Article

Understanding and Mitigating the Dissolution and Delamination Issues Encountered with High-Voltage \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \)

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Abstract: In our initial study on the high-voltage 5 V cobalt-free spinel \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) (LNMO) cathode, we discovered a severe delamination issue in the laminates when cycled at a high upper cut-off voltage (UCV) of 4.95 V, especially when a large cell format was used. This delamination problem prompted us to investigate further by studying the transition metal (TM) dissolution mechanism of cobalt-free LNMO cathodes, and as a comparison, some cobalt-containing lithium nickel manganese cobalt oxides (NMC) cathodes, as the leachates from the soaking experiment might be the culprit for the delamination. Unlike other previous reports, we are interested in the intrinsic stability of the cathode in the presence of a baseline Gen2 electrolyte consisting of 1.2 M of LiPF\(_6\) in ethylene carbonate/ethyl methyl carbonate (EC/EMC), similar to a storage condition. The electrode laminates (transition metal oxides, transition metal oxides, TMOs, coated on an Al current collector with a loading level of around 2.5 mAh/cm\(^2\)) or the TMO powders (pure commercial quality spinel LNMO, NMC, etc.) were stored in the baseline solution, and the transition metal dissolution was studied through nuclear magnetic resonance, such as \(^1\)H NMR, \(^{19}\)F NMR, scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS). Significant electrolyte decomposition was observed and could be the cause that leads to the TM dissolution of LNMO. To address this TM dissolution, additives were introduced into the baseline electrolyte, effectively alleviating the issue of TM dissolution. The results suggest that the observed delamination is caused by electrolyte decompositions that lead to etching, and additives such as lithium difluorooxalato borate and p-toluenesulfonyl isocyanate can alleviate this issue by forming a firm cathode electrolyte interface. This study provides a new perspective on cell degradation induced by electrode/electrolyte interactions under storage conditions.

Keywords: additives; delamination; transition metal dissolution; \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \); soaking

1. Introduction

The high-voltage 5 V spinel cathode \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) (LNMO) has an average working voltage of 4.6–4.7 V vs. Li, a high energy density of 650 Wh/kg at the material level, and a high rate performance with faster Li\(^+\) diffusion, and it is viewed as a promising cathode material for next-generation high-energy cobalt-free lithium-ion batteries [1–3]. However, the working voltage plateau above 4.7 V vs. Li/Li\(^+\) of LNMO exceeds the stability of the electrolyte’s operating window, and the usually observed rapid cell degradation hinders practical commercial applications [4,5]. Furthermore, cell degradation is exacerbated through other phenomena such as delamination, pitting, as well as corrosion that is a consequence of electrolyte decomposition [6].
This work mainly studies the stability of transition metal oxides (TMOs), either in powder form or as a laminate, when stored in Gen2 electrolytes. Laminate here is defined as coated products of cathode materials on top of an Al current collector, usually with a mixture of polyvinylidene fluoride (PVDF) binder and additives such as carbon black. The laminate information for each of the materials is listed in Table 1. Firstly, the delamination was observed using a special protocol (Section 3.1) designed to accelerate the degradation. Usually, due to the small size of coin cells, delamination can only be observed in larger format reference cells (area = 22.3 cm²) when cycled between 3.8 and 4.7 V (unpublished results). Significant pitting and corrosion were also observed when the cells were disassembled after aging. Secondly, in Section 3.2, the soaking experiments were designed, either in the form of electrode laminate or of the powder, using a baseline electrolyte of Gen2 electrolyte (1.2 M LiPF₆ in ethylene carbonate/ethyl methyl carbonate, EC/EMC 3/7 wt/wt). For example, LNMO electrode laminates with various compositions were first soaked in Gen2. Despite the difference in composition, such as PVDF binder sources and the carbon conductor types (as shown in Table 1 as entries 2 to 5), significant transition metal (TM) dissolutions were found regardless of the compositions (∼1898 to 4283 µg/g Mn dissolution after soaking in the Gen2). On the contrary, the LiNi₀.₅Mn₀.₂Co₀.₂O₂ (NMC532, Table 1, entry 1) electrode laminate showed much less TM dissolution (only 79 µg/g Mn dissolution after soaking in the Gen2). Herein, we ascribe the TM dissolution issue to the intrinsic reactivity between the electrode material and electrolyte. The study was further expanded to directly soaking different TMO powders into Gen2 under the same soaking conditions. The TMOs tested include spinel cathodes LNMO, LiMn₂O₄ (LMO), and layered cathodes of LiNi₀.₄Mn₀.₂Co₀.₂O₂ (NMC422), Li₁.₂Mn₀.₅₅Ni₀.₁₅Co₀.₁O₂ (LMR-NMC), and LiNi₀.₈Mn₀.₁Co₀.₁O₂ (NMC811). Characterizations of the electrolytes or electrodes were carried out via nuclear magnetic resonance (NMR), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma mass spectrometry (ICP-MS) to investigate the stability of electrolytes, the electrodes, and the interfaces. Overall, the results indicated that LNMO had the most severe TM dissolution through static electrode/electrolyte interactions compared to the other tested materials. Thirdly, in Section 3.3, using LNMO as the model cathode material, we designed electrolytes formulated with different categories of additives to test the additive’s ability to mitigate delamination both during the storage of LNMO and during cycling. The molecular structures of the additives are shown in Scheme 1, with each acronym listed here: vinylboronic anhydride pyridine complex (tVCBO), tris(trimethylsilyl) phosphite (TMSPi), lithium difluorooxalato borate (LiDFOB), prop-1-ene-1,3-sultone (PES), p-toluenesulfonyl isocyanate (PTSI), diethyl phenylphosphonite (DEPP), diphenyldimethoxysilane (DPDMS), succinic anhydride (SA), triphenylphosphate (TPP), and trimethylboroxine (TMB).

![Scheme 1. Molecular structures of the additives.](image-url)
Table 1. The electrode compositions for the soaking experiments and consequent soaking results with Gen2 stored at 45 °C for 3 months.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Active Materials (wt.%)</th>
<th>Timcal C45 (wt.%)</th>
<th>PVDF (wt.%)</th>
<th>SWCNT (wt.%)</th>
<th>Carbon Coated Al</th>
<th>Container Type</th>
<th>Color Change Observation</th>
<th>Delamination Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 NMC532</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td>Glass</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>2 LNMO</td>
<td>90</td>
<td>6</td>
<td>4 (Solvay)</td>
<td></td>
<td></td>
<td>PE</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>3 LNMO</td>
<td>90</td>
<td>6</td>
<td>4 (Solvay)</td>
<td></td>
<td></td>
<td>Glass</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4 LNMO-1</td>
<td>90</td>
<td>6</td>
<td>4 (Kynar)</td>
<td></td>
<td></td>
<td>Glass</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>5 LNMO-2</td>
<td>90</td>
<td>5.69</td>
<td>4.26 (Solvay)</td>
<td>0.05</td>
<td></td>
<td>Glass</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

2. Experimental
2.1. Electrolyte and Electrodes

Gen2 electrolyte containing 1.2 M LiPF₆ in EC/EMC (3:7 w/w ratio) and another electrolyte with a low EC (denoted as low-EC electrolyte) containing 1.0 M LiPF₆ in EC/EMC (1.9 v/v ratio) were purchased from Tomiyama Chemical Industry, Japan. Gen2 electrolyte was used for the soaking tests, while the low-EC electrolyte was used in the electrochemical tests. The additives employed in this study were all purchased from Sigma-Aldrich and were used without further purification. The electrode laminates of various LNMO and NMC532, and TMO powders, including LNMO (Targray SLM002001), LNMO (NEI Corporation Nanomyte SP-10), LMO (Targray SLM003001), LMR-NMC (Toda HE5050), NMC811 (Targray SNMC03008) and NMC442 (Toda NM-4100L), used in this study were provided by the Cell Analysis, Modeling and Prototyping (CAMP) facility in Argonne National Laboratory.

2.2. Electrochemical Measurement

The LNMO cathode was made from a mixture of 90 wt.% Targray LNMO “5 V spinel”, 4 wt.% PVDF (Solvay, 5130) and 6 wt.% conductive C45 carbon black particles (Timcal) coated on an aluminum current collector. The loading density for LNMO was 14.47 mg/cm². Li chips were used as anodes. The microporous separator Celgard 2325 was used in the coin cell assembly. All electrodes were dried at 110 °C under vacuum in an argon-filled glovebox prior to use, and coin cell parts (except the separators) were dried in an oven at 100 °C. The separators were dried at 50 °C overnight. The 2032-type coin cells were assembled in a glovebox. The diameters of the cathode, lithium metal anode, and separator were 14, 15.6, and 16 mm, respectively. The total amount of added electrolyte was 25 µL for each cell. Galvanostatic charge/discharge cycling between 3.3 and 4.95 V was conducted using MACCOR cyclers (www.maccor.com) at room temperature. The protocol comprised 3 formation cycles at a C/10 rate, followed by charging at 0.5 C and discharging at rates of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0 C, respectively.

2.3. Soaking Test

2.3.1. Electrode Soaking Test

Two discs of the laminate (LNMO, modified LNMO or NMC532, see Table 1 for detailed information) with a diameter of 14 mm were soaked in individual vials with 2 mL of Gen2 electrolyte. Glass or polythene (PE) containers were used for soaking. The samples were prepared in an Ar-filled glovebox and well-sealed in mason jars to prevent moisture and oxygen contamination. Subsequently, all the samples were stored for a duration of 3 months at 45 °C. Gen2 control samples without electrode laminates, soaked in either a glass or polyethylene (PE) container, were also performed in the study for comparison.

2.3.2. Powder Soaking Test

Instead of electrode laminates, 50 mg of TMO powders (LNMO from Targray, LNMO from NEI Corporation (www.neicorporation.com), LMO, LMR-NMC, NMC811 and NMC442, respectively) were soaked with 2 mL of Gen2 electrolyte in a glass vial under the same soaking conditions as the electrode soaking test.
2.3.3. Additive Soaking Test

For each soaking experiment involving an additive, two discs of the LNMO electrode laminate with a diameter of 14 mm were soaked in a glass vial containing 2 mL of Gen2 electrolyte, to which 3 wt.% (72 mg) of the specific additive was added and well dissolved. Other soaking conditions remained consistent with the previously conducted ones.

2.4. Characterizations of Electrode and Electrolyte

2.4.1. $^1$H and $^{19}$F Nuclear Magnetic Resonance (NMR) Spectroscopy

After soaking, the electrolyte was first filtered using a 0.22 µm pore size syringe filter to remove any potential particles. Subsequently, the filtered electrolyte was filled into a fluorinated ethylene propylene (FEP) sample tube liner, and the liner was then placed into an NMR tube containing a suitable amount of CDCl$_3$. The collected soaking electrolyte samples were then subjected to $^1$H and $^{19}$F NMR analyses. In the case of electrolytes obtained from the cycled coin cells, the cells were first disassembled in an Ar-filled glovebox, and the electrolytes were then collected by dipping the LNMO electrode and separator in 1.0 mL CDCl$_3$. The resulting solutions were subjected to $^1$H NMR analyses. NMR spectra were acquired using a Bruker Avance III HD 300 MHz spectrometer, and the chemical shifts in parts per million ($\delta$, ppm) were referenced to CDCl$_3$ at 7.26 ppm.

2.4.2. X-ray Photoelectron Spectra (XPS) Characterization

XPS measurements were conducted using a PHI 5000 VersaProbe II System (Physical Electronics, www.phi.com) under a base pressure of $2 \times 10^{-9}$ Torr. Prior to the measurements, the soaked electrodes were thoroughly washed with dimethyl carbonate. The photoelectron spectra were obtained in the fixed analyzer transmission mode using an Al Kα radiation ($h\nu = 1486.6$ eV, 100 µm beam, 25 W) with Ar$^+$ and electron beam sample neutralization. XPS spectra were aligned to the graphitic carbon at 284.5 eV.

2.4.3. Inductively Coupled Plasma-Mass Spectra (ICP-MS) Characterization

To quantify the amount of metal dissolution in each electrolyte after soaking, the soaking electrolyte was filtered using a 0.22 µm pore size syringe filter, and the measured volume of the sample liquid was transferred to a 15 mL polypropylene centrifuge tube. The sample was then allowed to evaporate to a minimum volume for three days or longer and was then added with 2 mL of 2% nitric acid (prepared from optima grade nitric acid) and mixed. Each sample was diluted to a final volume with 2% nitric acid, and then the sample was transferred to a quartz beaker and burned in a furnace at 700 °C for 12 h to remove organic constituents and carbon. The ash was then refluxed with a mixture of nitric and hydrochloric acids at 220 °C for 1 h, and the resulting solutions were diluted with water. The samples were analyzed using inductively coupled plasma–mass spectrometry to determine the concentrations of transition metals, which were referred to the weight of the anode. Measurements were made using a PerkinElmer NexION 2000 ICP Mass Spectrometer calibrated with the NIST(National Institute of Standards and Technology) traceable standards.

2.4.4. Scanning Electron Microscopy (SEM) Characterization

The LNMO electrodes, after soaking or cycling, were collected and washed with dimethyl carbonate. Afterwards, the electrode materials were peeled off with a blade to obtain the Al foils. SEM images of the Al foils were taken using a JEOL JSM-6610LV.

2.4.5. Powder X-ray Diffraction (XRD) Characterization

The LNMO electrode materials were peeled off from the laminates using a blade and then stuck to a piece of Kapton polyimide tape. The tape was then stuck to an XRD sample holder to ensure that all of the measurements were at the same height. Then, the structures of pristine LNMO and LNMOs after soaking were characterized using a laboratory Rigaku MiniFlex 600 diffractometer with Cu Kα radiation (1.5406 Å).
3. Results and Discussions

3.1. Observation of Delamination

When LNMO/Li half cells were cycled under a high upper cut-off voltage (UCV) of 4.95 V with a low-EC electrolyte (1.0 M LiPF$_6$ in EC/EMC 1/9), a delamination issue was observed after just 10 cycles of discharging at different rates. The cycling condition aggressively (4.95 V compared to the regular 4.8 V UCV) exacerbated the dissolution process. Upon examining the delaminated electrode using SEM, we observed the presence of etched dents (indicated by red circles in Figure 1b) on the aluminum foil, which were not present on the pristine electrode (Figure 1a).

![Figure 1. (a) The SEM image of pristine Al current collector foil. (b) The SEM image of cycled Al current collector with examples of dents marked in the red cycles; insert: the disassembled LNMO laminate showing delamination after cycling with the applied protocol.](image)

3.2. Mechanism of Transition Metal Dissolution in LNMO Cells When Stored in Gen2

The delamination phenomenon was attributed to the formation of acidic electrolyte decomposition/hydrolysis products and consequent etching of the electrode materials and current collectors [7,8]. To further investigate the reactivity of the electrolyte with transition metal oxides under static conditions, the following soaking experiments and discussions were carried out: (1) the stability of Gen2 by itself in different storage vessels (Section 3.2.1); (2) the reactivity of Gen2 with various LNMO and NMC532 electrodes (Section 3.2.2) under static conditions; and (3), the reactivity of Gen2 with TMOs powders (Section 3.2.3) under static conditions. The soaking experiments were intentionally kept at 45 °C to accelerate degradation and facilitate easier tracking of the degradation changes.

3.2.1. Comparison of Vessels for the Soaking Test: Glass vs. PE Vials

It is well documented that Gen2 is not stable when exposed to moderately elevated temperatures in glass or PE vials [9,10]. Particularly, not only the hydrolysis products from PF$_6^-$ (OPF$_3$, OPF$_2$OH, OPF(OH)$_2$) were observed, but the secondary products through the reactions with dimethyl carbonate (OPF$_2$OMe, OPF(OMe)$_2$, OPFOMeOH, and OPF$_2$(OCH$_2$CH$_2$OMe), etc.), were also detected [10,11]. These secondary products were also found to appear later in the stage of decomposition.

The choice of vials (glass and PE) is important for the stability of Gen2, as it has been proven that Gen2 stored in PE is generally more stable than Gen2 storage in a glass vial (scintillation vial), which consists mainly of sodium borosilicate. As depicted in Figure 2a, when Gen2 was stored in a glass vial, peaks of dimethyl carbonate (DMC) and diethyl carbonate (DEC) were observed due to transesterification (Figure 2a), and its $^{19}$F NMR spectra showed late-stage electrolyte decompositions of OPF$_2$(OCH$_2$CH$_2$OMe) (compound 2) and OPF$_2$OMe (compound 3) dominating its decomposition products (see Figure 2b,d). However, when Gen2 was stored in a PE vial, only peaks for EC and EMC in
its $^1$H NMR spectra (Figure 2c) were observed, and with only one decomposition product OPF$_2$(OH) (compound 1) based on $^{19}$F NMR analysis (Figure 2d). In contrast, more side reactions and decompositions occurred when Gen2 was stored in the glass container, likely due to the catalytic effect of borosilicate in a glass vial. As depicted in Figure 2b, the presence of fluoroborate species, namely OPF$_2$(OH)-BF$_3$ at $-149.5$ ppm and BF$_4$ at $-156.4$ ppm in the $^{19}$F NMR spectra, provided additional confirmation of the direct involvement of borosilicate in the side reactions. The peak assignments presented in Figure 2 were based on documented chemical shifts for existing oxyfluorophosphates and their J-coupling constants (see Figure S1) [10,12].

![Figure 2](image-url)

**Figure 2.** (a) $^1$H NMR spectra of Gen2 soaked in a glass vial; (b) $^{19}$F NMR spectra of Gen2 soaked in a glass vial; (c) $^1$H NMR spectra of Gen2 soaked in a PE vial; and (d) $^{19}$F NMR spectra of Gen2 soaked in a PE vial.

### 3.2.2. Gen2 Soaking with Various LNMO and NMC532 Laminates

To determine which component of the LNMO electrode was more responsible for the observed delamination issue in the aged coin cell, LNMO electrodes with different compositions were used in the electrode soaking test, as shown in Table 1. Table 1 also lists NMC532 electrodes to understand the component of Co in the TMO, as NMC532 batteries are widely used in commercial electric vehicles, including Tesla Model 3, Nissan Leaf, BMW i3, and Chevrolet Bolt, and thus can serve as a valuable reference material. Detailed composition information for each electrode and the corresponding observations of soaking results were recorded in Table 1. After soaking for 3 months, NMC532 soaked in glass and LNMO soaked in PE did not exhibit electrolyte color changes or delamination issues (entries 1 and 2). However, all LNMO electrodes soaked in glass (entries 3–5) showed electrolyte color change and delamination. The modifications made to the LNMO electrodes in entries 4 and 5, including using a different PVDF binder source (LNMO-1), and incorporating single-walled carbon nanotubes (SWCNT) as an additional carbon conductor (LNMO-2), did not resolve the delamination problem. This suggests that the issue of delamination and etching is solely attributed to the LNMO active material itself and not to the PVDF, SWCNT, or carbon.

The findings from SEM, NMR, and ICP-MS characterizations further support this conclusion, as elaborated below.

1. The SEM images of Al foils from soaked LNMO electrodes (Figure 3) revealed that there was no obvious corrosion observed on the Al foil from LNMO soaked in PE, while the etching dents presented on all the Al foils obtained from the glass vial LNMO soaking samples and were consistent with those observed in the cycled LNMO cells (Figure 1). These dents were accompanied by the appearance of electrolyte color change and observed delamination, which should be ascribed to the corrosion from generated HF and/or late-stage electrolyte decompositions (such as compounds 1–3 in Figure 2) during electrolyte aging.
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Figure 3. SEM images of the Al foils after the soaking test. (a) LNMO electrode soaked in PE; (b) LNMO electrode soaked in glass; (c) LNMO electrode with Kynar PVDF (LNMO-1) soaked in glass; and (d) LNMO electrode with SWCNT added (LNMO-2) soaked in glass.

(2) Figure 4a,b shows the $^1$H NMR and $^{19}$F NMR spectra, respectively, of the electrolytes collected from the electrode soaking test. From the spectra, it is depicted that the electrolytes soaked with LNMO samples showed severely broadened peaks and only retained the pattern and shape of the relative peaks in the spectra, especially for the $^1$H NMR spectra. Meanwhile, the spectra of NMC532 were remarkably similar to the Gen2 control sample soaked in PE. In addition, the peaks shifting and broadening were in order of LNMO (including LNMO, LNMO-1, and LNMO-2) soaked in Glass > LNMO soaked in PE > NMC532 soaked in Glass ≈ Gen2 control samples using the full width at half maximum (FWHM) measurements (Figure S2).

(3) The metal contents characterized using ICP-MS for each soaking electrolyte sample are plotted in Figure 5. As a result, the Mn dissolution is found to be in the same order as LNMO soaked in Glass > LNMO soaked in PE > NMC532 soaked in Glass ≈ Gen2 control samples, meaning that the NMR peak shifting and broadening were directly related to Mn dissolution in the electrolyte, and the greater the Mn dissolution, the greater the NMR peak shifting and broadening. This result also indicated that the electrode/electrolyte interaction was much more severe for LNMO compared to NMC532.
Figure 4. (a) $^1$H NMR spectra and (b) $^{19}$F NMR spectra of each soaked electrolyte with different electrodes. Each sample was assigned based on the line’s color as noted.

Figure 5. ICP-MS data of the Mn (red), Ni (Navy) and Al (grey) content of the soaked electrolyte for each electrode soaking test sample (NMC532, LNMO, LNMO-1 and LNMO-2 are the samples corresponding to the electrodes listed in Table 1). The suffix _G denotes the sample soaked in a glass vial, and _PE denotes the sample soaked in a PE vial.

3.2.3. Gen2 Soaking with Different TMO Powders

From the electrode soaking test, different electrode/electrolyte interaction results were observed between LNMO and NMC532, which clearly indicates the importance of cathode materials in terms of the dissolution of Mn and Ni. To further explore this difference, a series of TMOs were selected to represent a broad range of compositions, company sources, and transition metal types: NMC442, NMC811, LMR-NMC, LMO, LNMO from Targray and LNMO from the NEI Corporation. The selection of LMO, which shares the Co-free spinel characteristics with LNMO, alongside the choice of NMC-based materials as representatives of widely utilized commercial cathode electrode materials spanning a broad range of cobalt content, was made in order to provide a comprehensive assessment of the studied systems for LNMO. The electrode material powders were soaked with Gen2 in glass vials under the same conditions with the aim of understanding how the TMO materials themselves would impact the composition of Gen2 upon soaking. As previously observed, the use of glass vessels, as compared to PE vessels, resulted in accelerated electrolyte decomposition and more pronounced electrode/electrolyte interactions. After soaking, the electrolytes soaked with LNMO (both for the Targary and NEI Corporation) turned black, the electrolyte soaked with LMO turned purple, while all the electrolytes soaked with the NMC-based materials (NMC442, NMC811, and LMR-NMC) remained colorless (see Figure S3).
The $^1$H NMR and $^{19}$F NMR spectra of the electrolytes collected after the powder soaking test (shown in Figure 6a,b, respectively) displayed similar peaks shifting and broadening with an order of LNMO (Targary or NEI Corporation) > LMO > NMC442 > LMR-NMC/NMC811. The ICP-MS data (Figure 7) were also plotted in this order, and an increase in Mn dissolution content was observed along this order, further demonstrating that the NMR peaks shifting and broadening was caused by the paramagnetic Mn$^{2+}$ dissolution [13,14]. Based on the results from NMR and ICP-MS measurements, it can be concluded that compared to layered structure NMC, spinel LNMO and LMO suffered much more severe Mn dissolution when in contact with the carbonate-based electrolyte. This indicates that the electrode/electrolyte interaction for LNMO was harsher, which could explain the delamination issue observed in its high-voltage cycled cells.

![Figure 6](image-url)  
**Figure 6.** (a) $^1$H NMR spectra and (b) $^{19}$F NMR spectra of each soaked Gen2 electrolyte with or without different TMO powders. Each sample was assigned based on the line’s color as noted.

![Figure 7](image-url)  
**Figure 7.** ICP-MS data of the Mn (red) and Ni (Navy) content of the soaked electrolyte for each powder soaking test sample.

When LMO was soaked in Gen2, 4354 µg/g Mn dissolution was found to be relatively close to 12,208 or 10,037 µg/g Mn dissolution measured from the LNMO powders (Targray or NEI Corporation, respectively) soaking test. Surprisingly, when various amounts of cobalt were introduced, Mn dissolution was significantly inhibited. The Mn dissolutions were only 294, 46 and 0.8 µg/g for the soaked Gen2 collected from NMC442, LMR-NMC and NMC 811 samples, respectively.
3.3. Additives Effect in Mitigating TM Dissolution

To address the severe electrode/electrolyte interaction between LNMO and the electrolyte as well as the delamination issue encountered in the aged LNMO coin cells, both additives soaking tests and electrochemical cycling of LNMO in the presence of additives were carried out.

3.3.1. Gen2 Soaking with LNMO Electrodes Adding Additives

In this test, 3 wt.% of each selected additive was added to Gen2 as the soaking solutions for the LNMO electrodes in a glass vial under the same conditions. As the electrolytes undergo deliberate degradation, a higher-than-usual amount of 3 wt.% additive was selected here to ensure the pronounced manifestation of the additives’ effects during the soaking investigations. Glass vials were utilized here due to their catalytic effect on electrolyte decompositions, which consequently led to more pronounced etching of the electrodes, as previously discussed. Out of the 10 additives tested (summarized in Table 2), 7 of the additives could prevent the delamination of LNMO electrodes, and three soaked electrolytes (TMSPi, LiDFOB and PTSI containing samples) did not show up an obvious color change, presumably implying a depressed electrolyte decomposition. Especially, LiDFOB and PTSI, the Gen2 were still colorless, with no electrode delamination observed after soaking.

Table 2. Summary of delamination and electrolyte color change observations for additives soaking test.

<table>
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<tr>
<th>Additives</th>
<th>Delamination Observation</th>
<th>Color Change Observation</th>
</tr>
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<tbody>
<tr>
<td>1 tVCBO</td>
<td>Yes</td>
<td>Light brown</td>
</tr>
<tr>
<td>2 TMSPi</td>
<td>No</td>
<td>Light yellow</td>
</tr>
<tr>
<td>3 LiDFOB</td>
<td>No</td>
<td>Colorless</td>
</tr>
<tr>
<td>4 PES</td>
<td>Yes</td>
<td>Brown</td>
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<td>5 PTSI</td>
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</tbody>
</table>

Again, we utilized $^1$H and $^{19}$F NMR shift as indicators of Mn dissolution to monitor the severity of electrode/electrolyte interaction (see Figure 8a,b). Both LiDFOB and PTSI showed minimal NMR peak shifting, suggesting that they effectively reduced Mn dissolution [15]. tVCBO also showed relatively small NMR peak shifting, but it failed to prevent delamination and electrolyte color change during the soaking test, indicating that the electrode/electrolyte interaction was still notable. On the other hand, though TMSPi was satisfactory in preventing soaking delamination and electrolyte color change, its NMR peak shifting was still significant, so a high Mn dissolution could thus be expected. Therefore, only LiDFOB and PTSI were deemed promising in solving the LNMO delamination problem during cycling from a chemical standpoint. To further confirm this expectation, dissolution metal contents were measured via ICP-MS for the TMSPi-, LiDFOB- and PTSI-containing samples (shown in Figure 9). We found that LiDFOB was exceptionally effective in reducing Mn dissolution, with almost no Ni and Al present in the soaked electrolyte. Additionally, compared to the LNMO soaking sample containing no additive, the PTSI also showed its effectiveness in mitigating LNMO/Gen2 interactions. Additionally, not surprisingly, the metal contents in TMSPi added electrolyte were still high, even higher than the Gen2 control soaking sample, indicating that the electrolyte decompositions and etching were still dramatic.
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effective in reducing Mn dissolution, with almost no Ni and Al present in the soaked elec-
cathode laminates in a cycling coin cell.

Figure 8. (a) $^1$H NMR spectra and (b) $^{19}$F NMR spectra of each soaked electrolyte with LNMO electrodes adding additives. Each sample was assigned based on the line’s color as noted.

Figure 9. ICP-MS data of the Mn (red), Ni (Navy), and Al (grey) contents of the soaked electrolyte with LNMO electrodes adding or not adding additives. The additives are TMSPi, LiDFOB and PTSI, respectively.

Figure 10a–c show the morphologies of the LNMO electrode Al foils after soaking with LiDFOB, PTSI and TMSPi, respectively. However, dents appeared for all these samples, which could be due to the harsh soaking conditions employed. Despite LiDFOB and PTSI being very competent in depressing the electrode/electrolyte interactions, electrolyte decompositions would still accumulate and eventually erode the electrodes during the long time and elevated temperature soaking test. As will be discussed later in the text (Section 3.3.2), LiDFOB and PTSI are effective in preventing pitting and corrosion on the cathode laminates in a cycling coin cell.

To have a deeper insight into how the additives alleviated the electrode degradation during soaking, XPS analyses (see Figure 11) of electrode surfaces were performed for the following six samples, including (1) soaked NMC532 electrode in glass; (2) soaked LNMO electrode in PE; (3) soaked LNMO electrode in glass; (4) soaked LNMO electrode in glass with TMSPi; (5) soaked LNMO electrode in glass with LiDFOB; and (6) soaked LNMO electrode in glass with PTSI. In accordance with prior observations, it was anticipated that the NMC electrode would serve as a reference, exhibiting favorable stability in terms of electrode/electrolyte interaction as compared to LNMO. The LNMO samples soaked in
PE were expected to undergo a mild etching process, resulting in a modest alteration in the composition of the LNMO interface, whereas the LNMO samples soaked in glass were anticipated to exhibit more pronounced etching effects, indicative of severe alterations in the behavior of the LNMO interface. The additives TMSPi, LiDFOB, and PTSI effectively hindered electrolyte color change upon soaking, with LiDFOB and PTSI additionally demonstrating notable efficacy in suppressing TM dissolution. In the C 1s spectra, the peak at 284.8 eV was assigned to C-C binding from electrode carbon particles and PVDF binder; the CF2 peaks at 291 eV originated from PVDF, while the C=O peaks at 286.68 eV and (CO3)2− peaks at 290.1 eV came from the interface formed from electrode/electrolyte interaction. For the F 1s spectra, the CF2 peaks at 688.04 eV raised from PVDF binder while Li3PO3F2 peaks at 686.19 eV and LiF peaks at 685.18 eV were due to the formation of the contacting interface. Additionally, for the O 1s spectra, C-O peaks at 534.13 eV and C=O peaks at 532.43 eV came from the interface while metal-O peaks at 529.57 eV came from the LNMO electrodes [16]. As a result, the LNMO soaked in glass and in glass with TMSPi exhibited similar signal patterns, with signals predominantly arising from the LNMO electrode (including PVDF, carbon particles and metal oxide), while the signals from the interface were weak. In contrast, LNMO soaked in PE, LNMO soaked in glass with LiDFOB and LNMO soaked in glass with PTSI showed similar signals patterns, with peaks primarily assigned to the formation of the contacting interface. Hence, we conclude that both LiDFOB and PTSI help to form a stable interface between the LNMO electrode and Gen2 electrolyte upon contact, which effectively prevents LNMO electrode degradation caused by electrolyte decompositions. Moreover, the NMC532 soaked in glass showed a mixture of signals from the electrode and the interface, indicating a different interaction mechanism than that of LNMO.

Figure 10. SEM images of the Al foils of LNMO electrode soaked in glass adding (a) LiDFOB, (b) PTSI or (c) TMSPi.

As shown in Figure S4, the X-ray diffraction (XRD) patterns of the pristine LNMO laminates were compared to those of LNMO laminates collected after soaking in glass with Gen2 (red), Gen2 with TMSPi (blue), Gen2 with LiDFOB (green), and Gen2 with PTSI (purple). The Gen2-soaked LNMO exhibited an additional 20 peaks at 21.5 (insignificant), 42.6, and 55.6 (insignificant) degrees. However, in the presence of additives, the soaked LNMO displayed patterns similar to the pristine LNMO, with no extra peaks.

The underlying reasoning is that Gen2 decompositions introduced etchings, resulting in the appearance of additional peaks, which were subsequently prohibited in the presence of additives. Notably, TMSPi, while not significantly preventing Mn dissolution, effectively halted other deterioration processes responsible for the occurrence of these extra peaks, as well as delamination and electrolyte color change observed upon soaking.
3.3.2. Additives Cycling Results

To examine if the additives can finally mitigate the delamination in aged LNMO coin cells, low-EC electrolytes added with different additives were tested using the same protocol. In this study, 1 wt.% LiDFOB, 0.5 wt.% PTSI, 2 wt.% TMSPi, 1 wt.% LiDFOB + 1 wt.% TMSPi and 1 wt.% LiDFOB + 0.5 wt.% PTSI were incorporated into the low-EC electrolyte, respectively, and their cycling performance is presented in Figure 12. In our other works (unpublished yet), we found that a single additive can barely improve the electrochemical performance of LNMO cells, while proper dual additives provide enhanced performance. So, dual additives of 1 wt.% LiDFOB + 1 wt.% TMSPi and 1 wt.% LiDFOB + 0.5 wt.% PTSI were also used here to achieve a more favorable outcome. 1 wt.% LiDFOB + 1 wt.% TMSPi exhibited enhancement in the electrochemical performance of LNMO/Gr full cells operating at a UCV of 4.7 V in our other studies, and 1 wt.% LiDFOB + 0.5 wt.% PTSI was applied here to evaluate if dual additives containing both of the additives that demonstrated promising results in the soaking test would also be beneficial in the electrochemical test. Figure 12 illustrates that both 1 wt.% LiDFOB + 1 wt.% TMSPi and 1 wt.% LiDFOB outperformed the baseline. The TMSPi cell showed slightly inferior performance compared to the baseline, while the PTSI, despite its impressive results in the soaking test, exhibited disappointing electrochemical performance. However, when LiDFOB was combined with PTSI, the electrochemical performance, especially at the high rates, was significantly enhanced, further validating LiDFOB’s role in reducing the impedance of LNMO cells. The SEM images of the Al foils from the cycled LNMO half cells, along with the corresponding pictures of the disassembled LNMO electrodes in the inserts, are presented in Figure 13. No delamination was observed in cells containing any of the tested additives, and no etching dents on Al foils were observed for the LiDFOB- or PTSI-containing cells. These observations are consistent with our previous soaking findings. Figure 14 shows the $^1$H NMR spectra of the electrolytes collected from each cycled cell. The additives were found to suppress electrolyte decomposition.
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In summary, the results of this study establish that LiDFOB can resolve the LNMO delamination issue during high-voltage cycling by forming a firm interface to mitigate electrode/electrolyte interactions. Additionally, it can improve the electrochemical performance of LNMO, especially when employing the dual additives strategy. LiDFOB and PTSI significantly mitigated Mn dissolution in the soaking test, and the delamination of LNMO was not observed in all aged coin cells with the chosen additives applied in the electrolyte. Notably, electrolytes containing 1 wt.% LiDFOB or 1 wt.% LiDFOB + 1 wt.% TMSPi also exhibited improvements in the electrochemical performance of LNMO in both specific capacity and rate performance. Note that positive effects can also be observed from the SEI, which affect both the cathode degradation process and the battery cycle life.
However, SEI mainly infers interfaces on the graphite anode and electrolytes. The focus of our work is on cathode delamination and TM dissolution that are the preceding events before the TM deposition on the graphite anode.

![1H NMR spectra of electrolytes collected from the cycled LNMO//Li half cells. Each sample was assigned based on the line’s color as noted.](image)

**Figure 14.** 1H NMR spectra of electrolytes collected from the cycled LNMO//Li half cells. Each sample was assigned based on the line’s color as noted.

### 4. Conclusions

As LNMO delamination is a universal problem for aged coin cells with a high upper cut-off voltage above 4.7 V, this study aimed to figure out the cause of it and solve it chemically by conducting a series of soaking tests in a view of electrolyte decompositions etching. The results indicate that the dissolution mechanism of the soaking tests comes from the decomposition of a Gen2 electrolyte. The decomposition was further catalyzed by the borosilicate of the glass vials, and the LNMO delamination is confirmed to be caused by the electrolyte decompositions into acidic side products, which in turn lead to the etching of the electrode materials and current collectors. Furthermore, the decomposition process, which can be ascribed to the electrode/electrolyte interaction, is more severe for spinel LNMO and LMO materials compared to the layered structure NMC-based materials. Though the underlying mechanism remains unclear, it is believed that the poor electrode/electrolyte contacting stability of LNMO with the electrolyte can result in cell degradation both in cycling and calendar life and thus hinder its application as a promising Co-free cathode material. Both LiDFOB and PTSI can prevent Mn dissolution by forming a firm interface and further mitigate the harsh LNMO reactivity with carbonate-based electrolytes in both soaking and electrochemical experiments. Especially for the LiDFOB, it can also improve the electrochemical performance of LNMO in both energy and power densities.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/batteries9090435/s1](https://www.mdpi.com/article/10.3390/batteries9090435/s1), Figure S1: 19F NMR and the multiplet assignment of each compound in the aged Gen2 in a glass. Figure S2: Full width at half maximum measurements from 1H NMR and 19F NMR spectra of the laminates soaking test. Normalized Width = Σ (Peak Width/Peak Area)⁰.⁵. Figure S3: Gen2 electrolytes collected after electrode powder soaking test (samples from left to right are LMO, LNMO from NEI Corporation, LNMO from Targray, LMR-NMC, NMC811 and NMC442, respectively).

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