



Article Effects of Coating on the Electrochemical Performance of a Nickel-Rich Cathode Active Material

Eman Hassan ^{1,2}, Mahdi Amiriyan ², Dominic Frisone ¹, Joshua Dunham ^{1,2}, Rashid Farahati ^{2,*} and Siamak Farhad ^{1,*}

- ¹ Advanced Energy and Manufacturing Laboratory, Department of Mechanical Engineering, University of Akron, Akron, OH 44325, USA; eh40@uakron.edu (E.H.); df99@uakron.edu (D.F.); dunhajsh@schaeffler.com (J.D.)
- ² Schaeffler Group, Wooster, OH 44691, USA; amirimhd@schaeffler.com
- * Correspondence: farahrsh@schaeffler.com (R.F.); sfarhad@uakron.edu (S.F.)

Abstract: Due to their safety and high power density, one of the most promising types of all-solid-state lithium batteries is the one made with the argyrodite solid electrolyte (ASE). Although substantial efforts have been made toward the commercialization of this battery, it is still challenged by some technical issues. One of these issues is to prevent the side reactions at the interface of the ASE and the cathode active material (CAM). A solution to address this issue is to coat the CAM particles with a material that is compatible with both ASE and CAM. Prior studies show that the lithium niobate, LiNbO₃, (LNO) is a promising material for coating CAM particles to reduce the interfacial side reactions. However, no systematic study is available in the literature to show the effect of coating LNO on CAM performance. This paper aims to quantify the effect of LNO coating on the electrochemical performance of a nickel-rich CAM. The electrochemical performance parameters that are studied are the capacity, cycling performance, and rate performance of the coated-CAM; and the effectiveness of the coating to prevent the side reactions at the ASE and CAM interface is out of the scope of this study. To eliminate the effect of side reactions at the ASE and CAM interface, we conduct all tests in the organic liquid electrolyte (OLE) cells to solely present the effect of coating on the CAM performance. For this purpose, 0.5 wt.% and 1 wt.% LNO are used to coat the LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC-60) CAM through two synthesizing methods. Consequently, the effects of the synthesizing method and the coating weight percentage on the NMC-60 performance are presented.

Keywords: coating; wet process; nickel-rich NMC; lithium niobate; electrochemical performance

1. Introduction

In traditional commercial lithium-ion batteries (LIBs), the use of liquid electrolytes containing flammable organic solvents creates potential safety issues [1]. All-solid-state lithium batteries (ASSLB), on the other hand, utilize intrinsically safe solid-state electrolytes [2,3]. Hence, they are considered safe next-generation battery systems, especially for applications in electric vehicles (EVs). There are several types of ASSLBs, depending on the type of solidstate electrolyte used to make the battery. Among all types of solid-state electrolytes, the argyrodite electrolyte (ASE), for example, Li₆PS₅Cl_{0.5}Br_{0.5} (LPSCB), is considered one of the most promising electrolytes due to its high ionic conductivity and special mechanical properties [4]. The high ionic conductivity makes this solid electrolyte suitable for applications where high power density is required, for example, in hybrid electric vehicles (HEVs).

Significant efforts have been devoted toward the development of ASE-type ASSLBs by researchers. However, some technical issues still need to be addressed before the commercialization of these batteries. Some of these issues are (1) the interfacial resistance between the ASE and the cathode active material (CAM) in the cathode that causes an increase in the cathode ohmic resistance, consequently, the battery capacity decreases and the heat generation in the battery increases, (2) the side-reactions at the interface of



Citation: Hassan, E.; Amiriyan, M.; Frisone, D.; Dunham, J.; Farahati, R.; Farhad, S. Effects of Coating on the Electrochemical Performance of a Nickel-Rich Cathode Active Material. *Energies* **2022**, *15*, 4886. https:// doi.org/10.3390/en15134886

Academic Editor: Cai Shen

Received: 8 June 2022 Accepted: 28 June 2022 Published: 3 July 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the ASE and CAM that causes fast battery degradation, and (3) the scalability for largescale manufacturing [4,5]. As proposed by Divakaran et al. [6] and other researchers, one practical method to suppress side reactions at the interface of the ASE, such as LPSCB, and CAM, such as lithium nickel manganese cobalt oxide (NMC) or lithium nickel cobalt aluminum oxide (NCA), is to coat them with a material that is not only ionically conductive and acts as a second electrolyte, but also it is compatible with ASE, CAM, conductive material, and cathode current collector [6,7]. The interface between the coating material and each of these materials is schematically shown in Figure 1.



Figure 1. Interface of the coating material with other components of the cathode. The red particles are argyrodite electrolyte, the blue particles are the cathode active material, the black particles are the electron conductive materials, the gray layer is the cathode current collector, and the green layers are the coating (Reprinted/adapted with permission from Ref. [7]. Copyright year: 2022, copyright owner's name: Eman Hassan).

Several coating materials and procedures have been developed by researchers to suppress the interfacial side reactions between the electrolyte and electrode active materials. However, the addition of a surface coating layer can negatively impact ionic conductivity and decrease the cathode capacity and the rate performance [8]. Accordingly, researchers have reported compounds containing lithium as viable candidates for the coating of nickel-rich metal oxides because of their low impedance, increased ionic conductivity, and increased chemical stability [9,10]. Some compounds that have shown promise in resolving these issues are Li₂ZrO₃, LiAlO₂, Li₂TiO₃, and LiNbO₃ [11–14]. Lithium niobate, LiNbO₃, (LNO) has been suggested as a suitable coating material in several studies [3,14,15]. Due to its low detriment to conductivity [16,17], LNO has recently proven to be a viable transition metal oxide contender for coating as it increases Li⁺ mobility at the cathode surface. Additionally, due to its high thermal stability, LNO allows for operation at high temperatures for long periods of time without negative levels of dissolution. Despite the above-mentioned benefits, the effects of coating this material, along with its synthesis methods and coating thicknesses, on the performance of CAM still need to be systematically investigated.

Various methods can be employed to deposit coatings on the surface of cathode active material particles. Examples of methods that have been utilized by researchers for this purpose are dry coating, atomic layer deposition (ALD), and wet mixing [18–21]. Among these processes to coat NMC with LNO, the application of a relatively simple wet process followed by heat treatment has shown merits, while ALD is also promising. The procedure for this method is simple enough that issues of scalability for mass manufacturing can be resolved. The initial step of the wet process method involves the dissolution of LNO precursors in a solvent. Mereacre et al. [22] have shown that along with this solvent the addition of hydrogen peroxide might improve the LNO coating through surface activation [22]. Li et al. [20] investigated the effect of LNO coating on nickel-rich NMC using a wet mixing method followed by heat treatment. Their study into NMC structure and particle morphology showed that LNO-coated NMC was very stable and presented a uniform coating on NMC particles. By evaluating the effects of LNO coating on the chemical, structural, and thermal stability of nickel-rich NMC, it was proven that LNO coating can improve the electrochemical performance of the cathode, especially at elevated temperatures [20]. Furthermore, there is much flexibility regarding heat treatment of the coated NMC. As shown by Kim et al. [21], the development of the LNO surface coating is contingent upon the sintering temperature. Kim et al. [21] sought several benefits from coating NMC with LNO, which were namely chemical, structural, and thermal stability. For their study, when LNO coating was heated at 450 °C, it was amorphously present on the surface of NMC. However, it showed crystallinity when heated at 800 °C. They found that desirable properties were provided by both the crystalline and amorphous structures. However, these valuable properties were found to a larger degree in the crystalline coating than in the amorphous coating [21].

There is not any systematic study in the literature to show the effect of coating LNO material on the CAM performance. This paper aims to quantify the effect of LNO coating on the electrochemical performance of the nickel-rich LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC-60) cathode active material. The electrochemical performance parameters that are studied are the capacity, cycling performance, and rate performance of the LNO-coated NMC-60. It is noted that the study on the effectiveness of the coating to prevent side reactions at the ASE and CAM interface is out of the scope of this paper. To eliminate the effect of the ASE and CAM side reactions, we conduct all tests in the organic liquid electrolyte (OLE) environment to solely study the effect of coating on the NMC-60 material performance. It is also noted that the reason for coating the CAM is to use them in the ASE-type ASSLBs, rather than increasing the CAM performance to use it in conventional OLE-type LIBs. The only reason that we choose testing cells in the OLE environment is to separate the effect of side reactions at the interface of the ASE and CAM from the effect of the LNO coating layer on the NMC-60 material performance. For this purpose, we (a) compare two methods of synthesizing and coating LNO on nickel-rich NMC-60 cathode active material, and (b) evaluate the effects of coating thickness on the capacity, cycling performance, and rate performance of the coated-NMC-60. This study not only helps to fabricate high-performance solidstate lithium batteries, but it also aids several other studies such as modeling solid-state lithium batteries for investigation of cell operating voltage and capacity [23], microstructure heterogeneity [24], battery energy efficiency [25], and designing an appropriate cooling system for the battery [26].

2. Materials and Methods

To synthesize the LNO coating, the following chemical reaction was utilized.

 $1 \text{ CH}_3\text{CH}_2\text{OLi} + 1 \text{ Nb}(\text{CH}_3\text{CH}_2\text{O})_5 + 3\text{H}_2\text{O} \rightarrow 1 \text{ LiNbO}_3 + 6 \text{ CH}_3\text{CH}_2\text{OH}$

The synthesizing and coating methods of LNO that we used in this study are briefly explained below.

Method-I: For coating NMC-60 using Method-I, appropriate amounts of lithium ethoxide (CH₃CH₂OLi, 95%, Sigma-Aldrich, St. Louis, MO, USA) and niobium ethoxide

 $(Nb(CH_3CH_2O)_5, 99\%)$, Sigma-Aldrich) are dissolved in dry isopropanol (99%, Sigma-Aldrich) and continuously stirred at room temperature for 10 min. Then, NMC-60 is added to the solution and mixed at 80 °C until evaporation.

Method-II: In this method, lithium ethoxide (CH₃CH₂OLi, 95%, Sigma-Aldrich) and niobium ethoxide (Nb(CH₃CH₂O)₅, 99%, Sigma-Aldrich) are mixed in dry ethanol (99%, Sigma-Aldrich) and hydrogen peroxide (H₂O₂, 30%, Sigma-Aldrich). After dissolution of precursors under stirring for 10 min, NMC-60 is added to the solution and mixed at 100 °C until evaporation.

For both methods, the resulting dried powders are placed in zirconia combustion boats (AdValue Technology) and sealed in a quartz tube furnace (GSL-1100X, MTI Corporation). Powders are then annealed under flowing O₂ atmosphere at 450 °C for 1 h with a ramp of 5 °C/min. The coated powders are collected, ground, and kept overnight at 100 °C in a vacuum oven before making electrodes.

3. Coating Formulations

The entire mass of coating material does not participate in forming a solid and dense coating layer on the surface of CAM particles and remains as loosely connected LNO to CAM particles or agglomerated LNO as impurities in the obtained coated-CAM. Hence, we define the coating efficiency as the ratio of the mass of the dense coating layer to the total mass of the coating material as stated in Equation (1).

$$\eta_{coating} = \frac{m_{DCL}}{m_{CAM}} \tag{1}$$

where, $\eta_{coating}$ is the coating efficiency and *m* is the mass. The subscripts of *DCL* and *CAM* denote the dense coating layer and cathode active material, respectively. For one of the samples of 1 wt.% of LNO coating on NMC-60, we did the transmission electron microscopy (TEM) characterization at Argonne National Laboratory, Center for Nanoscale Materials (CNM). Based on the TEM image in Figure 2, the thickness of the dense coating layer on the NMC-60 is about 14 nm, while the 1 wt.% LNO is enough to make a 21 nm coating layer. Therefore, about two-thirds of the theoretical LNO thickness is formed as a dense coating layer. The other one-third of LNO material remains as loosely connected to NMC-60, or agglomerated LNO as impurities in the obtained coated-NMC-60. If required, the loosely connected LNO and the LNO impurities may be removed by rinsing the coated-NMC after the coating process is done. Therefore, we assume a coating efficiency of 66% for the calculation of the LNO coating layer thickness, which may be only valid for our lab with its available equipment and technology. It is also noted that the thickness of the LNO coating on the NMC-60 may not be uniform. This may affect the value of the coating efficiency.

The mass fraction ratio (MFR) of the coating material (LNO in this study) and the uncoated active material (NMC-60 in this study) is defined in Equation (2).

$$MFR = \frac{MF_{CM}}{MF_{CAM}} = \frac{m_{CM}/m_{tot}}{m_{CAM}/m_{tot}} = \frac{m_{CM}}{m_{CAM}} = \frac{1}{\eta_{coating}} \times \frac{m_{DCL}}{m_{CAM}} = \frac{1}{\eta_{coating}} \times \frac{\sum \rho_{CM} N_{p,i} V_{DCL,i}}{\sum \rho_{CAM} N_{p,i} V_{am,i}}$$
$$= \frac{1}{\eta_{coating}} \times \frac{\rho_{CM}}{\rho_{CAM}} \times \frac{\sum N_{p,i} \pi D_{CAM,i}^2}{\sum N_{p,i} \frac{\pi}{D} D_{CAM,i}^2}$$
$$= \frac{1}{\eta_{coating}} \times \left(6 \frac{\rho_{CM}}{\rho_{CAM}} \times \frac{\sum N_{p,i} D_{CAM,i}^2}{\sum N_{p,i} D_{CAM,i}^2} \right) \delta_{DCL}$$
$$= \frac{1}{\eta_{coating}} \times \left(6 \frac{\rho_{CM}}{\rho_{CAM}} \times \frac{D_{s,CAM}^2}{D_{s,CAM}} \right) \delta_{DCL}$$
(2)

where, *MF* is the mass fraction, ρ is the density, N_p is the number of CAM particles, *V* is the volume, and δ_{DCL} is the dense coating thickness on the active material. The subscripts of *s* and *v* denote the diameter of uncoated CAM, the surface mean diameter of particles, and the volume mean diameter of particles, respectively. The density of the LNO and NMC are approximately 4.65 g/cm³ and 4.76 g/cm³, respectively.



Figure 2. TEM image of the LNO coated NMC-60 showing a dense coating layer with a thickness of 14 nm has been formed, which is two-thirds of the theoretical thickness of 21 nm for a 1 wt.% of LNO coating on NMC-60 (work performed at the Center for Nanoscale Materials at Argonne National Laboratory).

To calculate the *MFR*, we need to determine the surface mean and volume mean diameters of uncoated CAM particles. For this purpose, the morphology of the NMC-60 was determined using Tescan Lyra 3 XMU scanning electron microscopy (SEM) at an operating voltage of 15 kV with an EDAX Element energy-dispersive X-ray spectroscopy (EDX) detector. The SEM image of the uncoated NMC-60 is taken as shown in Figure 3a. As seen, the shape of particles is close to a sphere. Thus, to obtain the sizes of particles, we assumed that the particles are spherical, and using the *ImageJ* software, we measured the diameter of more than 300 particles of NMC-60. Then, the measured particles are divided into several intervals and the histogram of the particle size distribution is plotted. Based on the obtained histogram, it was determined that a log-normal distribution is the best fit to the size distribution of NMC-60 particles, as shown in Figure 3b.





$$D_{s} = \left(\frac{\sum N_{p_{i}} D_{i}^{2}}{N_{p}}\right)^{1/2} = \frac{D_{50}}{exp\left(-\left(ln\left(\frac{D_{84.13}}{D_{50}}\right)\right)^{2}\right)}$$
(3)

$$D_{v} = \left(\frac{\sum N_{p_{i}} D_{i}^{3}}{N_{p}}\right)^{1/3} = \frac{D_{50}}{\left[exp\left(-\left(ln\left(\frac{D_{84.13}}{D_{50}}\right)\right)^{2}\right)\right]^{1.5}}$$
(4)

where, D_s is the surface mean diameter, D_v is the volume mean diameter, D_{50} is the median diameter, and $D_{84.15}$ is the diameter that 84.15% of particles are smaller than. The D_{50} and $D_{84.15}$ are determined by analyzing SEM images of NMC-60 particles using *ImageJ* software. For NMC-60, we obtained D_{50} and $D_{84.15}$ are 10.9 µm and 13.7 µm, respectively. Finally, we calculated that the D_s and D_v are 11.5 µm, and 11.8 µm, respectively.

For preparation of the LNO coated NMC-60 with the desired coating thickness, whether using Method-I or Method-II, the mass fraction of initial materials for CH_3CH_2OLi , Nb(CH_3CH_2O)₅, and uncoated NMC-60 are obtained from Equations (5)–(7).

$$MF_{\rm CH_3CH_2OLi} = \frac{MW_{\rm CH_3CH_2OLi}}{MW_{\rm LNO}} \times \left(1 + \frac{1}{MFR}\right)^{-1}$$
(5)

$$MF_{\rm Nb(CH_3CH_2O)_5} = \frac{MW_{\rm Nb(CH_3CH_2O)_5}}{MW_{\rm LNO}} \times \left(1 + \frac{1}{MFR}\right)^{-1}$$
(6)

$$MF_{\rm NMC_60} = \frac{1}{1 + MFR} \tag{7}$$

The molecular weights of CH₃CH₂Oli, Nb(CH₃CH₂O)₅, and LNO are 52.0 g/mol, 318.21 g/mol, and 147.85 g/mol, respectively.

4. Electrode and Cell Fabrication and Testing

Several OLE-type half-cell cathodes with mass loading of ~7 mg/cm² were made to evaluate and compare the performance of the coated and uncoated NMC-60. The cathodes were made from four types of coated NMC-60: 0.5% LNO coated NMC-60 using Method-I (Method-I-0.5%), 1% LNO coated NMC-60 using Method-I (Method-I-1%), 0.5% LNO coated NMC-60 using Method-II (Method-II-1%), 0.5% LNO coated NMC-60 using Method-II (Method-II-1%). First, a 6 wt.% PVDF (Sigma-Aldrich) solution is made by dissolution in NMP (99.5%, Sigma-Aldrich) and allowed to mix. A cathode slurry comprising of 90 wt.% active material, 5 wt.% conductive material and 5 wt.% binder was then made. The appropriate amounts of acetylene black (MTI corporation) and the PVDF solution were mixed in a planetary centrifugal mixer. One-third of the coated active material is then mixed with the acetylene black and PVDF solution. This step is repeated until the total amount of active material has been added and mixed. Then, several coin type half cells were fabricated using the OLE (LiPF₆), coated NMC-60 as the cathode, and the lithium metal as anode (reference electrode) with a separator in between.

Before testing the half-cells, a formation process was completed. For the rate performance test, we cycled the cathode half-cells at c-rates of C/10, C/5, C/3, 1C, 2C, and C/10, with five cycles at each C-rate (CC C/25 CV Charge; Discharge: No CV mode). The C-rate is defined as the rate at which a cell completely discharges its maximum capacity. To test half-cells using NMC-60 as cathode, a theoretical maximum capacity of 178 mAhg⁻¹ is assumed.

5. Results and Discussion

5.1. Coating Formation

The mass fractions of initial materials for coating NMC-60 were calculated from the desired coating thickness and shown in Figure 4. The red and orange lines in this figure represent the mass fractions of lithium ethoxide and niobium ethoxide in the synthesizing process, respectively. The green line indicates the mass fraction of the total LNO coating material synthesized, while the blue line indicates the mass fraction of LNO participated to form the dense coating layer on NMC-60 particles. The LNO that has not participated in formation of the dense coating layer remains as loosely connected LNO to NMC-60 particles, or agglomerated LNO as impurities in the obtained coated- NMC-60, as demonstrated in red circles in Figure 5.







Figure 5. Materials in red circles seem to be the agglomerated LNO with sizes < 1 µm produced during synthesizing, but has not participated in coating layer formation on the NMC-60 particles.

The SEM images was used to evaluate the morphology of LNO coating on NMC-60 using Method-I and Method-II. A comparison of changes in morphology between uncoated NMC-60, Method-I-1%, and Method-II-1% can be seen through the SEM images in Figure 6a–c, respectively. As shown in Figure 6a, the uncoated NMC-60 appears to have particles that are mostly spherical with some irregular edges. On the other hand, images of the coated NMC-60 show, in appearance, a white material sitting on the surface of particles. This is most clearly seen on the large particles of Method-I coated NMC-60 in Figure 6b. Method-I also showed agglomeration of secondary particles, which is not present in uncoated NMC-60 nor Method-II-1%. It is essential to note how the primary and secondary particles become less defined for the coated powders when compared to uncoated NMC-60. For instance, in the Method-II coating, the white material appearing in the images of the coated NMC-60 takes on a feathery appearance, which covers the entirety of some NMC particles. An enlarged image of a particle which exhibits this phenomenon is inset in Figure 6c. Figure 7 shows the corresponding EDX analysis for SEM imaging of the coated particles. Formation of LNO coating on NMC-60 particles is indicated through the presence of niobium elemental peaks for Method-I and Method-II, respectively.



Figure 6. SEM imaging of (**a**) uncoated NMC-60, (**b**) Method-I-1%, and (**c**) Method-II-1% with inset exhibiting LNO as soft or feathery surface material in appearance.



Figure 7. EDX analysis of 1% LNO coating using (a) Method-I and (b) Method-II.

The powder XRD measurements were taken using Rietveld analysis to compare the effect of LNO coating on NMC-60. Patterns of uncoated and 1% LNO coated NMC-60 using Method-I and Method-II are shown in Figure 8a–c. The XRD patterns of the three materials can be indexed to a hexagonal α -NaFeO₂ structure [20]. Moreover, there are no extra peaks on the coated NMC-60 materials indicating that no structural changes occurred as a result of the LNO coating or annealing procedure. It is noted that the LNO peaks are not visible in the XRD patterns due to the very small composition in the overall material being analyzed.



Figure 8. XRD analysis of (**a**) uncoated NMC-60, (**b**) 1% LNO coated NMC-60 using Method-I, and (**c**) 1% LNO coated NMC-60 using Method-II.

5.2. Electrochemical Performance

Electrochemical performance study of uncoated NMC-60, coated using Method-I, and coated using Method-II, with 0.5 wt.% and 1 wt.% LNO content for both methods, was performed in the voltage range of 2.7 V to 4.3 V using coin half-cells. Two tests were performed. The cycling performance was the first test which was used to evaluate the stability and capacity retention of the cathode half-cells over time. The CAM capacity was also determined during this test. The rate performance was the second test used to evaluate the power performance under different current loadings.

5.2.1. Cycling Performance Test

Cycling performance was performed at a charge and discharge rate of C/3 for 50 cycles. The results of this performance for uncoated NMC-60, Method-I, and Method-II with 0.5% and 1% for both methods are shown in Figure 9. Each point in this graph was found through charge and discharge voltage versus capacity curves. These curves showed almost the same trend between uncoated and coated NMC-60 with only changes in values of the capacity. Half-cells made using uncoated NMC-60 show an initial capacity of \sim 164.0 mAhg⁻¹ and a capacity retention of 98.0%. Method-I-1% showed comparative values with an initial capacity of 166.4 mAhg $^{-1}$ and a capacity retention of 97.0%. In comparison, Method-I-0.5% has a higher initial capacity of ~167.0 mAhg⁻¹ with a much higher capacity retention of ~99.9%. This capacity retention is higher than the uncoated NMC-60, may be due to the protective coating layer formed around the NMC-60 particles. On the other hand, Method-II-1% showed an initial capacity of \sim 155.1 mAhg⁻¹, which is much lower than that of the uncoated NMC-60 or Method-I-1%. However, the capacity retentions of uncoated NMC-60 (98.0%) and Method-II-1% (97.7%) were very similar. Method-II-0.5% has an initial capacity of 171.0 mAhg⁻¹ which is higher than all other initial capacities. Contrastingly, while Method-II-0.5% has higher initial capacity, capacity retention is much greater for Method-I-0.5% with a value of ~99.9% versus 97.0% for Method-II-0.5%. It is apparent that Method-I-0.5% has very good stability with almost no capacity fade after 50 cycles. Furthermore, with special regard to capacity fade, Method-I-0.5% shows a clear improvement in electrochemical performance of NMC-60 with organic liquid electrolytes. This improvement should be checked with the argyrodite electrolyte as well, which is the out of the scope of this paper.



Figure 9. Cycling performance of the uncoated NMC-60 and 0.5 wt.% and 1 wt.% LNO coating NMC-60 using Method-I and Method-II.

We define the capacity retention ratio (CRR) as the ratio of the capacity retention of the coated-CAM to the capacity retention of the uncoated-CAM. The CRR of the coated-NMC-60 with methods I and II is shown in Figure 10. In this figure, the CRR of the uncoated NMC-60 has been represented by the LNO wt.% of 0, which is obviously equal to 1. The Method-I-0.5% exhibits CRR \approx 1.026 after 50 cycles, which is higher than other coated samples. The CRR of Method-I-1% and Method-II-0.5% are less than that of the uncoated-NMC-60, while Method-II-1% shows almost the same CRR compared to the uncoated-NMC-60.



Figure 10. Capacity retention ratio of the coated-NMC-60 for (a) Method-I, and (b) Method-II.

5.2.2. Rate Performance Test

Results of the rate performance test to compare the uncoated NMC-60 with the coated NMC-60 with Method-I and Method-II 0.5 wt.% and 1 wt.% LNO are shown in Figure 11. Tests were run in the same cut-off voltage range of 2.7 V to 4.3 V. Different C-rates of C/10, C/5, C/3, C/2, C, and 2C followed by a return to C/10 were each tested for 5 cycles. Regarding initial capacity, Method-I-1% has higher values than the uncoated NMC-60 and Method-I-0.5%. Method-I-1% also exhibits these higher capacities for all c-rates. Method-II-0.5% has higher capacity than all other samples for all c-rates. Conversely, Method-II-1% has lower capacities than uncoated NMC-60 for c-rates below 2C. Although Method-II-0.5% has the highest capacity overall, this sample has the lowest recuperation of capacity after returning to C/10, while Method-I-0.5% has the highest. For better comparison of rate capabilities, Table 1 features the initial capacities, capacities at 2C, and capacities after returning to C/10 for all five samples as well as their corresponding capacity retentions.

It is evident from the data that the most improvement of NMC-60 regarding rate capability is achieved through Method-II-0.5% and Method-I-1%. These two samples exhibit higher capacities and capacity retention than the uncoated NMC-60 even at high c-rates. This trend is maintained upon returning to C/10 discharge rate. It should also be noted that Method-I-0.5% performs better than the uncoated NMC-60 after returning to C/10.

We define the specific capacity ratio (SCR) as the ratio of the specific capacity of the coated-CAM to the specific capacity of the uncoated-CAM. The SCR of the coated-NMC-60 with methods I and II is shown in Figure 12. In this figure, the SCR of the uncoated NMC-60 has been represented by the LNO wt.% of 0, which is obviously equal to 1. The comparison is presented for low versus high c-rates. It is evident from Figure 12a that the 1 wt.% LNO for Method-I can keep the specific capacity of the coated-NMC-60 about 1 to 2 percent more than the specific capacity of the uncoated-NMC-60 at both low and high C-rates of C/10 and 2C. On the other hand, Figure 12b shows that the 0.5 wt.% LNO for Method-II can keep the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacity of the coated-NMC-60 about 6 percent more than the specific capacit



capacity of the uncoated-NMC-60 at both low and high C-rates of C/10 and 2C. Further investigations into the effects of various LNO wt.% are necessary to conclude a precise wt.% of LNO for each method.

Figure 11. Rate performance of the uncoated NMC-60 and 0.5 wt.% and 1 wt.% LNO coating NMC-60 using Method-I and Method-II.

Table 1. Comparison of rate performance at low and high C-rates.

	Initial Capacity (mAhg ⁻¹)	Capacity at 2C (mAhg ⁻¹)	Capacity Retention at 2C (%)	Capacity upon Return to C/10 (mAhg ⁻¹)	Capacity Retention at C/10 (%)
Uncoated NMC-60	167.6	146.1	87.2	172.6	103.1
Method-I-0.5%	167.3	140.0	83.7	175.6	105.0
Method-I-1%	168.9	148.7	88.0	174.1	103.1
Method-II-0.5%	176.9	154.8	87.5	178.8	101.1
Method-II-1%	159.1	135.4	85.1	163.2	102.6



Figure 12. Specific capacity ratio of the coated-NMC-60 for (**a**) Method-I, and (**b**) Method-II for low or high c-rates of C/10 and 2C.

6. Conclusions

This paper aimed to quantify the effect of LNO coating on the electrochemical performance of the nickel-rich NMC-60 cathode active material. The electrochemical performance parameters of the initial capacity, cycling performance, and rate performance were studied. To eliminate the effect of side reactions at the interface of the argyrodite solid electrolyte and NMC-60, we conduct all tests using organic liquid electrolyte cells to solely study the effect of coating on the NMC-60 electrochemical performance. We presented a model and formulation to control the coating thickness on the electrode active material particles. Based on these formulations and by using two synthesizing and coating methods, several coated-NMC-60 with 0.5 wt.% and 1 wt.% LNO were prepared. The effects of LNO on the morphology and electrochemical performance of the coated-NMC-60 were investigated. Using the TEM and SEM images and EDS analysis the presence of LNO coating on the surface of the NMC-60 was determined. Further characterization using XRD showed that the coating methods did not change the structure of NMC-60. The electrochemical performance analysis results indicated that the capacity, cycling performance, and the rate performance of the LNO coated-NMC60 are sensitive to the LNO coating thickness (or wt.%) and the synthesizing and coating method. It was found that the initial capacity and rate performance of the 0.5 wt.% LNO-coated-NMC-60 using Method II are noticeably higher than those of the uncoated-NMC-60. The initial capacity and rate performance of the 1 wt.% LNOcoated-NMC-60 using Method I are only slightly higher than the uncoated-NMC-60. The initial capacity and rate performance of the 0.5 wt.% LNO-coated-NMC-60 using Method I and 1 wt.% LNO-coated-NMC-60 using Method II are lower than the uncoated-NMC-60. Although the 0.5 wt.% LNO-coated-NMC-60 using Method II is promising, a more detailed study is required to determine the optimum LNO wt.% and the best synthesizing and coating methods. Although this study provided a baseline for electrochemical performance of the coated-NMC-60, further investigations are required by testing the coated-NMC-60 in solid state cells.

Author Contributions: Conceptualization, M.A. and S.F.; Data curation, E.H., M.A. and D.F.; Formal analysis, E.H., M.A. and S.F.; Funding acquisition, R.F. and S.F.; Investigation, E.H., M.A., D.F., J.D., R.F. and S.F.; Methodology, M.A. and S.F.; Project administration, M.A.; Resources, R.F.; Supervision, R.F.; Visualization, J.D.; Writing—original draft, E.H.; Writing—review & editing, M.A., R.F. and S.F. All authors have read and agreed to the published version of the manuscript.

Funding: The funding was provided internally by the Schaeffler Company and the University of Akron.

Informed Consent Statement: Not applicable.

Acknowledgments: The support of the Schaeffler Company and The University of Akron is highly appreciated. Work performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, was supported by the U.S. DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Goodenough, J.B.; Kim, Y. Challenges for Rechargeable Li Batteries. Chemistry of Materials. Am. Chem. Soc. 2010, 22, 587–603. [CrossRef]
- Hao, F.; Han, F.; Liang, Y.; Wang, C.; Yao, Y. Architectural Design and Fabrication Approaches for Solid-State Batteries. *MRS Bull.* 2018, 43, 775–781. [CrossRef]
- 3. Zubair, M.; Li, G.; Wang, B.; Wang, L.; Yu, H. Electrochemical Kinetics and Cycle Stability Improvement with Nb Doping for Lithium-Rich Layered Oxides. *ACS Appl. Energy Mater.* **2018**, *2*, 503–512. [CrossRef]
- 4. Zhu, X.; Wang, K.; Xu, Y.; Zhang, G.; Li, S.; Li, C.; Zhang, X.; Sun, X.; Ge, X.; Ma, Y. Strategies to Boost Ionic Conductivity and Interface Compatibility of Inorganic—Organic Solid Composite Electrolytes. *Energy Storage Mater.* **2021**, *36*, 291–308. [CrossRef]
- 5. Divakaran, A.M.; Hamilton, D.; Manjunatha, K.N.; Minakshi, M. Design, Development and Thermal Analysis of Reusable Li-Ion Battery Module for Future Mobile and Stationary Applications. *Energies* **2020**, *13*, 1477. [CrossRef]
- 6. Divakaran, A.M.; Minakshi, M.; Bahri, P.A.; Paul, S.; Kumari, P.; Divakaran, A.M.; Manjunatha, K.N. Rational Design on Materials for Developing next Generation Lithium-Ion Secondary Battery. *Prog. Solid State Chem.* **2021**, *62*, 100298. [CrossRef]
- Xiao, Y.; Wang, Y.; Bo, S.H.; Kim, J.C.; Miara, L.J.; Ceder, G. Understanding Interface Stability in Solid-State Batteries. *Nat. Rev. Mater.* 2020, 5, 105–126. [CrossRef]
- 8. Shi, J.L.; Qi, R.; Zhang, X.D.; Wang, P.F.; Fu, W.G.; Yin, Y.X.; Xu, J.; Wan, L.J.; Guo, Y.G. High-Thermal- and Air-Stability Cathode Material with Concentration-Gradient Buffer for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 42829–42835. [CrossRef]
- Ryu, W.G.; Shin, H.S.; Park, M.S.; Kim, H.; Jung, K.N.; Lee, J.W. Mitigating Storage-Induced Degradation of Ni-Rich LiNi_{0.8} Co_{0.1}Mn_{0.1}O₂ Cathode Material by Surface Tuning with Phosphate. *Ceram. Int.* 2019, 45, 13942–13950. [CrossRef]
- Cho, D.H.; Jo, C.H.; Cho, W.; Kim, Y.J.; Yashiro, H.; Sun, Y.K.; Myung, S.T. Effect of Residual Lithium Compounds on Layer Ni-Rich Li[Ni_{0.7} Mn_{0.3}]O₂. J. Electrochem. Soc. 2014, 161, A920–A926. [CrossRef]
- Meng, K.; Wang, Z.; Guo, H.; Li, X.; Wang, D. Improving the Cycling Performance of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ by Surface Coating with Li₂TiO₃. *Electrochim. Acta* 2016, 211, 822–831. [CrossRef]
- 12. Song, B.; Li, W.; Oh, S.M.; Manthiram, A. Long-Life Nickel-Rich Layered Oxide Cathodes with a Uniform Li₂ZrO₃ Surface Coating for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 9718–9725. [CrossRef] [PubMed]
- Srur-Lavi, O.; Miikkulainen, V.; Markovsky, B.; Grinblat, J.; Talianker, M.; Fleger, Y.; Cohen-Taguri, G.; Mor, A.; Tal-Yosef, Y.; Aurbach, D. Studies of the Electrochemical Behavior of LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ Electrodes Coated with LiAlO₂. *J. Electrochem. Soc.* 2017, 164, A3266–A3275. [CrossRef]
- Zhang, Z.J.; Chou, S.L.; Gu, Q.F.; Liu, H.K.; Li, H.J.; Ozawa, K.; Wang, J.Z. Enhancing the High Rate Capability and Cycling Stability of LiMn₂O₄ by Coating of Solid-State Electrolyte LiNbO₃. ACS Appl. Mater. Interfaces 2014, 6, 22155–22165. [CrossRef] [PubMed]
- Xin, F.; Zhou, H.; Chen, X.; Zuba, M.; Chernova, N.; Zhou, G.; Whittingham, M.S. Li–Nb–O Coating/Substitution Enhances the Electrochemical Performance of the LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC 811) Cathode. ACS Appl. Mater. Interfaces 2019, 11, 34889–34894. [CrossRef]
- 16. Ohta, N.; Takada, K.; Sakaguchi, I.; Zhang, L.; Ma, R.; Fukuda, K.; Osada, M.; Sasaki, T. LiNbO₃-Coated LiCoO₂ as Cathode Material for All Solid-State Lithium Secondary Batteries. *Electrochem. Commun.* **2007**, *9*, 1486–1490. [CrossRef]
- 17. Gabrielli, G.; Axmann, P.; Diemant, T.; Behm, R.J.; Wohlfahrt-Mehrens, M. Combining Optimized Particle Morphology with a Niobium-Based Coating for Long Cycling-Life, High-Voltage Lithium-Ion Batteries. *ChemSusChem* **2016**, *9*, 1670–1679. [CrossRef]
- Nakamura, H.; Kawaguchi, T.; Masuyama, T.; Sakuda, A.; Saito, T.; Kuratani, K.; Ohsaki, S.; Watano, S. Dry Coating of Active Material Particles with Sulfide Solid Electrolytes for an All-Solid-State Lithium Battery. J. Power Sources 2020, 448, 227579. [CrossRef]
- 19. Li, X.; Liu, J.; Banis, M.N.; Lushington, A.; Li, R.; Cai, M.; Sun, X. Atomic Layer Deposition of Solid-State Electrolyte Coated Cathode Materials with Superior High-Voltage Cycling Behavior for Lithium Ion Battery Application. *Energy Environ. Sci.* **2014**, *7*, 768–778. [CrossRef]
- 20. Li, X.; Jin, L.; Song, D.; Zhang, H.; Shi, X.; Wang, Z.; Zhang, L.; Zhu, L. LiNbO₃-Coated LiNi_{0.8}Co0.1Mn_{0.1}O₂ Cathode with High Discharge Capacity and Rate Performance for All-Solid-State Lithium Battery. *J. Energy Chem.* **2020**, *40*, 39–45. [CrossRef]
- Kim, J.H.; Kim, H.; Choi, W.; Park, M.S. Bifunctional Surface Coating of LiNbO₃ on High-Ni Layered Cathode Materials for Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2020, 12, 35098–35104. [CrossRef] [PubMed]
- Mereacre, V.; Stüble, P.; Ghamlouche, A.; Binder, J.R. Enhancing the Stability of Lini_{0.5}Mn_{1.5}O₄ by Coating with LinbO₃ Solid-State Electrolyte: Novel Chemically Activated Coating Process versus Sol-Gel Method. *Nanomaterials* 2021, *11*, 548. [CrossRef] [PubMed]

- 23. Mastali, M.; Samadani, E.; Farhad, S.; Fraser, R.; Fowler, M. Three-Dimensional Multi-Particle Electrochemical Model of LiFePO₄ Cells Based on a Resistor Network Methodology. *Electrochim. Acta* **2016**, *190*, 574–587. [CrossRef]
- Kashkooli, A.G.; Amirfazli, A.; Farhad, S.; Lee, D.U.; Felicelli, S.; Park, H.W.; Feng, K.; De Andrade, V.; Chen, Z. Representative Volume Element Model of Lithium-Ion Battery Electrodes Based on X-Ray Nano-Tomography. J. Appl. Electrochem. 2017, 47, 281–293. [CrossRef]
- Farhad, S.; Nazari, A. Introducing the Energy Efficiency Map of Lithium-Ion Batteries. Int. J. Energy Res. 2019, 43, 931–944. [CrossRef]
- Mohammed, A.H.; Esmaeeli, R.; Aliniagerdroudbari, H.; Alhadri, M.; Hashemi, S.R.; Nadkarni, G.; Farhad, S. Dual-Purpose Cooling Plate for Thermal Management of Prismatic Lithium-Ion Batteries during Normal Operation and Thermal Runaway. *Appl. Therm. Eng.* 2019, 160, 114106. [CrossRef]
- 27. Frisone, D.; Amiriyan, M.; Hassan, E.; Dunham, J.; Farahati, R.; Farhad, S. Effect of LiNbO₃ Coating on Capacity and Cycling of Nickle-Rich NMC Cathode Active Material. In Proceedings of the International Mechanical Engineering Congress and Exposition, Virtual, Online, 4 November 2021.