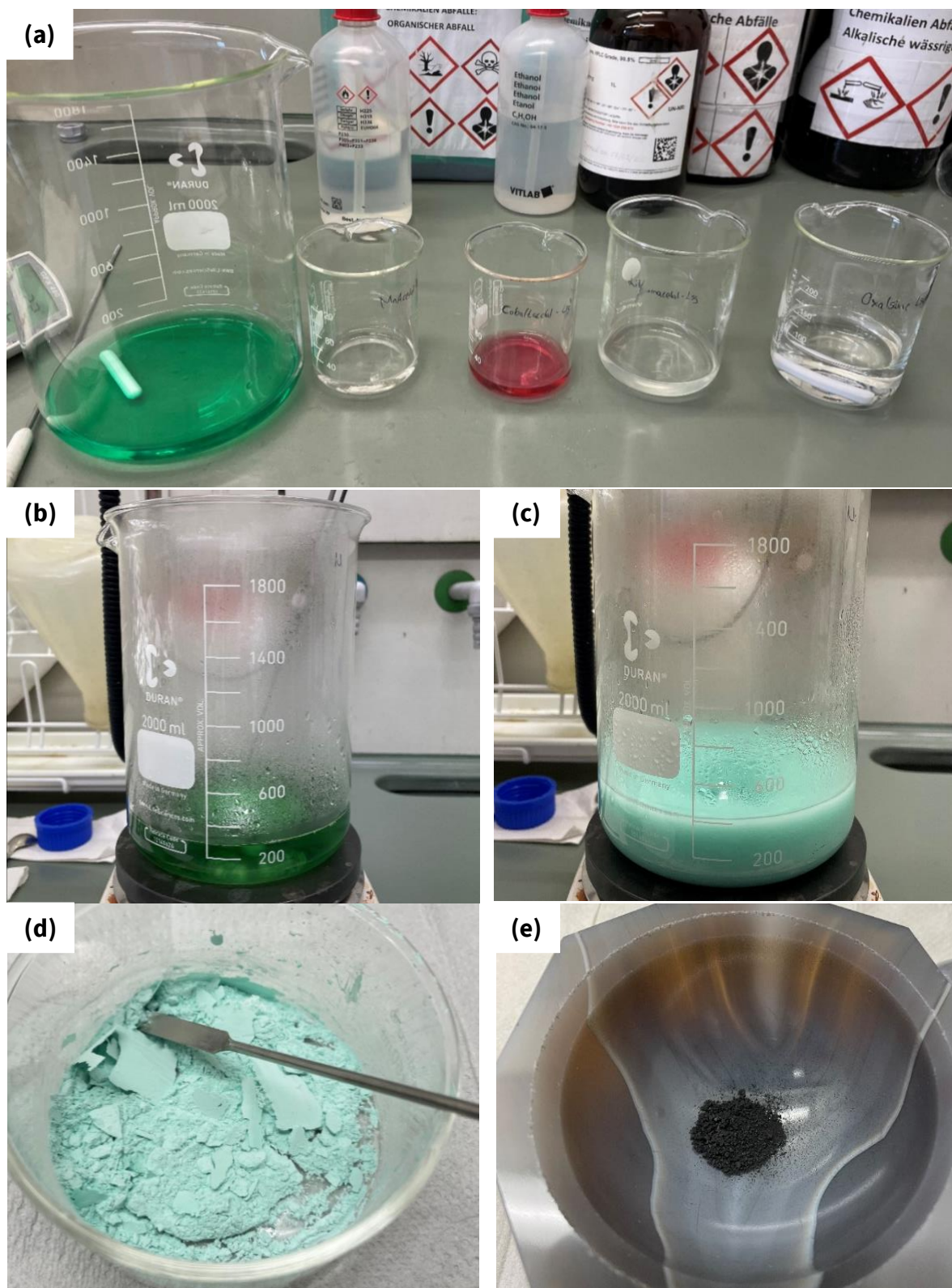


Figure 2 - Synthesis steps of NMC core particles: (a) precursor solutions; (b) mixed solution before adding oxalic acid; (c) mixed solution after adding oxalic acid; (d) dried precipitate; (e) calcined NMC powder



2.1.1 Microstructural and compositional powder characterization

To establish the proper synthesis protocols to fabricate NMC cathode powders with a good electrochemical performance for Li-ion batteries, the investigation of synthesis parameters, including heat treatment conditions and Li-infiltration approach, has been performed. SEM, EDX and XRD techniques have been used to study the compositional, morphological and structural relations within the core/shell particles.

2.1.2 Investigations of synthesis parameters of NMC 90 core powders

To study the effect of the heat treatment temperature on morphological and compositional characteristics, NMC90 core powders have been synthesized, following the synthesis route described in Section 2.1, and heat treated at temperatures in the range of 650-950 °C. The morphology of the NMC90 core samples has been observed with SEM investigations as shown in Figure 3. The surface morphology of NMC90 particles displays that smaller size particle (primary particles) agglomerated to form large secondary particles. Calcination temperature has a significant effect on the morphology of the samples. Thus, the increase of the heat treatment temperature from 650 to 950 °C results not only in the formation of bigger particles, but the heat treatment of powders at temperatures above 750 °C also leads to disappearance of define crystal facets of primary particles due to the heavy agglomeration at higher temperatures (see Figure 3, 850 and 950°C images). Particle agglomeration results in the decreasing of the active surface area, what may have a negative effect on the electrochemical performance of the synthesized cathode powders.

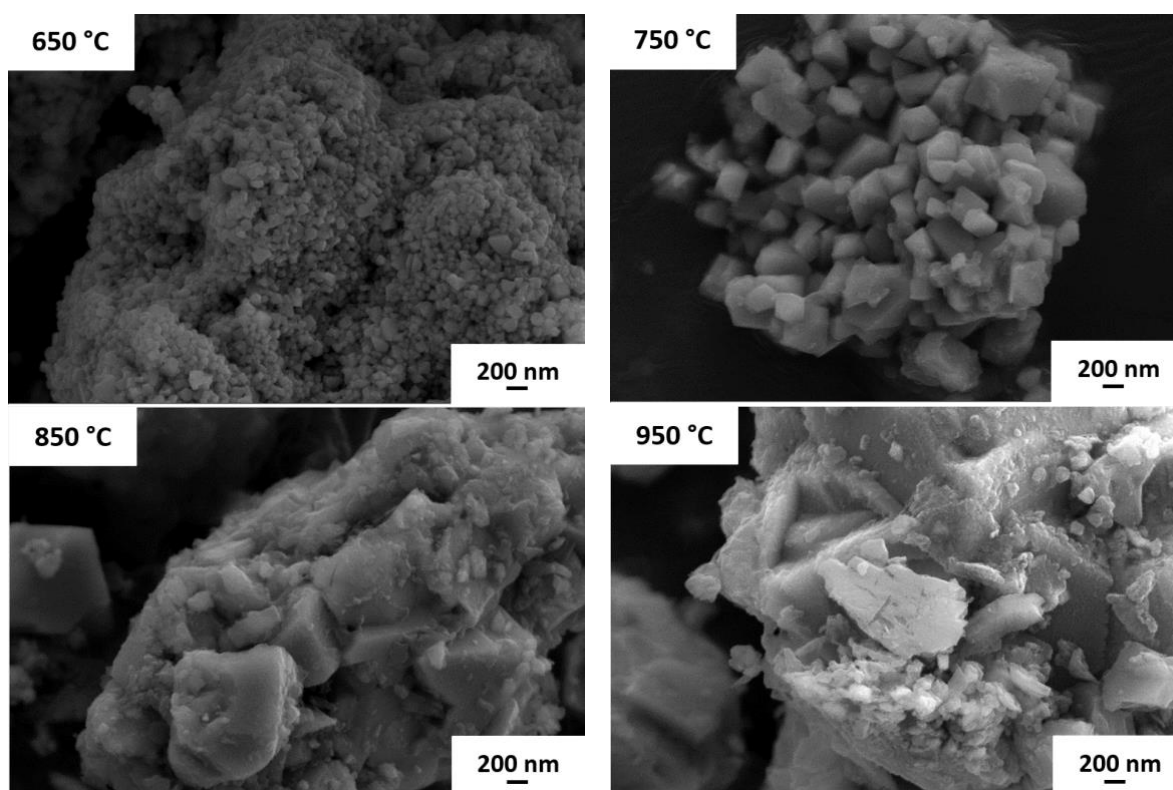


Figure 3 – SEM images of NMC90 core powders, heat treated at different temperatures



According to the XRD results (Figure 4), NMC crystalline structure is formed in the temperature range 750-850 °C. In the case of lower heat treatment temperatures, besides lower powder crystallinity, the small quantities of Li_2CO_3 can be observed in the samples. Higher heat treatment temperatures of 950 °C applied to the samples led to a decrease of $I(003)/I(104)$ ratio, what may be an indication for the NiO phase formation. At the same time, 850 °C is the optimal heat treatment temperature, allowing to obtain more ordered structure with higher crystallinity and phase pattern fitting perfectly to the $R\bar{3}m$ structure, which corresponds to the NMC layered crystal structure.

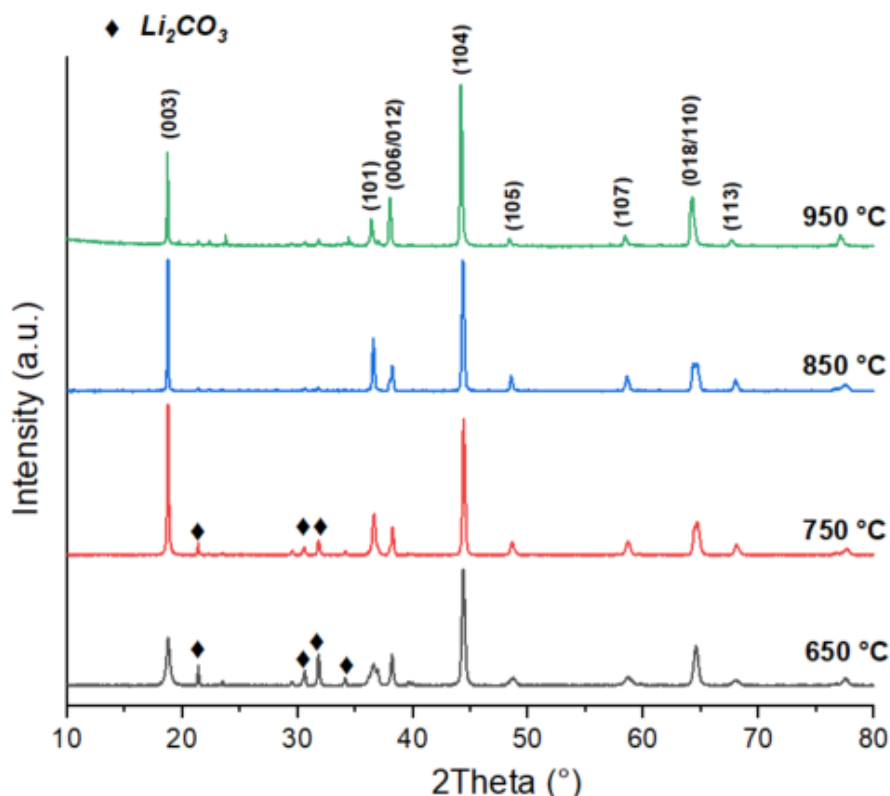


Figure 4 – XRD patterns of NMC90 core powders, heat treated at different temperatures

The Li content effect has been investigated by synthesis of NMC90 core powders with different amount of LiAc excess. The morphology of the NMC90 core particles, synthesized with 50%, 100% and 120% Li excess and heat treated at 850 °C is presented in Figure 5. As SEM pictures exhibit, no significant morphological changes can be observed depending on the employed Li content.



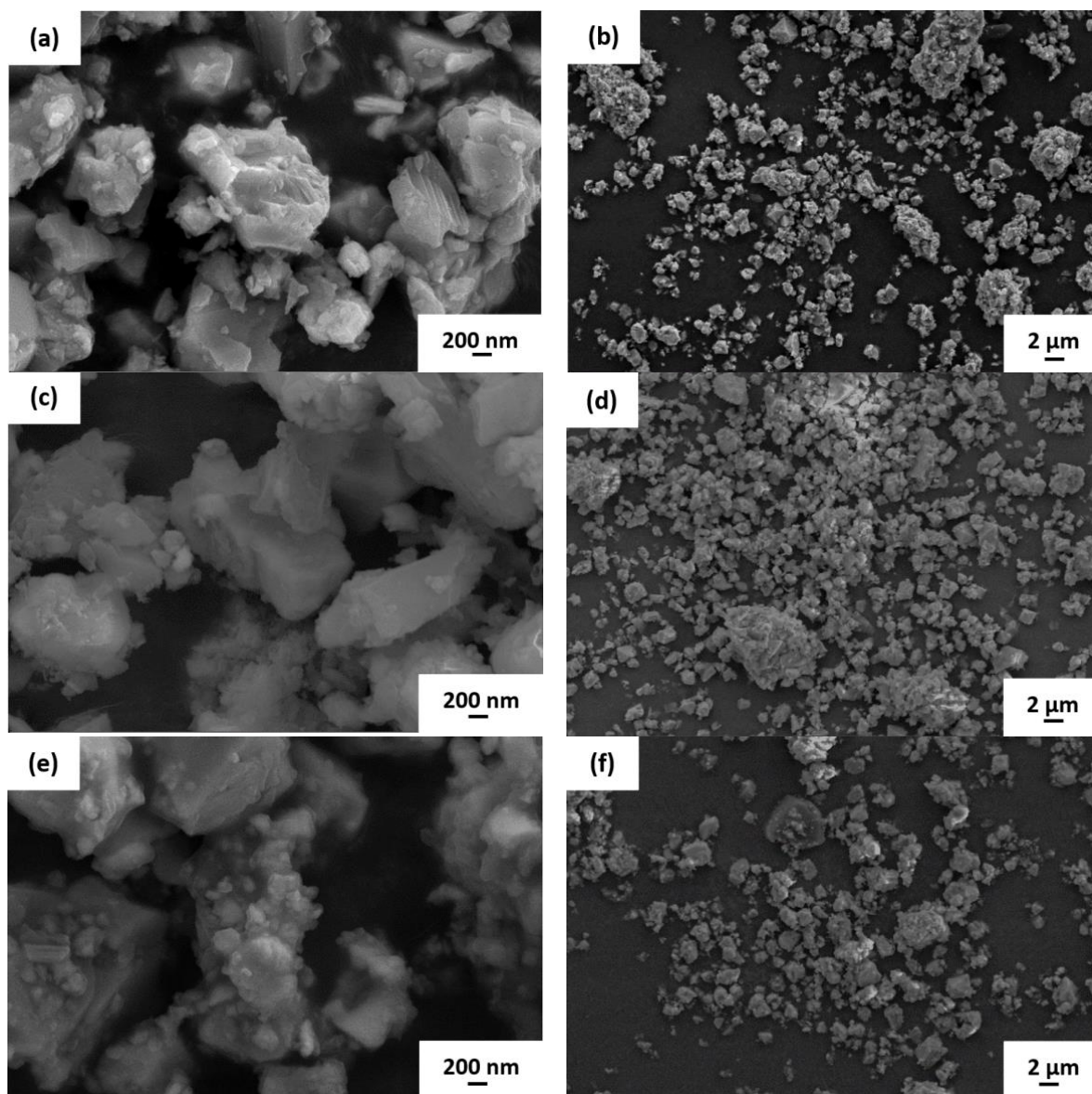


Figure 5 – SEM images of NMC90 core particles, synthesized with 50% (a,b), 100% (c,d) and 120% (e,f) LiAc excess and heat treated at 850°C

Figure 6 shows the XRD measurements of NMC90 core powders, synthesized with different LiAc excess. The obtained XRD patterns matched the diffraction peak of LiNiO_2 (PDF 85-1978). The crystal structure of the synthesized NMC90 samples belong to the R-3m layered structure. The good layered structure is confirmed by split of (006/012) and (018/110) diffraction peaks at 2θ around 38° and 65° [4]. Peak shape and intensity indicated a good crystallinity of material for all three samples. The calculated $I(003)/I(104)$ ratios of 1.59, 1.54 and 1.79 for samples with 50%, 100% and 120% LiAc excess, corresponding, indicate low cation disorder in crystal lattice of these samples, what is crucial for good electrochemical performance [5].



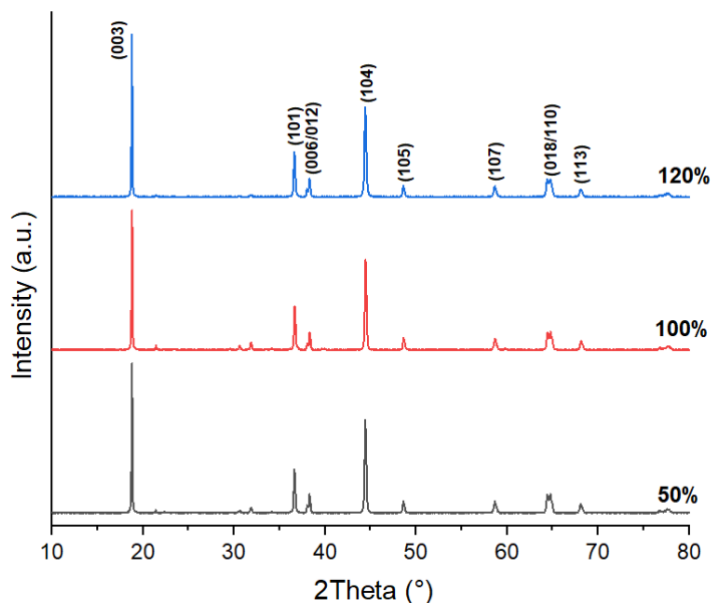


Figure 6 – XRD patterns of NMC90 core powders, synthesized with 50%, 100% and 120% LiAc excess and heat treated at 850°C

In the course of research, it was also established that the material of crucible, in which the heat treatment process is performed, has a crucial effect on the formation of NMC crystalline structure. Thus, it has been observed that the heat treatment of the NMC precursor powder in porcelain crucible resulted in the very low $I(003)/I(104)$ ratio of 0.18 (Figure 7) probably due to the chemical interaction of the NMC powder with the porcelain crucible. The $I(003)/I(104)$ intensity ratio serves to assess the Li/Ni disorder. The low $I(003)/I(104)$ ratio of 0.18 indicates the numerous cationic defects in the NMC crystalline lattice [6,7], predicting the poor electrochemical properties of the synthesized powder.

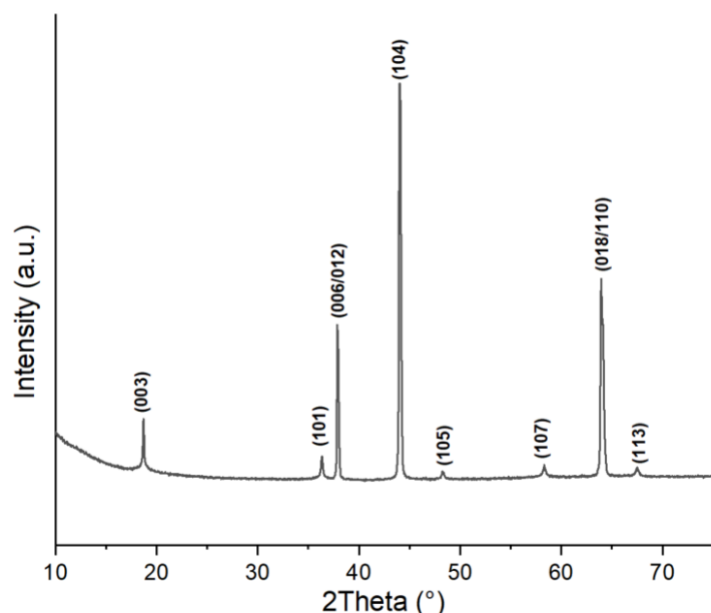


Figure 7 – XRD pattern of NMC90 core powders, heat treated in porcelain crucible



2.1.3 Investigations of synthesis parameters of WO_3 -coated NMC 90 core powders

As have been mentioned in the Section 2.1, two different approaches have been investigated to produce WO_3 -coated NMC90 core powders. For both approaches, additionally the effect of the heat treatment temperature on morphological and compositional characteristics of the synthesized powders has been studied. According to the SEM images (Figure 8), in the case of ammonium tungstate approach, powders consist of primary particles with define crystal facets and more or less uniform particle size distribution, what especially noticeable for the sample heat treated at 450 °C (Figure 8e). Synthesis of WO_3 -coated NMC90 core powders using WO_3 /ammonia solution led to the formation of the non-uniform particles in all range of the applied temperatures.

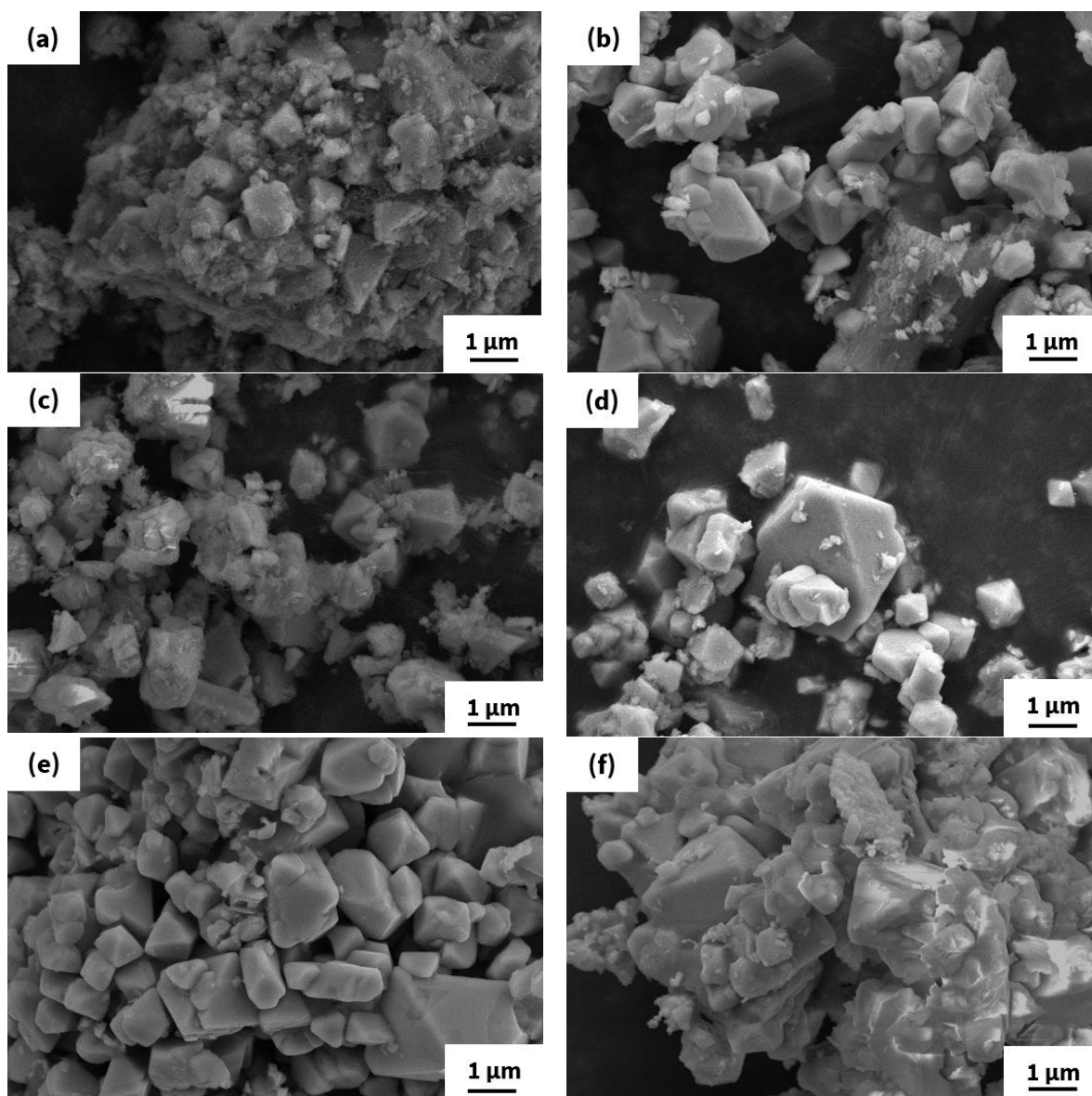


Figure 8 – SEM images of WO_3 -coated NMC90 core particles, synthesized using ammonium tungstate (a,c,e) and WO_3 / ammonia solution (b,d,f) and calcined at 250 °C (a,b), 350 °C (c,d) and 450 °C (e,f)



On the next step, the impact of WO_3 content on the phase structure of NMC90 powder has been studied. The diffraction peaks of WO_3 -coated NMC90 core powders with 1wt% and 2wt% WO_3 (**Error! Reference source not found.**) align with those in Powder Diffraction File Database (PDF card 85-1978), which corresponds to the characteristic hexagonal layered structure of LiNiO_2 within the R-3m space group, with no impurities detected. Analysis revealed that the addition of WO_3 did not alter the material's phase structure. Diffraction peaks corresponding to WO_3 were not detected by XRD, probably due to the small amount of WO_3 added.

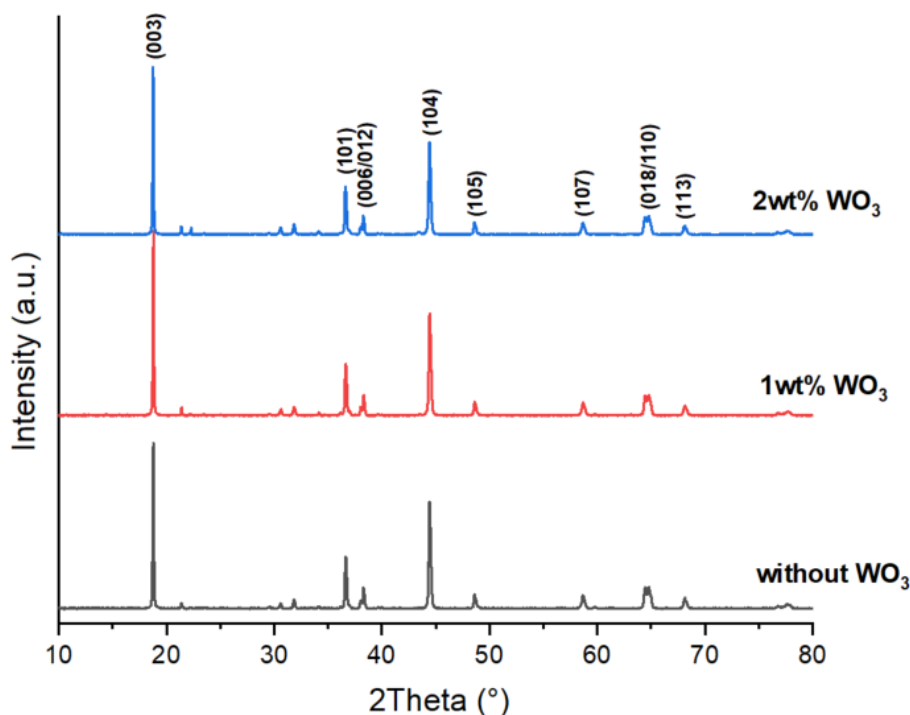


Figure 9 – XRD patterns of WO_3 -coated NMC90 core particles with 1wt% WO_3 and 2wt% WO_3 , synthesized in ammonium tungstate

In contrast to XRD investigation, EDX mapping of WO_3 -coated NMC90 core powders has confirmed the formation of the WO_3 layer on the NMC surface for both 1wt% and 2wt % WO_3 samples (Figure 10). Furthermore, it has been observed that increasing the WO_3 content resulted in agglomeration of WO_3 particles on the NMC90 surface (Figure 10b), while the coating with 1wt % WO_3 led to the formation of a very uniform thin layer (Figure 10a). The analysis of the elemental composition (at. %) of the synthesized samples is provided in Table 1.

Table 1: Elemental composition of WO_3 -coated NMC90 powders

NMC Sample	At. %				
	O	Ni	Mn	Co	W
NMC90 with 1%wt. WO_3	69.3	27.2	1.6	1.7	0.2
NMC90 with 2%wt. WO_3	73.7	23.2	1.3	1.4	0.4



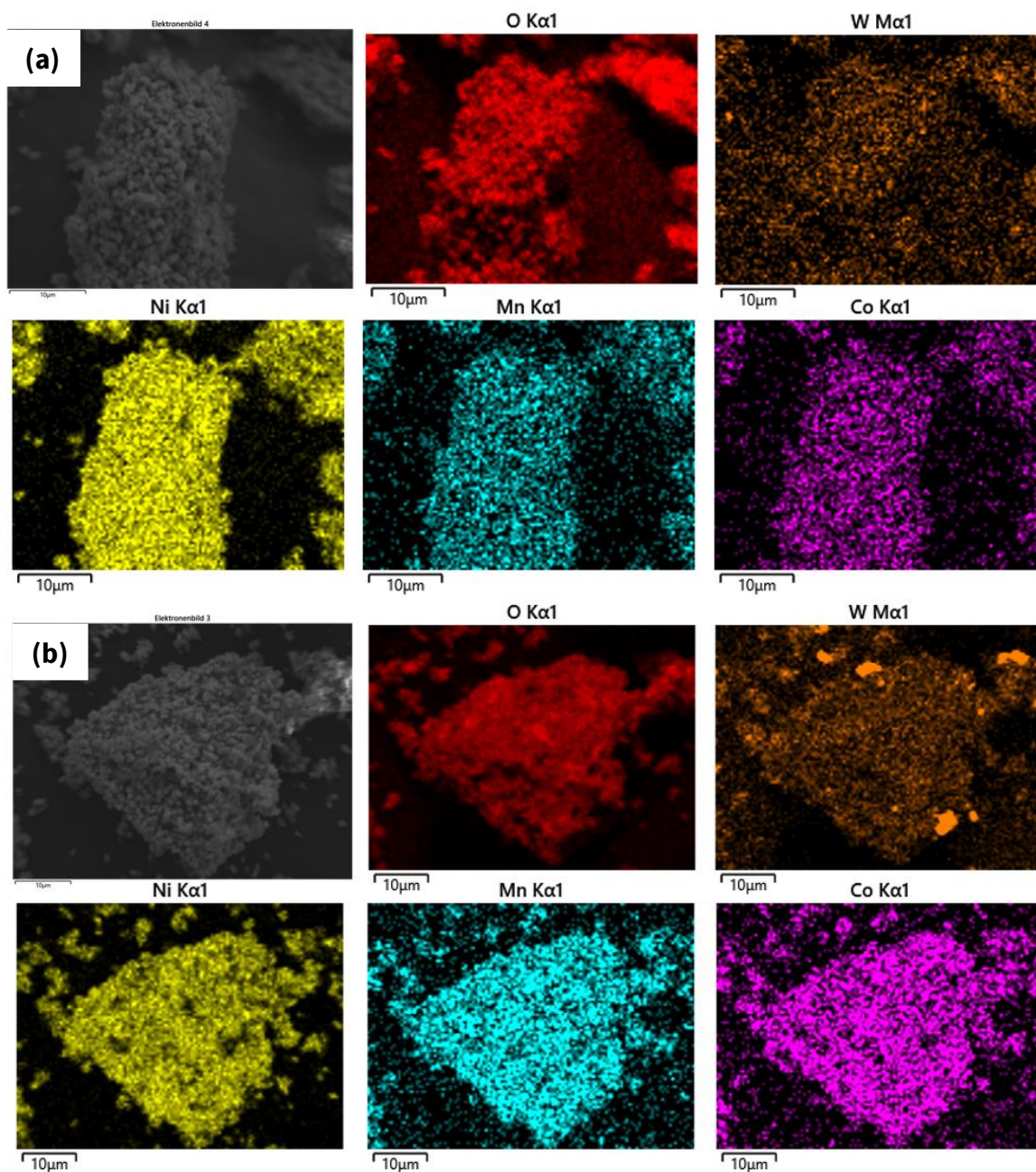


Figure 10 – EDX investigations of WO₃-coated NMC90 core particles with 1wt% WO₃ (a) and 2wt% WO₃(b), synthesized in ammonium tungstate

2.1.4 Investigations of synthesis parameters of NMC 622 shell powders

Similar, to the NMC90 investigations (Section 2.1.2), the effect of process parameters on microstructural and compositional characteristics of NMC622 shell powders has been studied. Thus, the increase of heat treatment temperature from 650 °C to 950 °C resulted in the formation of bigger primary particles, which is particularly noticeable for the sample heat treated at 950 °C (Figure 11). The increase in particle size can be explained due to faster crystallization at high-temperature what induced the growth of particles.



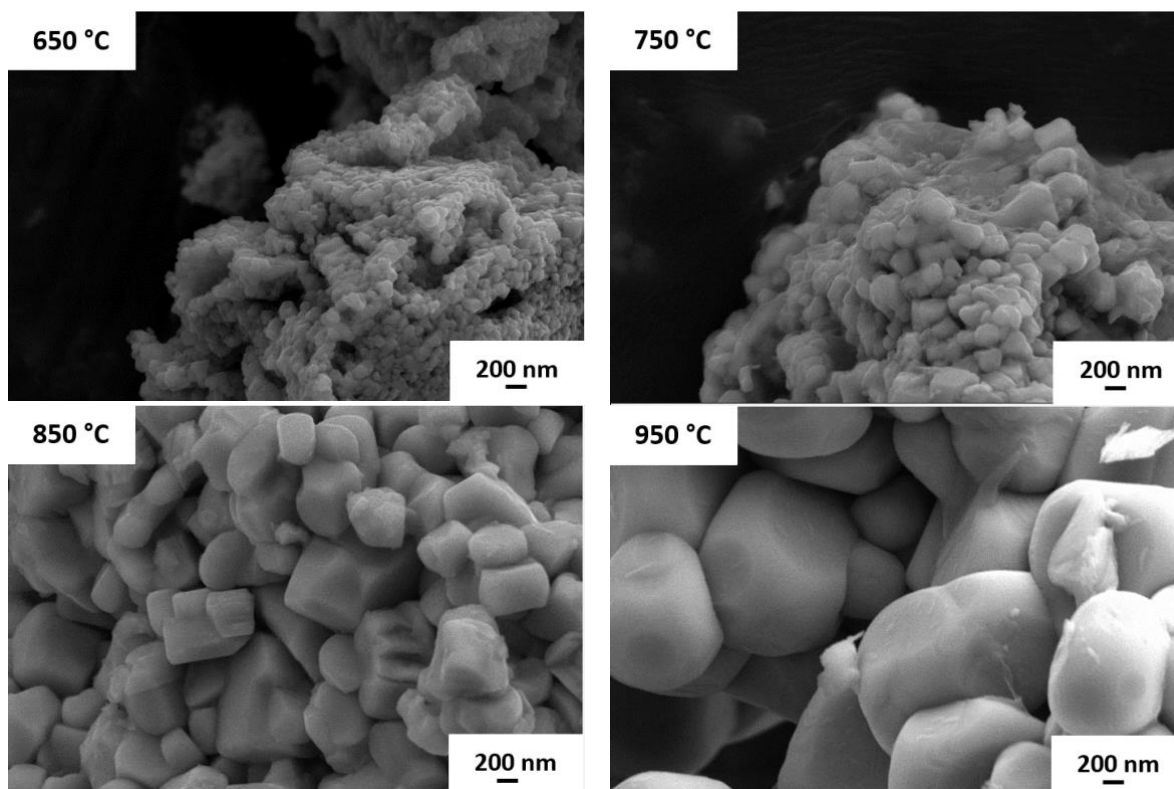


Figure 11 – SEM images of NMC622 shell powders, heat treated at different temperatures

Figure 12 shows the XRD patterns of NMC622 core powders, heat treated at different temperatures, according to which NMC crystalline structure is formed in the temperature range 750-950 °C. In the case of lower heat treatment temperatures of 650 and 750 °C, besides lower powder crystallinity, the small quantities of Li_2CO_3 can be observed in the samples. At the same time heat treatment of powders in the temperature range of 850-950 °C allows to obtain more ordered structure with higher crystallinity and phase pattern fits perfectly to the R3m structure. However, for further investigation the heat treatment temperature of 850 C has been chosen, considering the higher $I(003)/I(104)$ ratio of 2.18 in comparison with 1.27 for the sample heat treated at 950 C.

Figure 13 Error! Reference source not found. shows SEM images of NMC622 shell powders, synthesized with different amount of Li excess and heat treated at 850 °C. According to the obtained results, the primary particles of NMC622 sample with 50% Li excess (Figure 13a) have a diameter in the range of 200-600 nm. While secondary particles (Figure 13b), composed of densely packed primary particles, exhibit a close to round shape and vary in the size range of 5-20 μm . In turn, the increase of Li content led to the destroying of define crystal facets of primary facets and forming of bigger secondary particles agglomerates (Figure 13c, d).



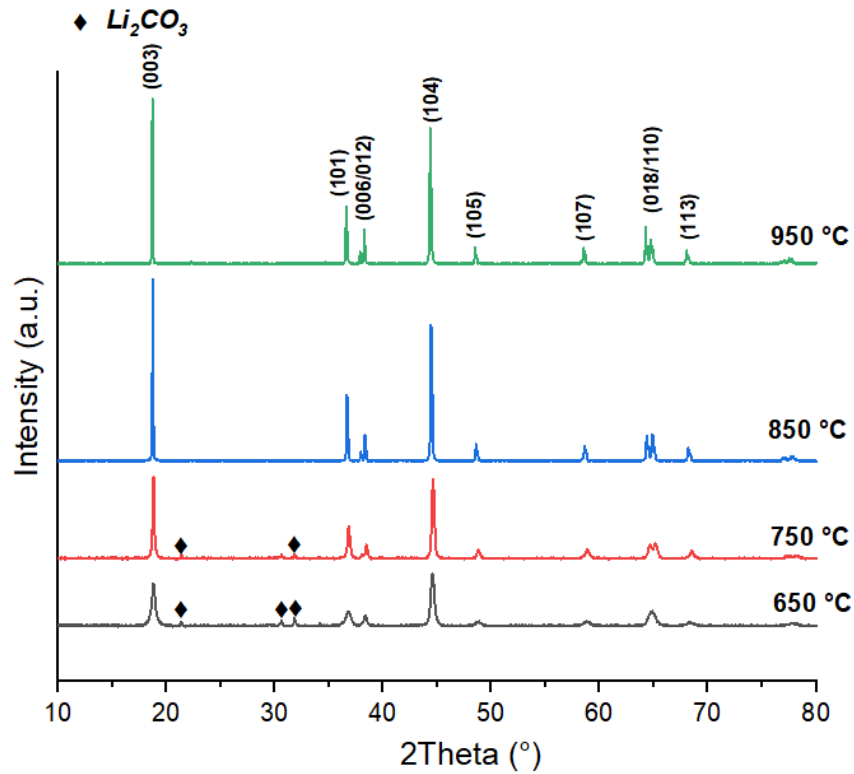


Figure 12 - XRD patterns of NMC622 core powders, heat treated at different temperatures

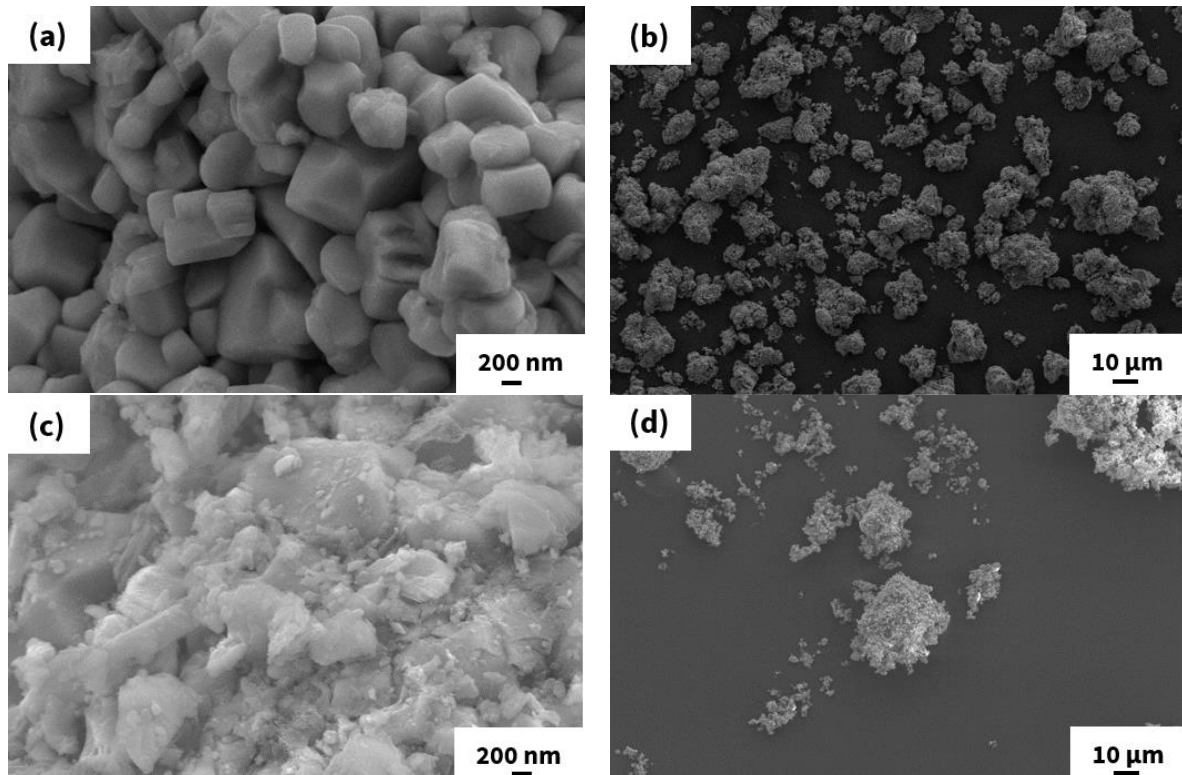


Figure 13 - SEM images of NMC622 shell particles, synthesized with 50% (a,b) and 100% (c,d) LiAc excess and heat treated at 850°C

The XRD patterns of NMC622 powders, synthesized with 50% and 100% LiAc excess and heat treated at 850°C (Figure 14), represent the R-3m space group with hexagonal crystallographic patterns. The distinct doublet-peak splits of the (006/012) and (018/110) at 2θ around 38° and 65° are visible, corresponding to well-ordered crystalline structures of NMC [4]. The calculated I(003)/I(104) ratios of 2.18 and 1.63 for samples with 50% and 100% LiAc excess, corresponding, indicate low cation disorder in crystal lattice of these samples [5].

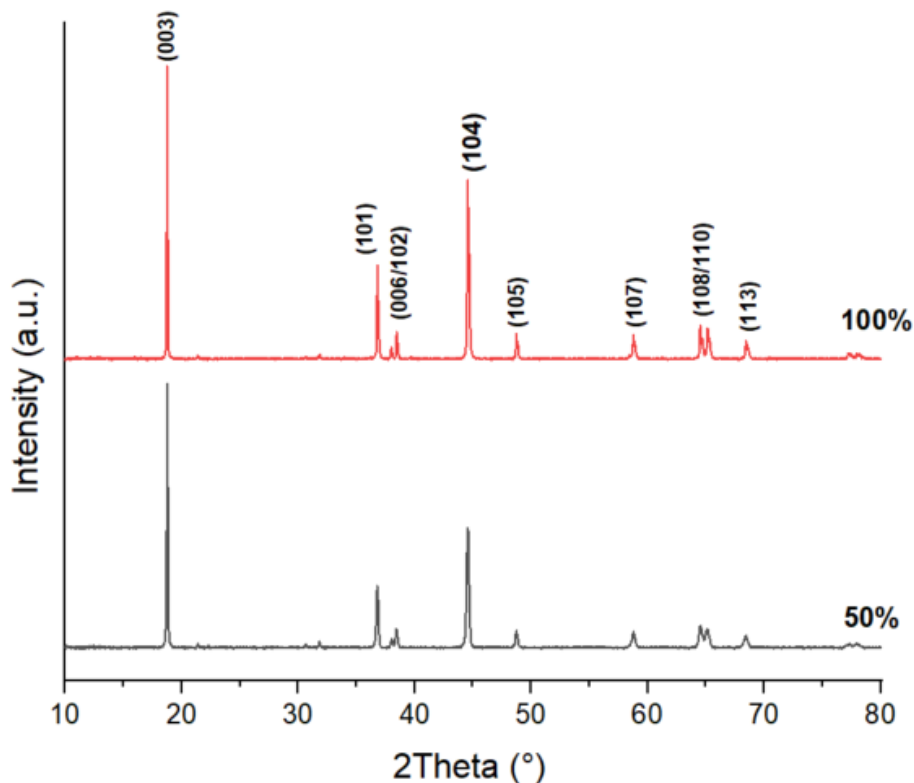


Figure 14 – XRD patterns of NMC622 shell powders, synthesized with 50% and 100% LiAc excess and heat treated at 850°C

Synthesis parameters to produce core/shell structured NMC cathode powder have been chosen based on the obtained results of microstructural and compositional characterisation. Accordingly, NMC90 core powder with 100% LiAc excess has been synthesized following the synthesis route described in Section 2.1 and heat treated at 850 °C. Afterwards, the surface of NMC90 core particles has been coated with thin layer of WO₃ (1wt% WO₃) via ammonium tungstate approach with following heat treatment at 450°C. On the last stage, NMC622 shell with 50% LiAc excess has been precipitated on WO₃-coated NMC90 core particles and obtained powder has been heat treated at 850°C. As reference for electrochemical trials, NMC core/shell structures without WO₃ have been also synthesized.



3. ELECTROCHEMICAL TESTS

NMC90/NMC622 core/shell samples with and without WO_3 interlayer have been selected for the electrochemical investigations. The preparation of cathode powder for electrochemical test has done as follows: the slurry with a composition ratio of 8:1:1 has been obtained by mixing 80% by weight NMC cathode powder, 10% Polyvinylidene fluoride (PVDF) and 10% of activated carbon (AC). First, PVDF has been dissolved in the N-Methyl-2-pyrrolidone (NMP) solvent under continuous stirring at 60-65°C. Afterwards, the PVDF solution has been cooled and AC and NMC powder have been added to the solution with following stirring of the mixture overnight at a high-speed of 1400 rpm. The resulted slurry has been coated on aluminum foil using a doctor blade coating device with a device set up for thickness of 600 μm (Figure 15a) and dried at 70°C for 4 hours (Figure 15b). The cathode mass loading was 11.10 and 22.20 mg/cm^2 for NMC90/NMC622 core/shell powder without and with WO_3 interlayer, respectively. Finally, 14 mm diameter discs have been punched out from the electrode (Figure 16) for assembling the CR2030 half-coin cells.

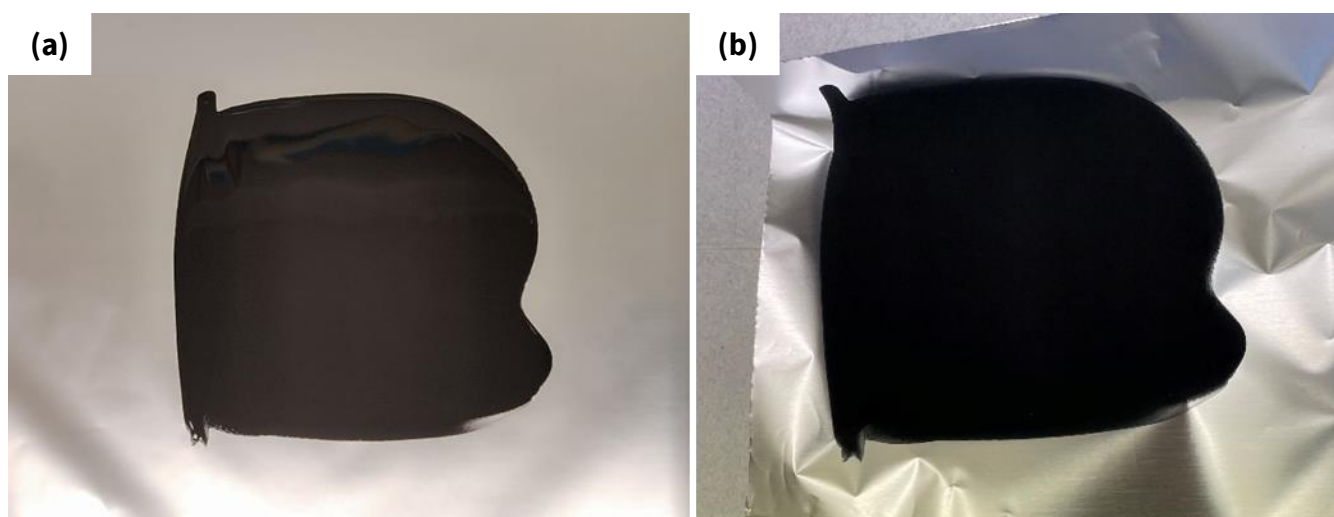


Figure 15 – NMC electrode sheet (a) immediately after coating with the doctor blade; (b) dried electrode



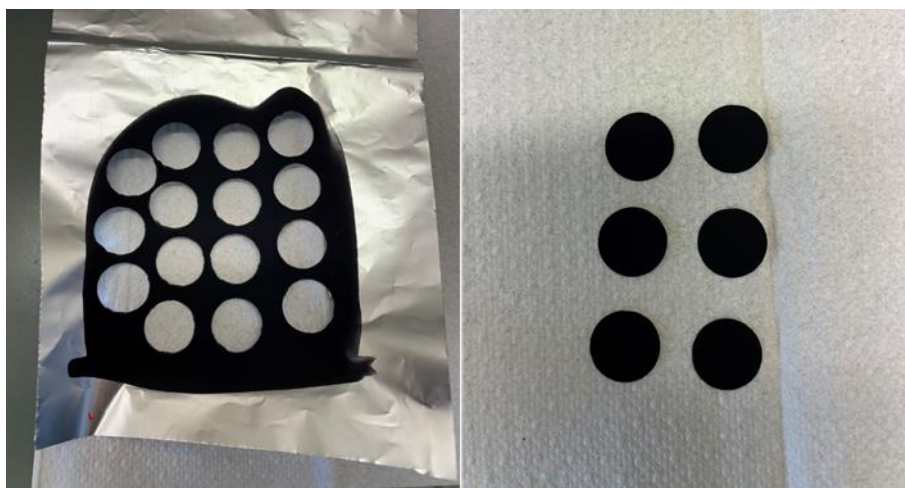


Figure 16 – Punched out electrodes with a diameter of 14 mm for coin cells assembling

Subsequently, the assembly of the coin cells has been carried out in a Glovebox under inert Ar-gas atmosphere and the electrolyte 1M LiPF₆ in ethylene carbonate (EC)/ dimethyl carbonate (DMC) = 50/50 (v/v) has been used. Cell assembly has been done according to the following scheme as shown in Figure 17 [8]:

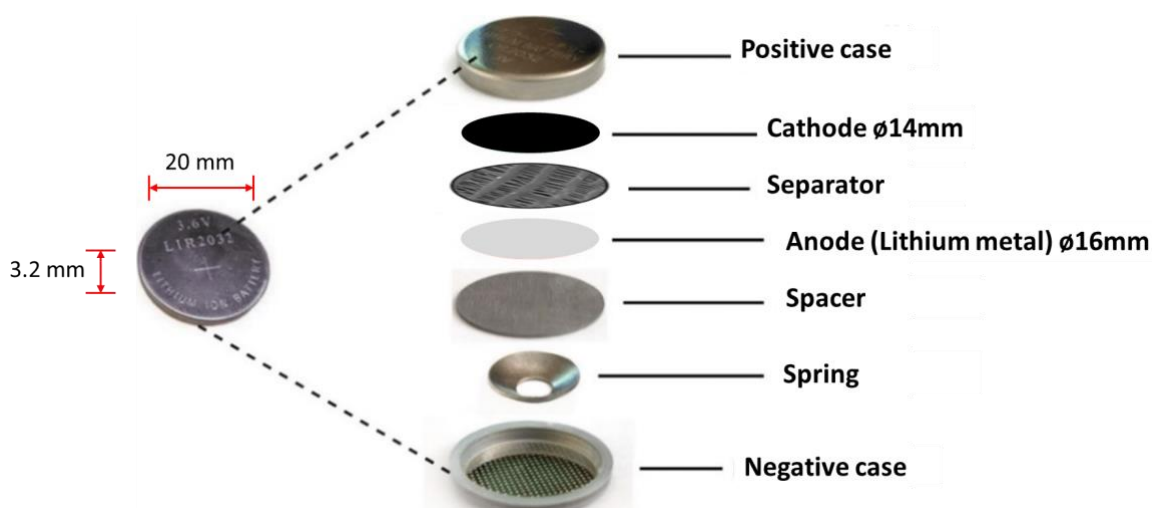


Figure 17 – Assembly of Coin Cell

The first five cycles of charge-discharge performance of NMC90/NMC622 core/shell powder with and without WO₃ interlayer as cathode materials are conducted at a rate of C/10 in the potential range of 2.7 V to 4.2 V. The galvanostatic charge-discharge (GCD) tests are carried out on half-cell form fabricated with metallic lithium (Li) as negative (anode) electrode and glass fiber (GF) as separator. The GCD curves in Figure 18 represent that compared to NMC core/shell powder with WO₃ interlayer material, the NMC core/shell powder without WO₃ interlayer materials show better performance by delivering higher capacity of 131 mAh/g at C/10. The first five cycle GCD curves of NMC core/shell powder without WO₃ interlayer



materials also shows better stability compared to the one with WO_3 interlayer materials. Lower specific capacity of NMC core/shell powder with WO_3 interlayer materials may be due to the reason that the interlayer of relatively low electrochemically active WO_3 significantly reduces the intercalation/deintercalation of Li^+ ions to NMC90 core and mostly NMC622 shell take part in the battery performance and contribute to the capacity of the half-cell battery. Further optimization of the position and thickness of WO_3 layer will be performed to achieve the high performance NMC core/shell materials. The mitigation strategies, among others, involve the reduction of thickness of the WO_3 interlayer to study the effect of WO_3 layer thickness on the electrochemical properties of the NMC core/shell structured powders.

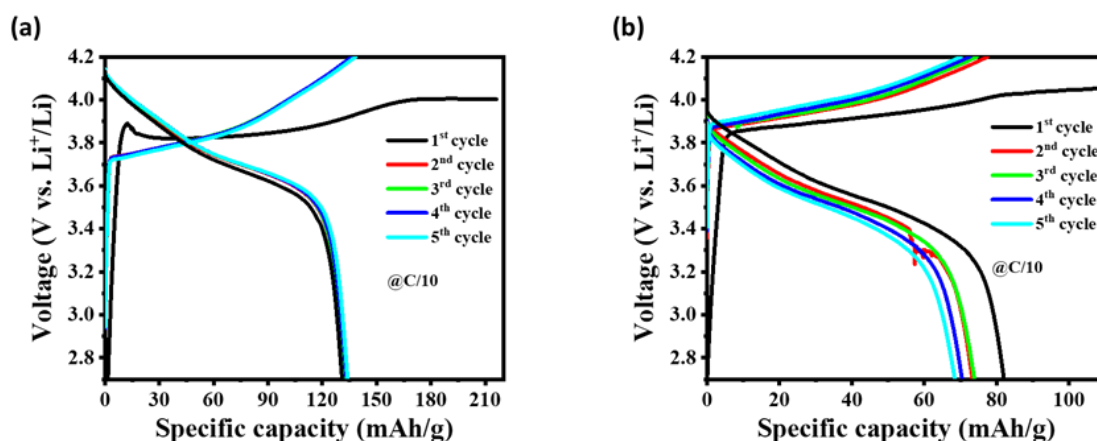


Figure 18 –Charge/discharge voltage curve as a function of specific capacity of core/shell structured NMC powders: (a) without WO_3 interlayer; (b) with WO_3 interlayer



4. CONCLUSIONS

The process parameters have been established for the synthesis of core/shell structured NMC cathode powders with additional WO_3 interlayer via easy process-controlled oxalate-assisted co-precipitation method. It has been shown that the formation of the pure NMC ($R\bar{3}m$) structure can be achieved for both NMC90 and NMC622 compositions at 850 °C. According to the XRD results, in-situ Li-infiltration approach results in the formation of NMC structures with a relatively high I(003)/I(104) ratio. The electrochemical performance of half-cell Li-ion battery using core/shell NMC cathode show promising battery properties in respect of capacity and cyclic stability. However, the WO_3 interlayer between NMC90 core and NMC622 shell Initially shows relatively lower capacity compared to core/shell NMC structure without WO_3 interlayer, more optimization in synthesis and electrode fabrication will be continued to achieve the desired properties according to the project requirements.



REFERENCES

1. Noh, H.-J.; Youn, S.; Yoon, C.S.; Sun, Y.-K. Comparison of the structural and electrochemical properties of layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x = 1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85) cathode material for lithium-ion batteries. *Journal of Power Sources* **2013**, 233, 121-130. doi:10.1016/j.jpowsour.2013.01.063.
2. Chen, Z.; Zhang, L.; Wu, X.; Song, K.; Ren, B.; Li, T.; Zhang, S. Effect of N/P ratios on the performance of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2\|\text{SiO}_x/\text{Graphite}$ lithium-ion batteries. *Journal of Power Sources* **2019**, 439: 227056. doi:10.1016/j.jpowsour.2019.227056.
3. Xu, L.; Bao, C.; Zhou, H.; Li, J. The Modification of WO_3 for Lithium Batteries with Nickel-Rich Ternary Cathode Materials. *Processes* **2023**, 11, 1756. doi:10.3390/pr11061756
4. Liu, Z.; Zhang, Z.; Liu, Y.; Li, L.; Fu, S. Facile and scalable fabrication of K^+ -doped $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Co}_{0.08}\text{Mn}_{0.52}\text{O}_2$ cathode with ultra high capacity and enhanced cycling stability for lithium ion batteries. *Solid State Ionics* **2019**, 332, 47-54. doi:10.1016/j.ssi.2018.12.021.
5. Ding, Y.; Mu, D.; Wu, B.; Zhao, Z.; Wang, R. Controllable synthesis of spherical precursor $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$ for nickel-rich cathode material in Li-ion batteries. *Ceramics International* **2020**, 46(7), 9436-9445. doi:10.1016/j.ceramint.2019.12.204.
6. Nam, K.-W.; Bak, S.-M.; Hu, E.; Yu, X.; Zhou, Y.; Wang, X.; Wu, L.; Zhu, Y.; Chung, K.Y.; Yang, X.-Q. Combining in situ synchrotron X-ray diffraction and absorption techniques with transmission electron microscopy to study the origin of thermal instability in overcharged cathode materials for Lithium-Ion batteries. *Adv. Funct. Mater.* **2012**, 23, 1047–1063. doi:10.1002/adfm.201200693.
7. Hua, W.; Zhang, J.; Zheng, Z.; Liu, W.; Peng, X.; Guo, X.-D.; Zhong, B.; Wang, Y.-J.; Wang, X. Na-doped Ni-rich $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material with both high rate capability and high tap density for lithium ion batteries. *Dalton Trans.* **2014**, 43, 14824–14832. doi:10.1039/C4DT01611D.
8. Park, B.H.; Kim, T.; Park, H.; Sohn, Y.; Shin, J.; Kang, M. Electrochemical performance of layer-structured $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode active materials synthesized by carbonate co-precipitation. *Nanomaterials* **2022**, 12, 3610. doi:10.3390/nano12203610

