Investigating the Synthesis of NMC and LCO Thin-Film Cathodes for Enhanced Performance in Lithium-Ion Batteries

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Abstract

Thin-film lithium batteries are designed to improve the longevity, storage capacity, energy density, and safety level of lithium batteries. The materials of the thin-film of electrodes should fit several criteria, such as ionic conductivity, electrochemical stability, and optimized solid electrolyte characteristics. This study investigated the electrochemical performance of an NMC-based lithium-ion battery, with a focus on understanding the voltage-capacity relationship and cycling performance. The obtained experimental results showed a peak voltage of 3.1 V, which is considerably lower than the expected value of 4.2 V for NMC-based cells. Additionally, the specific capacity was found to be 2.09 μAh/g, which is significantly lower than the reported capacities in the literature for similar battery chemistries. The deviation from the expected performance suggests potential issues in the materials, cell design, or experimental conditions. Despite the suboptimal performance, this study provides valuable insights into the challenges associated with NMC-based lithium-ion batteries and serves as a foundation for further investigations and optimizations. Future work should focus on identifying the factors contributing to the observed performance and exploring strategies to enhance the electrochemical behavior of NMC-based cells to make them suitable for various applications, such as electric vehicles and energy storage systems.

Keywords: NMC electrode, magnetron sputter deposition, lithium ion battery, coin cell, charge-discharge cycle

Contents

1. Introduction

The increase in usage of portable electronics and electric vehicles (EVs) caused the rise in demand for compact and lightweight power sources (Jetybayeva et al., 2021). Though lithium-ion batteries (LIB) are currently widely used, they have constrained longevity, storage capacity, and energy density (Phillip et al., 2019). Fortunately, recent studies (Uzakbaiuly, Mukanova, & Bakenov, 2022) show that these issues can be solved by using thin-film coatings of cathodes such as Lithium Nickel Manganese Cobalt Oxide also known as NMC and LCO. Similarly, Phillip and his colleagues (2019) claim that Ni-rich cathodes can eliminate all the above-mentioned disadvantages of LIB, and improve safety level due to the lack of flammable or toxic liquid electrolytes.

Despite the potential benefits of thin-film lithium batteries, their current form is still limited. Tan et al. (2014) report that this limitation is caused by the problem of finding suitable thin-film materials for the electrodes of the battery. In the search for new materials, the enhancement of the ionic conductivity and electrochemical stability as well as the optimization of the solid electrolyte characteristics should be taken into consideration (Tan et al., 2014).

According to Phillip et al. (2019), the surface reactivity, charge capacity, and degradation mechanisms of the electrode can be improved with the adhesive and binding current collector coating of electrochemically active elements such as Pt, Co, and Cr. They (2019) used magnetron sputter deposition to coat aluminum oxide (Al_2O_3) and stainless steel (SS) substrates with two distinct layers of Co and Pt (0.5-1.5 microns) targets. In their (2019) research, Co sub-layer was used to achieve a favorable crystalline allocation of NMC and LCO thin-films. Authors (2019) claim that this method helped them to achieve greater potential (up to 4.3V) and specific capacity (almost 200 mAh/g).

Because of the above-mentioned properties, the commercial interest in NMC cathode batteries increases which leads to more research on that topic (Phillip et al., 2019). In the same vein, this report replicates Phillip et al. (2019)'s method of NMC and LCO cathode synthesis process to achieve the enhanced performance of lithium ion batteries.

2. Materials and Methods

Coin cells: Typical coin cells were assembled at Nazarbayev University laboratory of solid-state batteries in an Argon-filled

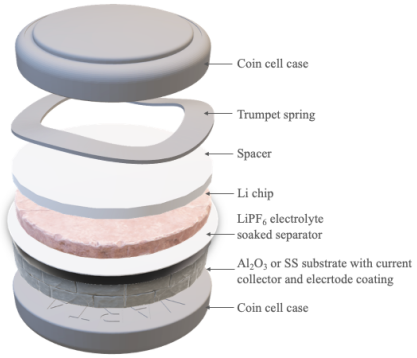


Figure 1: A coin cell structure

MBRAUN glovebox. The composition of the cell is illustrated in Figure 1. The diagram shows the internal components of the coin cell. It consists of a negative cap, trumpet spring, a SS spacer, a Li metal chip, a separator immersed in Lithium hexafluorophosphate (LiPF6) electrolyte, an NMC or LCO cathode, and a positive case (Varta CR2032). All components after the assembling were pressed in the Automatic Coin Cell Crimper by Hohsen.

Electrolyte: Lithium hexafluorophosphate (LiPF6) solution in ethylene carbonate and ethyl methyl carbonate by Sigma-Aldrich was used as the electrolyte (1.0 M LiPF6 in EC/EMC=50/50 (v/v)).

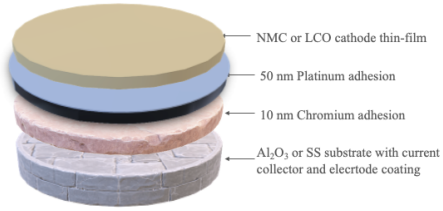


Figure 2: A composite electrode structure (not to scale)

Electrodes: A composite cathode electrode composition is illustrated in Figure 2. As shown in the diagram, it consists of Al_2O_3 or SS substrate coated with 10nm sublayer of Chrome, 50 nm of Platimum current collector, and NMC or LCO cathode. The substrate weight was measured prior to any coating. A radio frequency (RF) magnetron sputtering (MS) deposition (equipment by ANGSTSROM) was used to prepare electrodes. Thin (1 mm) and thick (2 mm) Al_2O_3 and SS substrates (1 cm in diameter) were first coated with Cr target and then with Pr target in RFMS chamber under the following conditions: 15 mTorr pressure/15 sccm, 45W power, and 5:1 Argon to Oxygen ratio environment with 30 min pre-sputter phases to remove any remaining impurities from the surface. Then, 100 microns of NMC111 or LCO (depending on the sample) was deposited on one surface of the substrate under 5nTorr pressure/15sccm, 60W power (20% of maximum), 5:1 Ar:O_2 ration for about 33 hours. Sputtered electrodes were kept in an Ar-filled glovebox after being annealed under high-purity airflow. At the end of the process, the electrodes' weight was measured to find the mass of the cathode film.

Electrochemical testing: A 15-channeled coin cells testing board was used to do electrochemical testing. All (successfully) assembled cells were tested in 50 charge-discharge cycles to measure charge capacity (μAh) and voltage (V). NMC111 has the theoretical specific capacity of 150 μAh/g and theoretic potential up to 4.2V (Tan et al., 2014). However, since the experimental values will not reach 4.2V of potential, the initial voltage window was 2.2V-4.0V. Finally, the graphs of voltage (V) against capacity (μAh) and capacity against cycle number were plotted. The results of electrochemical testing are shown in the Results and Discussion section.

3. Results and Discussion

Table 1: The average mass of electrodes measured before and after thin-film coating

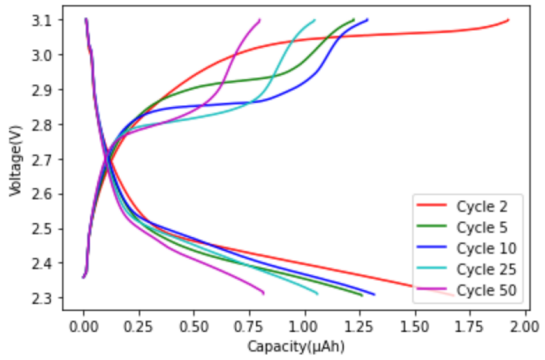
Average mass in mg			
Electrode (Substrate and cathode materials)	Substrate	Substrate with film	Film only (Difference of mass)
SS LCO	821.0838	821.8004	0.7166
SS NMC	795.1424	795.8483	0.7059
Al_2O_3 LCO	576.4768	576.9610	0.4842
Al_2O_3 NMC	580.5276	580.9866	0.4590

In the experiment, a total of eight batteries were assembled. The cathode masses are given in Table 1. However, two batteries were not sealed properly and two batteries did not provide the planned 50 charge-discharge cycles. Unfortunately, all electrochemical data on LCO cathodes was lost.

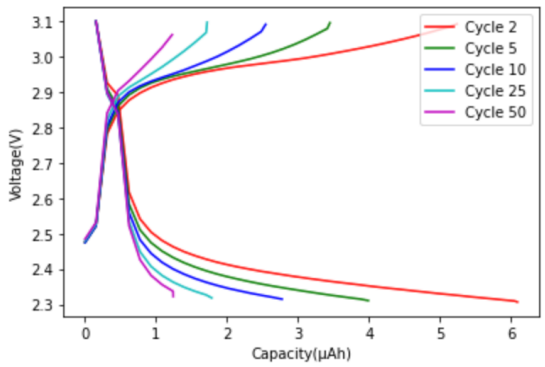
Figure 3(a and b) reveals the plot of Voltage (V) against Capacity (μAh) for cycles 2, 5, 10, 25, and 50 for SS and Al_2O_3 substrates, respectively. During the electrochemical testing, the potentials of the cells did not reach the theoretical voltage of 4.2V. Therefore, the voltage window was changed to 2.2V-3.2V. Consequently, the first cycle was not included in the plot since it was used to calibrate the voltage window. Although it was not described, cycle 1 still contained valuable information so it is included in Appendix A.

Figure 3 depicts charge-discharge patterns for 50 cycles. For SS substrate (Figure 3(a)), there is an irregularity of charging during cycles 5, 10, 25, and 50. The curve is sigmoidal in shape, with an initial rapid increase in voltage, followed by a plateau at around 2.8 V, and then a sharp increase to a peak voltage of 3.1 V. The voltage begins to decrease after reaching the peak, indicating a transition to a lower voltage plateau at around 2.1 V during discharge. Charge and discharge plots intersect at roughly 2.7V mark with a capacity range from 0μAh to 2μAh and voltage range from 2.3V to 3.1V. The capacity decreases from cycle 2 to cycle 50 from 2μAh to 0.8μAh, respectively.

A similar tendency can be seen in Al_2O_3 substrate (Figure 3(b)), the curve shows that there is a clear pattern in the charge-discharge process. Curves meet at 2.85V and have a plateau

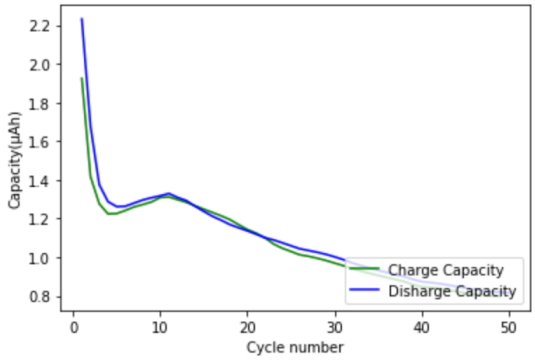


(a) SS substrate

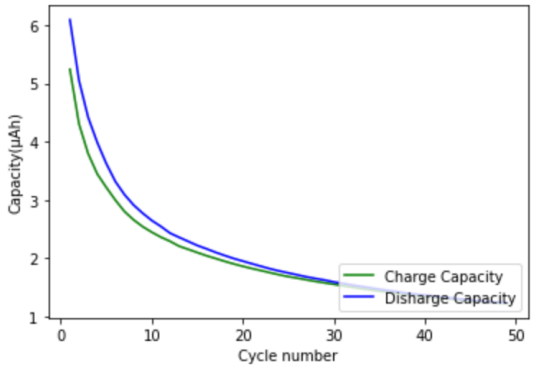


(b) Aluminum oxide substrate

Figure 3: (a) and (b) NMC-cathode potential of different substrates during 50 charge and discharge cycles with voltage window of 2.2 to 3.2V



(a) SS substrate



(b) Aluminum oxide substrate

Figure 4: Average charge and discharge capacity of different substrates during 50 cycles

shape. For Al_2O_3, capacity ranges from 0μAh to 6μAh and voltage ranges from 2.3V to 3.1V. The sigmoidal shape of the curve is typical for layered transition metal oxide cathodes, such as NMC, and indicates a two-phase reaction during charge and discharge (Tariq et al., 2021). According to Abraham et al. (2021), the plateau at 3.1 V may represent the main lithium intercalation/deintercalation process in the NMC cathode. The peak voltage of 3.1 V is much lower that the theoretical value of 4.2 V, which could be due to limitations in the materials or experimental setup, such as impurities or non-optimal electrolyte composition. The lower voltage plateau during discharge suggests that the battery undergoes a different mechanism during discharge, which may be due to the structural changes in the cathode material or side reactions.

Figure 4(a)(b) demonstrates the change in charge and discharge capacity (μAh) through the 50 cycles from SS and Al_2O_3 substrates, respectively. The capacity shows an initial drop after the first few cycles, followed by a gradual decrease in capacity over 50 cycles. The initial capacity is 2.2 μAh for SS and 6μAh for Al_2O_3, and after 50 cycles, the capacity drops to 1μAh. The initial drop in capacity may be attributed to the formation of a solid electrolyte interphase (SEI) layer on the electrode surfaces or irreversible side reactions that consume lithium (Phillip et al., 2019). The severe capacity fade over 50 cycles suggests that the battery experienced some degradation, such as structural changes in the cathode, electrolyte decomposition, or loss of active lithium. A capacity retention of 16% after 100 cycles is considered poor and indicates that the battery's performance is far from optimal for practical applications. Comparing the cycling performance to other studies on NMC cathodes, it is evident that the capacity retention is substantially lower, which could be attributed to differences in the materials, experimental setup, or operating conditions.

The experimental capacity of the cells after 50 cycles was 1.24 μAh in average. The average cathode mass is 0.5924 mg (Table 1). By dividing capacity to mass we get specific capacity 2.09 μAh/g, which is only 1.4% of the theoretical value.

Limitations and future work: The poor cycling performance may be due to several factors, including impurities in the active materials, non-optimal electrolyte composition, manufacturing defects in the cell, and operating conditions. Future work could involve optimizing the synthesis and fabrication processes to improve the material purity and electrode quality, which may help enhance the cycling performance. The electrolyte composition and additives could also be examined and modified to improve the stability of the battery during cycling. According to (Phillip et al., 2019) additional characterization techniques, such as X-ray diffraction, scanning electron microscopy, and electrochemical impedance spectroscopy, could be employed to further investigate the observed trends and provide insights into the underlying mechanisms and degradation processes. The study of the impact of operating conditions, such as temperature and charge/discharge rates, could help identify factors contributing to the rapid capacity fade and guide the development

of strategies for improving the battery's performance (Phillip et al., 2019).

4. Summary and conclusions

In conclusion, this study focused on the voltage-capacity relationship and performance during charge-discharge cycles to analyze the electrochemical performance of an NMC-based lithium ion battery. The voltage versus capacity plot demonstrated a typical sigmoidal curve, with an observed peak voltage of 3.1 V, which was lower than the theoretical value of 4.2 V. The capacity versus cycle number plot revealed a dramatic decline in capacity, with a poor retention of only 16% after 50 cycles.

The revealed electrochemical behavior shows that the battery is significantly degrading during cycling. This is likely due to a combination of factors, including structural changes in the cathode, electrolyte decomposition, loss of active lithium, and continuous development of the SEI layer on the electrode surfaces. In comparison with the literature materials, the specific capacity is substantially less than expected, showing that there is a potential for further improvement in the battery's performance.

Further work should focus on optimizing the synthesis and production processes to enhance the material purity and electrode quality. Investigating the electrolyte composition, additives, and the effects of operating conditions like temperature and charge-discharge rates, could help to determine factors contributing to the rapid capacity decline and suggest ways of improving battery performance. Moreover, using advanced characterization methods can offer valuable information about the fundamental mechanisms and degradation processes.

Though the experimental results did not meet the expected performance criteria, this study proved to be a great possibility for learning. The process of identifying possible issues and understanding the fundamental mechanisms behind the battery's degradation has provided valuable insights and contributed significantly to my overall knowledge and experience in the field of battery research.

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Appendix A. First cycle

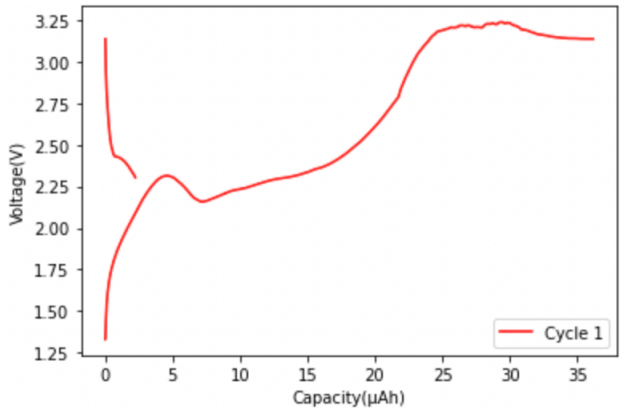

Figure A.1: Voltage versus charge-discharge capacity for the first cycle for SS

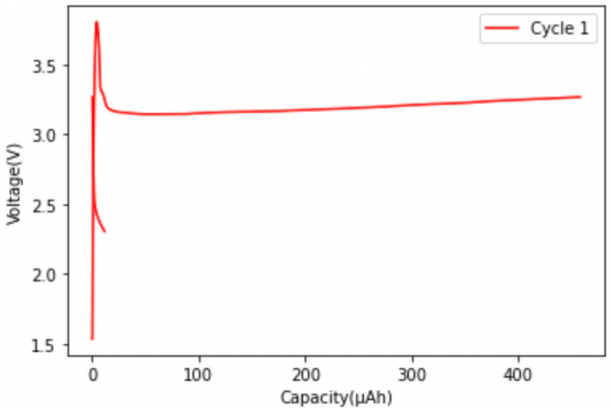

Figure A.2: Voltage versus charge-discharge capacity for the first cycle for Al_2O_3 substrate