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Lithium-Rich Cobalt-Free Manganese-Based Layered Cathode Materials for Li-Ion Batteries: Suppressing the Voltage Fading

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Abstract: Lithium-rich layered oxides are recognized as promising materials for Li-ion batteries, owing to higher capacity than the currently available commercialized cathode, for their lower cost. However, their voltage decay and cycling instability during the charge/discharge process are problems that need to be solved before their practical application can be envisioned. These problems are mainly associated with a phase transition of the surface layer from the layered structure to the spinel structure. In this paper, we report the AlF₃-coating of the Li-rich Co-free layered Li₁₂Ni₀₂Mn₀₆O₂ (LLNMO) oxide as an effective strategy to solve these problems. The samples were synthesized via the hydrothermal route that insures a very good crystallization in the layered structure, probed by XRD, energy-dispersive X-ray (EDX) spectroscopy, and Raman spectroscopy. The hydrothermally synthesized samples before and after AlF₃ coating are well crystallized in the layered structure with particle sizes of about 180 nm (crystallites of ~65 nm), with high porosity (pore size 5 nm) determined by Brunauer–Emmett–Teller (BET) specific surface area method. Subsequent improvements in discharge capacity are obtained with a ~5-nm thick coating layer. AlF₃-coated Li₁₂Ni₀₂Mn₀₆O₂ delivers a capacity of 248 mAh g⁻¹ stable over the 100 cycles, and it exhibits a voltage fading rate of 1.40 mV per cycle. According to the analysis from galvanostatic charge-discharge and electrochemical impedance spectroscopy, the electrochemical performance enhancement is discussed and compared with literature data. Post-mortem analysis confirms that the AlF₃ coating is a very efficient surface modification to improve the stability of the layered phase of the Li-rich material, at the origin of the significant improvement of the electrochemical properties.

Keywords: Li-rich oxide; layered structure; cathode; voltage decay; Li-ion batteries

1. Introduction

The energy density (E in Wh g⁻¹) of a battery is determined by the amount of charge it can hold (Ah kg⁻¹) and by the voltage across its terminal (V); optimization of its electrochemical performance is achieved by an appropriate selection of anode and cathode materials [1]. In this context, layered Li-rich materials are attracting a lot of attention, because their capacity is the best among the lithium intercalation materials. In addition, they are not expensive and non-toxic when they are cobalt-free. Layered lithium-rich cobalt-free manganese-based oxides (LLNMOs) have been widely considered as new cathode materials for Li-ion batteries [2–40]. They are constituted by the architectural solid solution yLi₂MnO₃ (1−y)LiMO₂ (M = Mn, Ni), which includes the monoclinic Li₂MnO₃ (C2/m space group) and the rhombohedral LiMO₂ (R₃m space group) phase. Both R₃m and C2/m phases have a
layered structure with a repeating transition-metal layer, oxygen layer, and lithium layer as shown in Figure 1 [2]. The high specific capacity (>250 mAh g\(^{-1}\)) with an average discharge voltage of >3.5 V vs. Li\(^+\)/Li and the high energy density approaching 1000 Wh kg\(^{-1}\) are due to the activation of the Li\(_2\)MnO\(_3\) component at potential >4.4 V vs. Li\(^+\)/Li during the first charge and the structural stability due to the Mn-rich composition. The early work by Lu et al. [3,4] demonstrated the stable reversible capacity in the potential window 2.0–4.6 V of the series Li\(_{4/3}\)-2xNi\(_x\)Mn\(_{2/3}\)-x/3O\(_2\), in which Li\(_{1.11}\)Ni\(_{0.33}\)Mn\(_{0.56}\)O\(_2\) (x = 0.33) exhibited a specific capacity of ~230 mAh g\(^{-1}\). Then Kang et al. [5] reported the strong correlation between structure and electrochemical performance. Among various LLNMO compositions, Li\(_{1.5}\)Ni\(_{0.25}\)Mn\(_{0.75}\)O\(_{2.5}\) (Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) or 0.5Li\(_2\)MnO\(_3\) 0.5LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) in layered notation) has attracted much interest because it is also considered as an inter-grown composite; this Co-free structure exhibited the lowest voltage decay rate [6] and was easily synthesized by wet-chemical methods.

In spite of the efforts to obtain good reproducible electrochemical performance, practical applications of LLNMOs are still hindered by a large irreversible capacity loss in the initial cycle, severe capacity and voltage fading during long-term cycling, and poor rate capability [7,8]. Upon successive charge-discharge reactions, a surface reconstruction layer (SRL) occurs, which directly correlates to the electrochemical performance of the electrode. The SRL features are as follows: (1) creation of oxygen vacancies; (2) migration of transition metal (TM) cations into Li-sites; (3) reduction of the TM cations to low valence state; and (4) transformation of the lattice structure [9,10]. Zheng et al. [11] evidenced the influence of the synthesis conditions on the voltage decay rate, concluding that the sol-gel method provides better performance than the co-precipitation technique. It has been suggested that one of the main reasons for voltage fade is the irreversible migration of TM to the Li layer promoted by oxygen vacancies [12].

![Figure 1](https://example.com/fig1.png)

**Figure 1.** Schematic view of the crystal structure of Li-rich Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\). The red, green, silver, and purple spheres represent O, Li, Ni, and Mn atoms, respectively. Reproduced with permission from [2]. Copyright 2018 Wiley.

Several strategies have been employed to enhance the electrochemical properties of any cathode materials and reduce the voltage decay rate upon long-term cycling. The first approach is surface modification, since the coat can protect the active particles against corrosion and dissolution, and improve the electrical contact between powders (for a review, see [1]). Various substances have been deposited on the surface of active particles such as Li\(^+\)-conductor (Li\(_2\)ZrO\(_3\), LiAlO\(_2\)) [13,14], inert compound (AlF\(_3\), Al\(_2\)O\(_3\)) [15], wide-gap semiconductor (ZnO) [16], and carbon [17,18]. Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) nanoparticles (100–200 nm in size) coated with a thin layer of Li\(_2\)ZrO\(_3\) obtained through a synchronous lithiation strategy delivered a capacity of circa 169 mAh g\(^{-1}\) over 100 cycles at current density 200 mA g\(^{-1}\) [13]. ZnO coating also improved the electrochemical properties of 0.5Li\(_2\)MnO\(_3\) 0.5LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\); a specific discharge capacity of 215 mAh g\(^{-1}\) was reported after 10 cycles for ZnO treated LLNMO against 181 mAh g\(^{-1}\) for pristine electrode [19]. Enhanced electrochemical properties were observed for Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) synthesized nickel enrichment is a second way to mitigate the voltage fading. For example, Shi et al. [20] demonstrated that Ni ions act as stabilizing ions to inhibit the Jahn–Teller effect of active Mn\(^{3+}\) ions in 0.5Li\(_2\)MnO\(_3\) 0.5LiNi\(_{0.8}\)Co\(_{0.1}\)Mn\(_{0.1}\)O\(_2\). Doping or
cationic substitution is another successful method to reduce the voltage drop [21,22]. Substitution of a small amount of $M^{3+}$ ($M = \text{Al, Cr, Fe, Co}$) for $\text{Mn}^{4+}$ and $\text{Ni}^{2+}$ in $\text{Li(Li}_{0.2}\text{Mn}_{0.6}\text{Ni}_{0.2})\text{O}_2$ sensitively influences the length of the plateau region due to the changes in the metal–oxygen bond covalence [23]. Ba doping improves the first-cycle Coulombic efficiency of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ by mitigating the oxidation of $\text{O}^{2-}$ ions [24]. The synergetic effects of coating and doping were used by Liu et al. who synthesized $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ by co-precipitation technique with 3 wt.% LiAlO$_2$ coat and 0.8% Cr doping [14]: (i) the spinel phase was suppressed, (ii) the midpoint voltage increased from 2.746 to 3.128 V, and (iii) higher $D_{\text{Li}}$ contributed to good rate capability. Nevertheless, even though doping was able to significantly improve the electrochemical performance of the material, it did not solve the problem of side reactions with the electrolyte, dissolution, and phase transition of the surface layer to the spinel phase. Surface modification remains mandatory. However, the efficiency of the coating is also debated, because it depends on several parameters, including full surface coverage, thickness of the coating layer, the composition of the coat, and the morphology of the particles. This last parameter also plays an important role. In particular, use of nano-sized particles is needed for any cathode element to shorten the diffusion path. However, in the particular case of the $\alpha$-NaFeO$_2$ structure of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ considered here, it is also necessary to increase the size of the active (010) lattice planes at the surface.

As an experimental fact, the crystal morphology of LLNMOs and subsequent electrochemical performance are strongly dependent on the synthesis technique. Many methods have been tested to prepare “optimized” $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6} \text{O}_2$ powders such as the solid state reaction [17,25], sol-gel process [15,26], co-precipitation method [27–29], combustion process [30,31], sol-freeze-drying method [32], ball-milling [33], hydrothermal [34–37], templating process [38], microwave heating process [39,40], and lithium ion-exchange reaction [41]. Currently, well-crystallized LLNMO materials prepared via wet-chemical synthesis are subjected to post-annealing treatment, i.e., typically a two-step calcination at ~350/900 °C for 10/4 h in air [36,42–44]. Among these methods, the co-precipitation process is a widely used synthesis approach to obtain spherical and mono-dispersed materials [45]. However, prolonged post-treatment provide big particles that limit the rate capability. Liu et al. [35] revealed the influence of the synthesis techniques on the voltage fading rate in the $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ electrode, with a decrease of this rate in the sequence co-precipitation > sol-gel > hydrothermal method. Therefore, hydrothermal synthesis seems to be the best synthesis route.

In the present work, the voltage decay in long-term cycled $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6} \text{O}_2$ is investigated for pristine and AlF$_3$-coated samples. AlF$_3$ has been chosen as the inert material to coat the particles. The hydrothermal method has been chosen not only to minimize the fading rate, but also because it is well suited for the preparation of nano-sized powders with a spherical-like shape that is considered as the best morphology to optimize the electrochemical properties. The structure and morphology of the as-prepared sample are analyzed by X-ray diffraction (XRD), Raman spectroscopy, Brunauer–Emmett–Teller (BET) specific surface area method, scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). Electrochemical properties are studied using galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) experiments. Chemical diffusion coefficients of Li$^+$ ions in LLNMO lattices are evaluated. Finally, the rate capability and cycle ability of LLNMO electrodes are further investigated and discussed. As a result, importantly, both the rate capability and cycle ability have been improved, with a capacity of 248 mAh g$^{-1}$ stable over the 100 cycles. Moreover, the voltage fading rate has been reduced to 1.40 mV per cycle. These results prove the efficiency of the AlF$_3$ coating to protect the surface layer of the Li-rich particles.
2. Materials and Methods

2.1. Preparation of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ Nanoparticles

Li-rich layered Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ powders were prepared by a two-step process, i.e., a hydrothermal synthesis followed by a solid-state calcination. Lithium and transition-metal (TM) acetates (analytical grade from Merck KGaA, Darmstadt, Germany) were mixed in distilled water at the stoichiometric composition and stirred for 15 min. A homogeneous slurry was obtained after adding citric acid drop-wise to the solution under continuous stirring for 6 h with molar ratio 1:1 of (Li+Ni+Mn):C$_6$H$_8$O$_7$. The pH value was adjusted to 7-8 with ammonium hydroxide. The slurry was transferred into a 100 mL Teflon-lined stainless-steel autoclave maintained at a constant temperature of 180 °C for 12 h. Then the product was dried and calcined at 500 °C for 3 h, and thereafter post-treated at 900 °C for 12 h in air. The AlF$_3$-coating layer was fabricated by the chemical deposition method. The as-prepared Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ powders were immersed in the Al(NO$_3$)$_3$ dilute aqueous solution heated to 50 °C and stirred vigorously. NH$_4$F dilute solution was then added into the solution with the molar ratio of Al to F of 1:3 corresponding to the 5-wt.% AlF$_3$ coat. After drying at 60 °C in a vacuum oven, the obtained products were heated at 400 °C in ambient argon for 4 h to prevent the formation of Al$_2$O$_3$ and secure the formation of AlF$_3$-coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$. Figure 2 displays the pictures of both Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ samples.

![Photographs of pristine and AlF$_3$-coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ specimens.](image)

2.2. Material Characterization

The crystalline phase was identified by XRD using a Philips X’Pert diffractometer (PANalytical, Orsay, France) equipped with CuKα radiation source (λ = 1.5406 Å). The diffractograms were recorded at room temperature in the 2θ-range 10–80°. The experimental patterns were refined by the Rietveld method with FULLPROF software program. The variance of the relative amounts of atomic components in the samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 7000DV, Perkin Elmer Co., Ltd., UK). The morphology and composition were studied by SEM (ZEISS model ULTRA 55) coupled with an energy-dispersive X-ray attached analyzer (EDX). HRTEM images were obtained using an electronic microscope JEOL model JEM-2010. Raman spectra were taken using a micro-Raman spectrophotometer (Horiba, Longjumeau, France) equipped with an optical microscope (×100 objective) and a 633 nm He–Ne laser excitation line. Data were recorded in steps of 1.6 cm$^{-1}$ with an acquisition time of 30 s. The wavenumber calibration was regularly verified by using the Raman peak at 520 cm$^{-1}$ of a silicon crystal as a reference. BET specific surface area was measured by nitrogen adsorption/desorption at 77 K in a relative pressure $P/P_0 = 0.0$–1.0, with $P$ and $P_0$ being the equilibrium and saturation pressure, respectively, using a Quantachrome NOVA automated gas sorption analyzer (Anton Paar GmbH, Blankenfelde-Mahlow, Germany). The pore size distribution and pore volume were estimated using the Barrett–Joyner–Halenda (BJH) method [46].

Electrochemical tests were conducted on CR2025-type coin cells assembled in a glove box (moisture and oxygen content ≤5 ppm) under argon atmosphere. The procedure to fabricate the
cathode was as follows: 85 wt.% active material, 10 wt.% carbon black as conductive medium, and 5 wt.% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) solvent were mixed and ground to generate a homogeneous slurry. The slurry was then spread onto an aluminum foil current collector and dried at 80 °C for 2 h to remove the solvent before being pressed. Using such a cathode (loading of ~2 mg cm⁻²), the electrochemical cells fabricated with lithium sheet as the counter electrode, Celgard 2500 film as the separator filled with 1 mol L⁻¹ LiPF₆ in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1) solution (LP30, Merk) as electrolyte. The galvanostatic charge–discharge GCD cycles were performed using a potentiostat/galvanostat (workstation VMP3 Bio-Logic, Seyssinet-Pariset, France) in the potential range 2.0–4.8 V. EIS data were collected using a phase sensitive multimeter (model PSM 1700, UK) in the frequency range 0.01 Hz–100 kHz using a voltage bias of 5 mV.

3. Results

3.1. Structure and Composition

The relative concentration of atoms was measured by ICP-AES. Results listed in Table 1 show that the chemical composition of the LLNMO samples is close to the theoretical stoichiometry. Moreover, the amount of Al is consistent with the value expected by the surface treatment. The ~2% loss of Li in pristine LLNMO should be attributed to its departure from the surface during the calcination process. Figure 3 displays the Rietveld refinement of the XRD patterns of pristine and AlF₃-coated Li₁.₂Ni₀.₂Mn₀.₆O₂ oxides. For both samples, these results suggest the structural co-existence of the Li₂MnO₃ (C₂/m S.G.) and LiNi₀.₅Mn₀.₅O₂ (R₃m S.G.) phases. XRD diagrams exhibit the typical diffraction patterns of the α-NaFeO₂-type layered structure with the R₃m space group (hexagonal setting) [47]. Additional reflections appeared in the 20–21° 2θ-region that are the fingerprints of the Li₂MnO₃-type C₂/m phase. Such a superstructure suggests the presence of Li⁺ ions in the transition-metal layer of Li₁.₂Ni₀.₂Mn₀.₆O₂. The existence of this secondary phase is also detected by Raman spectroscopy, as it will be evidenced in the following. For the coated sample, the XRD features are unchanged in agreement with other works [48,49].

| Table 1. Elemental composition of LLNMO samples analyzed by ICP-AES. |
|-------------------------|-----|-----|-----|-----|
| Sample                  | Li  | Ni  | Mn  | Al  |
| Pristine                | 1.18| 0.21| 0.59| -   |
| AlF₃-coated             | 1.20| 0.19| 0.61| 0.048|

From the Rietveld refinement results (Table 2), the lattice expansion occurred in both the a and c directions when LLNMO particles are coated with AlF₃. Thus, the volume of the elementary unit...
cell increases slightly with the coating. In stoichiometric Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, the valence state of Mn and Ni ions are +4 and +2, respectively [50,51]. The primary effect of the AlF$_3$ coating is a reduction of the loss of Li ions at the surface of particles that provokes an increase of the Li$_2$MnO$_3$ component content and, consequently, an increase of the amount of Mn$^{3+}$ ions. The slight change of the lattice parameters is explained by consideration of the ionic radii of Mn ions. The increase in $a$ and $c$ is attributable to the bigger ionic radius of Mn$^{3+}$ ions in octahedral coordination (58 pm against 53 pm for Mn$^{4+}$ ions) [52]. It also gives evidence that an internal composite structure exists in the Li-rich oxide framework. This increasing concentration of Mn$^{3+}$ has been reported to be beneficial to the electrochemical performance. The existence of Mn$^{3+}$ causes a gradual activation of Li$_2$MnO$_3$, which results in a capacity increase upon cycling [53].

For the $R3m$ phase of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, the refinement involved fixing the Mn occupancy and varying the ratios of the Ni and Li occupancies on the TM and Li sites. The degree of Ni occupancy in the interlayer Li sites (cationic mixing) is rather low at 1.33% and 1.25% for pristine and coated LLNMO samples, respectively. There are several indicators to evaluate the presence of Li-Ni anti-sites (cation mixing). First, the $c/a$ lattice parameter ratio evidences the deviation of the rock-salt structure (i.e., $c/a > 4.90$). The second indicator is the peak intensity ratio $R_1 = I_{003}/I_{104}$; the higher $R_1$, the lower amount of undesirable Li-Ni anti-sites and better hexagonal structure [54]. The third fingerprint of the hexagonal ordering is defined by the factor $R_2 = (I_{006} + I_{102})/I_{101}$; the lower the $R_2$, the better the hexagonal ordering [55,56]. The values of $R_1$ and $R_2$ reveal that the hydrothermally synthesized LLNMO samples have a perfect layered structure. As seen in Table 2, the Rietveld refinement results are consistent with the direct observation of the XRD peak intensity ratios showing the lower cation mixing with well-ordered rhombohedral structures for the AlF$_3$ coated LLNMO sample.

Table 2. The structural parameters obtained from Rietveld refinements for pristine and AlF$_3$-coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ powders prepared by hydrothermal method via citric acid chelator.

| Crystal Data       | Pristine LLNMO | AlF$_3$-Coated LLNMO |
|--------------------|----------------|----------------------|
| $a$ (Å)            | 2847(3)        | 2852(1)              |
| $c$ (Å)            | 14.216(6)      | 14.235(0)            |
| $V$ (Å$^3$)        | 99.82          | 99.97                |
| $c/a$              | 4.992          | 4991                 |
| $I_{003}/I_{104}$  | 1.41           | 1.45                 |
| $(I_{006} + I_{102})/I_{101}$ | 0.42 | 0.41                 |
| Coherent length ($L_c$) (nm) | 68  | 65                  |
| Strain $\times 10^{-2}$ | 2.45 | 2.12                |
| Reliability factors |                |                      |
| $R_w$ (%)          | 6.22           | 7.55                 |
| $R_{exp}$ (%)      | 4.71           | 6.23                 |
| Ni$^{2+}$ (in Li layer of $R3m$) | 0.0133 | 0.0125
| Phase fraction (mol %) | 48.2 | 49.5               |
| $R3m$              |                |                      |
| $C2/m$             | 51.8           | 50.5                 |

The local deformation of the crystal structure is investigated by the analysis of the broadening of the XRD reflections according to the Williamson–Hall relationship [57,58]:

$$B \cos \theta = 4 <e> \sin \theta + K \lambda/L_c$$

where $B$ is the full-width at half-maximum (FWHM), $K$ is the crystallite shape factor (assumed to be 0.9), $<e>$ is the micro-strain field, $L_c$ is the size of the crystallites (coherence length), $\theta$ is the diffraction angle and $\lambda$ is the X-ray wavelength of the source. The microstrain is extracted from the slope of the plot of $B \cos \theta$ vs. $\sin \theta$ in Figure 4, and $L_c$ is determined by extrapolation of the straight line to $\sin \theta = 0$.  
Both samples have identical $L_c$ of $65 \pm 5$ nm. The results show that the microstrain of $2.45 \times 10^{-2}$ for pristine LLNMO slightly reduces to $2.12 \times 10^{-2}$ for the coated sample. The smaller value of $\langle c \rangle$ in the AlF$_3$-coated sample proves that the thin layer stabilizes the lattice structure, a consistent result with the fact that the coating process has reduced the number Li-Ni anti-sites by $\sim$7%. The decrease of the strain field gives evidence of a better structural stability of the coated sample than the pristine one, as expected from the above discussion devoted to the lattice parameters and the consideration of ionic radii.

**Figure 4.** Analysis of the full-width at half-maximum (FWHM) of the XRD reflections according to Equation (1).

The porosity of hydrothermally synthesized LLNMO samples was studied by N$_2$ adsorption/desorption tests. Figure 5a,b presents the N$_2$ adsorption/desorption isotherm and the pore-size distribution (inset) for pristine and AlF$_3$-coated LLNMO samples. An increase in the amount of adsorbed N$_2$ with increase of the $P/P_0$ value and the appearance of a hysteresis loop are observed in the isotherm curves. Results obtained from BJH analysis are listed in Table 3. The average BJH pore width is in the range 4.5–5.5 nm, which indicates that these holes are mainly mesopores with total pore volume of 0.45 cm$^3$ g$^{-1}$. These features are fingerprints of a hierarchical mesoporous structure of LLNMO powders that promotes the Li$^+$ ion kinetics [59]. Suib et al. [60] described the formation of mesoporosity by aggregation of nanoparticles along their lateral faces. In the same way, the mesopores (~5 nm) correspond here to the voids existing between randomly-packed nanoparticles of ~150 nm in diameter inside secondary particles (agglomerates) of ~600 nm in size, as we will see on TEM images reported later in this work.

BET analysis shows that pristine and AlF$_3$-coated LLNMO samples have a specific surface area of 11.5 and 9.2 m$^2$ g$^{-1}$, respectively, which is advantageous for enhancing the transport of Li$^+$ ions in the secondary particles. These values are comparable with those reported by Chang et al. [61] for Li-rich Li$_{1.27}$Cr$_{0.2}$Mn$_{0.53}$O$_2$ oxides prepared by milling-assisted solid-state process. Xiang et al. [62] reported the influence of polyvinyl alcohol (PVA) as chelating agent on the BET surface area for Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ prepared by sol-gel technique (varying from $\sim$10 m$^2$ g$^{-1}$ for PVA-0% to $\sim$33 m$^2$ g$^{-1}$ for PVA-15%). Zhang et al. [63] showed that 3-µm sized secondary particles, which consisted of self-assembled crystallites ~150 nm in size, demonstrated optimized mesostructuration partially mitigating the voltage fading. The equivalent particle size of the samples can be calculated from the BET data and compare with SEM images. The average particle diameter (in nm) is expressed by the relation [64]:

$$L_{BET} = \frac{6000}{S_{BET}d}$$  \hspace{1cm} (2)

where $S_{BET}$ is the specific surface area (in m$^2$ g$^{-1}$) measured by BET experiments and $d$ the gravimetric density ($4.53$ g cm$^{-3}$ for NMO). The BET surface area and the average particle size results are found in Table 3. We observe a relatively good agreement between particle size values $L_{BET}$ and $L_{TEM}$ evaluated from BET and measured from TEM images, respectively.
Table 3. Brunauer–Emmett–Teller (BET) specific surface area, calculated average particle size from BET data ($L_{\text{BET}}$) using Equation (2), mean particle size measured using TEM imaging ($L_{\text{TEM}}$) and results obtained from Brunauer–Joyner–Halenda (BJH) analysis for hydrothermally prepared LLNMO samples.

| Sample          | BET ($m^2 g^{-1}$) | $L_{\text{BET}}$ (nm) | $L_{\text{TEM}}$ (nm) | Pore Size (nm) | Pore Volume ($cm^3 g^{-1}$) |
|-----------------|---------------------|------------------------|------------------------|----------------|-----------------------------|
| Pristine        | 11.5                | 115                    | 150                    | 4.6            | 0.45                        |
| AlF$_3$ coated  | 9.2                 | 144                    | 180                    | 5.2            | 0.49                        |

The crystal structure of Li-rich layered oxides is currently discussed assuming either the existence of solid solution according to the substitution of $M$ in LiMO$_2$ [65,66] or the formation of a composite of LiMO$_2$ and Li$_2$MnO$_3$ [67,68]. The X-ray diffraction analysis clearly pleads for the second model. This hypothesis is also confirmed by Raman spectroscopy, which is efficient in probing the short-range order (local structure) of materials. Regarding the vibrational modes of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ (0.5Li$_2$MnO$_3$, 0.5LiNi$_{0.5}$Mn$_{0.5}$O$_2$ in layered notation), two Raman-active modes ($A_{1g} + E_g$) are expected for LiMO$_2$ ($M = \text{Ni or Mn, } D_{3d}^5 \text{ symmetry}$) [69,70], while six Raman active modes ($4A_g + 2B_g$) are predicted for Li$_2$MnO$_3$ ($C_{2v}^3 \text{ symmetry}$) [71]. In Figure 6, we observe two peaks at 603 and 482 cm$^{-1}$, which are assigned to the stretching $\nu$(MO$_6$) and bending $\delta$(O–M–O) vibration with $M = \text{Mn}^{4+}, \text{Ni}^{2+}$ belonging to the LiNi$_{0.5}$Mn$_{0.5}$O$_2$ phase and three peaks at 587, 437, and 416 cm$^{-1}$ attributed to the Li$_2$MnO$_3$ phase. The extra-peak at ca. 650 cm$^{-1}$ is attributed to the stretching vibration $\nu$(Mn$^{3+}$O$_6$). The calculated spectrum is shown in Figure 6 (black line). The Raman spectrum of the surface-modified LLNMO sample does not exhibit any frequency shift with respect to the pristine one. This indicates that the AlF$_3$ coating does not influence the Li-rich local structure, and that neither Al nor F penetrated into the samples in agreement with the XRD analysis.

Figure 5. N$_2$ adsorption desorption isotherm and Barrett–Joyner–Halenda (BJH) pore-size distribution for (a) pristine and (b) AlF$_3$-coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ oxides.

Figure 6. Raman spectra of LLNMO materials recorded with the laser excitation line at 532 nm. The solid black line represents the calculated spectrum.
3.2. Morphology

The morphology of LLNMO powders has been investigated by SEM and HRTEM imaging. Figure 7 presents the SEM images combined with the EDX spectrum of the surface of AlF3-coated sample. The SEM images show regular particles with similar morphology (almost monodisperse). The homogeneous size distribution of agglomerates ~200 nm is noticeable without difference between pristine and AlF3-coated particles. The EDX spectrum (Figure 7c) of the AlF3-coated sample exhibits only the additional peak of Al, because the peak of fluorine merges with that of Mn. No other element was detected, giving evidence of the absence of any impurity in all the samples. From this experiment, the concentration of Al is found to be 5.15 wt.%.

Figure 7. SEM images of (a) pristine LLNMO and (b) AlF3-coated LLNMO. (c) EDX spectrum of AlF3-coated LLNMO.

The HRTEM images for all the samples are reported in Figure 8. The 200 nm-thick agglomerates of the Li1.2Ni0.2Mn0.6O2 samples are made of well-crystallized particles 95 nm in size. The comparison between HRTEM images shows that the coating had no effect on the size of particles. There is no effect on the shape, confirming that the coating of only 5–7 nm thickness does not change the structure nor the morphology of the powders [72,73]. This is due to the relatively low temperature of 400 °C used during the coating process, which is much smaller than the temperature at which the particles could start to coalesce. The distance between neighboring fringes shown in insets is 0.47 nm, which is assigned to (003), (001), or both planes for rhombohedral, monoclinic, or both phases, respectively. Such features are commonly observed in Li-rich samples of different compositions [74].

Figure 8. TEM images of (a) pristine LLNMO and (b) AlF3-coated LLNMO. HRTEM images of (c) pristine LLNMO and (d) AlF3-coated LLNMO. Image (e) shows the morphology of the AlF3 coating.
3.3. Electrochemical Properties

Electrochemical properties of LLNMO samples have been investigated by galvanostatic charge-discharge and electrochemical impedance spectroscopy. In this study, we consider the total charge delivered by each component of the LLNMO cathodes (xLi2MnO3·(1−x)LiNi0.5Mn0.5O2). As x = 0.5 for Li1.2Ni0.2Mn0.6O2, the theoretical specific capacity is 369 mAh g\(^{-1}\) (229 mAh g\(^{-1}\) for 0.5Li2MnO3 + 140 mAh g\(^{-1}\) for 0.5LiNi0.5Mn0.5O2). This value is exactly the theoretical capacity, based on complete extraction of lithium (1.2 Li per Li1.2Ni0.2Mn0.6O2 formula unit) [75–77]. The theoretical discharge capacity, based on the mass of the discharged rock-salt product after the first charge/discharge cycle, is 280 mAh g\(^{-1}\). Note that for unknown reasons, some authors used the value of 200 mAh g\(^{-1}\).

For clarity, we use the current density expressed in mA g\(^{-1}\) with the correspondence 1C = 369 mA g\(^{-1}\) for all the electrodes.

Figure 9a,b display the GCD curves of pristine and AlF\(_3\)-coated Li1.2Ni0.2Mn0.6O2 electrodes, respectively, performed at 0.15C rate in the potential window 2.0–4.8 V. The shape and change after the first activation cycle are consistent with literature [9,41,44,50,78–82]. The initial charge occurred with a well-defined voltage plateau at 4.5 V, which correspond to the irreversible extraction of Li\(_2\)O from the Li\(_3\)MnO\(_3\) component [8]. Thus, the strong oxidation of O\(^{2-}\) is considered to occur at ca. 4.5 V.

The capacity corresponding to the oxidation of Ni from Ni\(^{2+}\) to Ni\(^{4+}\) (below 4.5 V) is ca. 100 mAh g\(^{-1}\) for both electrodes. During the initial discharge, the pristine and coated LLNMO electrodes delivered a specific capacity of 242 and 260 mAh g\(^{-1}\), respectively, which was maintained at 219 and 231 mAh g\(^{-1}\) after 50 cycles. After 100 cycles of charge-discharge at 600 mA g\(^{-1}\) current density, the capacity retention of ~91% for the coated electrode is higher than that of pristine LLNMO (~59%).

Figure 9. Galvanostatic charge-discharge of (a) pristine LLNMO and (b) AlF\(_3\)-coated LLNMO. Cycles were carried out at 30 mA g\(^{-1}\) current density (0.08C rate) in the potential range 2.0–4.8 V.

Figure 10. Incremental capacity (-dQ/dV vs. V) plots for (a) LiNi0.5Mn0.5O2, (b) pristine LLNMO, and (c) AlF\(_3\)-coated LLNMO.

Figure 10a–c present the differential capacity or incremental capacity (IC) plots (-dQ/dV vs. V) for discharge curves of LLNMO electrodes at the 3rd and 50th cycles, which not only specify the reduction potentials but also clearly display the voltage fade issue. In IC plots, the peaks correspond to the
pseudo plateaus in the GCD curves. The IC curve of the parent LiNi0.5Mn0.5O2 (Figure 10a) confirms that the peak at ca. 3.74 V is due to the reduction of Ni^{4+} to Ni^{3+} during the insertion of Li⁺ ions in the layered framework. This reduction peak (A) occurred at 3.75 and 3.77 V in the discharge profile of pristine and coated electrodes, respectively. It is shifted down to ~3.65 V after 50 cycles for pristine Li_{1.2Ni_{0.2}Mn_{0.6}O2}, whereas a shift by only 70 mV is observed for the AlF3-coated electrode. The main difference between Li_{1.2Ni_{0.5}Mn_{0.5}O2} and Li_{1.2Ni_{0.2}Mn_{0.8}O2} is the occurrence of the low-voltage cathodic peak (B) at ca. 3.25–3.35 V, which is assigned to the reduction of Mn^{4+} to Mn^{3+} in MnO2 formed during the first charging reaction [38,59,83]. Note that the reduction peak of Mn^{4+} is weaker for AlF3-coated Li_{1.2Ni_{0.2}Mn_{0.6}O2} than Li_{1.2Ni_{0.2}Mn_{0.8}O2}; however, the voltage decay of the B peak is higher than that of the A peak.

Figure 11 presents the rate capability and the cycling stability of LLNMO electrodes synthesized by the hydrothermal method assisted with citric acid. Experiments were carried out in the voltage range 2.0–4.8 V at various current densities in the range 30–900 mA g⁻¹. As shown in Figure 11a, specific capacities of 116 and 153 mAh g⁻¹ are obtained at the 900 mA g⁻¹ rate during the discharge process of pristine and AlF3-coated electrodes, respectively. The decay in the specific capacity was observed without significant change in the S-shape of the charge and discharge curves. From the cycling performance shown in Figure 11b, the loss of capacity calculated upon 100 cycles is found to be 0.75 and 0.20 mA h g⁻¹ per cycle for the pristine and AlF3-coated electrodes, respectively. The good reversibility of the AlF3-coated Li_{1.2Ni_{0.6}Mn_{0.4}O2} electrode is confirmed by the Coulombic efficiency remaining around 99.4% over 100 cycles (Figure 11b). The rates of capacity fade for the AlF3-coated electrode are 0.29 and 0.41 mAh g⁻¹ per cycle, when tested over 80 cycles at current densities of 300 and 900 mA g⁻¹, respectively (Figure 11c). The evolution of the Coulombic efficiency for pristine and AlF3-coated LLNMO electrodes is presented in Figure 11d. In comparison, the Coulombic efficiency of 76% for pristine LLNMO in the first cycle has increased to 87% after AlF3 coating. Similar behavior was reported by Liu et al. [43] for ZnAl₂O₄-coated Li_{1.2Ni_{0.2}Mn_{0.6}O2} material.

![Figure 11](image-url)  
**Figure 11.** (a) Rate performance (current densities in mA g⁻¹) and (b) cycling stability of pristine and AlF3-coated LLNMO electrodes tested at current density of 30 mA g⁻¹. (c) Cyclability of the AlF3-coated LLNMO electrode tested at current density of 300 and 900 mA g⁻¹. (d) Coulombic efficiency of pristine and AlF3-coated LLNMO electrodes.

The present electrochemical performances of LLNMO electrodes are comparable with previous data. However, there are some differences depending on the morphology of the active particles.
Hydrothermally synthesized rod-like hierarchical nano/micro \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) delivered a capacity of 212 mAh g\(^{-1}\) after 30 cycles at 1C rate (250 mA g\(^{-1}\)) [36]. Yang et al. [32] reported a specific capacity of \( \sim 190 \) mAh g\(^{-1}\) at 1C rate (250 mA g\(^{-1}\)) for agglomerated \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) particles with a large pore volume of \( 9.2 \times 10^{-3} \) cm\(^3\) g\(^{-1}\) prepared by sol-freeze-drying method. \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) nanoparticles (100–200 nm in size) coated with a thin layer of Li\(^+\)-conductive \( \text{Li}_2\text{ZrO}_3 \) coating obtained through a synchronous lithiation strategy delivered a capacity of circa 169 mAh g\(^{-1}\) over 100 cycles at current density 200 mA g\(^{-1}\) [13].

To further investigate the effect of the AlF\(_3\) coating on resistances and lithium kinetics in LLNMO, EIS measurements were carried out. Figure 12 presents the EIS spectra investigated after the first cycle performed at 0.15C rate. As shown in Figure 12a, all of the Nyquist plots of the cells are composed of three contributions that can be modeled using the equivalent circuit shown as inset: (i) an intercept of x-axis at high-frequency corresponds to the ohmic resistance (\( R_s \)), i.e., electrodes and electrolyte contributions; (ii) a depressed semicircle in the high-frequency region is ascribed to the charge transfer impedance (\( R_{ct} \), CPE\(_{ct} \)) at the electrode/electrolyte interface, in which the constant phase element is expressed by CPE = \( 1/\omega^p \) with \( \omega \) the angular frequency, \( T \) a CPE constant and \( p \) an exponent (0 \( \leq p \leq 1 \), \( p = 1 \) for pure capacitance) and \( j \) is the imaginary number (\( j = \sqrt{-1} \)); and finally (iii) an inclined line (with a slope of \( \sim 45^\circ \)) at low-frequency reflects the diffusion-controlled process characterized by a Warburg impedance taken in the infinite limit and expressed by the relation \( Z_W(\omega) = \sigma_w (1 - j \omega)^{-1/2} \), where \( \sigma_w \) is the Warburg factor [84]. The real part of the impedance \( Z'(\omega) \) is the sum of the components:

\[
Z'(\omega) = R_s + R_{ct} + R_{SEI} + \sigma_w \omega^{-1/2}
\]  

(3)

From the slope of the \( Z' \) vs. \( \omega^{-1/2} \) curves (Figure 12b), we can calculate the apparent chemical diffusion coefficient of Li\(^+\) ions (\( D_{Li^+} \)) in the electrode using the relation [85]:

\[
D_{Li^+} = \frac{1}{2} \left( \frac{RT}{F^2 A C_{Li} \sigma_W} \right)^2
\]  

(4)

where \( R \) is the gas constant, \( F \) is Faraday’s constant, \( T \) the absolute temperature, \( A \) the surface area of the electrode-electrolyte interface, and \( C_{Li} \) the molar concentration of Li\(^+\) ions in the electrode (0.8 mmol cm\(^{-3}\)). The fitting parameters are reported in Table 4. Results can be summarized as follows. The value of \( R_{ct} \) for the cell with AlF\(_3\)-coated \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) (65.5 \( \Omega \)) is smaller than that of pristine \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) (100.3 \( \Omega \)), demonstrating that the AlF\(_3\) coating layer effectively decreases the interface contact resistance. In addition, the exponent \( p \) of the CPE component associated with the charge transfer is close to unity for both cells, which means that the CPE contribution is essentially capacitive. This gives evidence of a good homogeneity of the electrode. Note that the contribution of the SEI layer can be neglected. As a result, the apparent diffusion coefficients of Li\(^+\) ions are found to be \( 2.8 \times 10^{-15} \) and \( 1.1 \times 10^{-14} \) cm\(^2\) s\(^{-1}\) in pristine and AlF\(_3\)-coated \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) electrodes, respectively.

![Figure 12. (a) Nyquist plots of the cell with pristine and AlF\(_3\)-coated \( \text{Li}_1.2\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2 \) cathodes. (b) plots of \( Z' \) vs. \( \omega^{-1/2} \). Solid lines are the fits using the equivalent circuit shown as inset.](image-url)
The $D_{Li}^+$ calculated values of our hydrothermally synthesized LLNMO samples are slightly higher than the values reported from Yang et al. [39] and Lin et al. [44]. $D_{Li}^+$ of of $2.34 \times 10^{-17}$ and $1.03 \times 10^{-14}$ cm$^2$ s$^{-1}$ was reported for pristine LLNMO and LLNMO/graphene structures synthesized by sonication in ethylene glycol solution [39]. $D_{Li}^+$ measured for LLNMO prepared by a sol-gel method assisted with carbon felt as reactive carrier was $2.49 \times 10^{-16}$ cm$^2$ s$^{-1}$ before charging, which is slightly smaller than $4.71 \times 10^{-16}$ cm$^2$ s$^{-1}$ obtained under charge at 4.8 V [44]. In contrast, Sasakawa et al. [86] reported a higher $D_{Li}^+$ value of $1.6 \times 10^{-13}$ cm$^2$ s$^{-1}$ in the discharge state of LLNMO particles prepared by combustion method. The same group of researchers showed that $D_{Li}^+$ increased with increasing the charge rate in the potential range 2.5–4.4 V with an average value of $4.5 \times 10^{-13}$ cm$^2$ s$^{-1}$ at mid-voltage.

| Sample                | $R_s$ (Ω) | $R_{ct}$ (Ω) | CPE$_{ct}$ | $\sigma_w$ (Ω s$^{-1/2}$) | $D_{Li}$ (cm$^2$ s$^{-1}$) |
|-----------------------|------------|--------------|------------|----------------------------|----------------------------|
| pristine              | 8.4        | 100.3        | 2.6 $\times$ 10$^{-5}$ | 0.91 | 40.5 | 2.8 $\times$ 10$^{-15}$ |
| AlF$_3$ coated         | 9.1        | 65.5         | 4.8 $\times$ 10$^{-6}$ | 0.94 | 34.6 | 1.1 $\times$ 10$^{-14}$ |

Generally, a high $D_{Li}^+$ value implies a well-ordered layer structure of the cathode material and a minimum cationic disorder in the Li slabs [87]. Such an Li$^+$ diffusion enhancement is attributed to the presence of the thin AlF$_3$ layer, which promotes the ionic transport at the electrode-electrolyte interface and partly suppresses the spinel layer formation. Liu et al. [29] reported $D_{Li}^+$ values of $8.2 \times 10^{-13}$ and $3.8 \times 10^{-12}$ cm$^2$ s$^{-1}$ for pristine and Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$PO$_{4}$ (LATP) coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, respectively. The samples were synthesized by co-precipitation with the LATP layer ~4 nm thick and exhibited a cationic mixing of 2%. Liu et al. [43] estimated $D_{Li}^+$ values of $8.2 \times 10^{-14}$ and $7.6 \times 10^{-12}$ cm$^2$ s$^{-1}$ at mid-voltage (3.5 V) for pristine and Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ coated with 1 wt.% ZnAl$_2$O$_4$. Recently, Ku et al. [88] proposed a new Li diffusion model based on the correlation between asymmetric TM migration and Li mobility that explained the non-equivalent intercalation and de-intercalation kinetics. Chang et al. [61] suggested that the high Li-ion diffusion coefficient of $3.9 \times 10^{-10}$ cm$^2$ s$^{-1}$ in Li-rich layered cathode material is caused by the mesoporous network composed of tiny primary particles.

To further verify the improvement of the electrochemical properties of the electrodes, EIS measurements were conducted at different discharge cycles. Figure 13a,b presents the variation of the transport parameters $R_s$, $R_{ct}$, and $\sigma_w$ for both LLNMO samples. Among those parameters listed, $R_{ct}$ is the most important since it represents the charge transfer within the cathode material. After 50 charge-discharge cycles, $R_s$ increased by a factor of 2 for both electrodes but seems to saturate at ca. 145 Ω for the AlF$_3$-coated LLNMO material. These results show that $\sigma_w$ for pristine LLNMO increases almost linearly upon cycling, while it reaches a value of 50 Ω s$^{-1/2}$ for the AlF$_3$ coated electrode after 30 cycles.

![Figure 13](image-url) Evolution of the transport parameters $R_s$, $R_{ct}$, and $\sigma_w$ as a function of cycling for (a) pristine and (b) AlF$_3$-coated LLNMO samples.
Raman spectroscopy is a non-destructive and sensitive method to perform post-mortem studies of cycled cathode materials [89]. This analytical technique allows the investigations of structural changes at the particle surface, the electrode degradation, and the formation of spinel-like layer [28,80,83,90]. In which case, such surface modifications are not detected by diffraction techniques. Figure 14 shows the ex situ Raman spectra of cycled pristine and AlF$_3$-coated LLNMO electrodes after 50 and 100 cycles. The formation of the spinel-like layer in all cycled LLNMO electrodes is indicated by the shoulder at ~650 cm$^{-1}$. After long-term cycling (100 cycles) of the pristine LLNMO sample, the intensity of this spectral feature becomes relatively strong, revealing the formation of a disorder on the particle surface. Simultaneously, a broadening and a frequency shift of the peak at 416 cm$^{-1}$, related to the monoclinic Li$_2$MnO$_3$ phase, are observed. In contrast, the AlF$_3$-coating retards the transformation to the spinel structure of the Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode surface. These studies confirm that the AlF$_3$ coating is a very efficient surface modification to improve the stability of the layered phase of the Li-rich material, at the origin of the significant improvement of the electrochemical properties.

![Ex situ Raman spectra of (a) pristine and (b) AlF$_3$-coated LLNMO electrodes after 50 and 100 cycles at 30 mA g$^{-1}$ current density.](image)

**Figure 14.** Ex situ Raman spectra of (a) pristine and (b) AlF$_3$-coated LLNMO electrodes after 50 and 100 cycles at 30 mA g$^{-1}$ current density.

4. Discussion

4.1. Structural Stability

The structural and electrochemical stability of LLNMO strongly depend on synthesis conditions and operating parameters. The stable performance in relation to initial charge condition shows that a fast rate of 3C induced a decrease of the $R_{ct}$ resistance and slight increase of the Li$^+$ diffusion coefficient in the bulk. Our results confirm the efficiency of the AlF$_3$ coating with the optimized concentration of 5 wt.% [86]. This layer is thick enough to protect the electrode material against the side reactions with the electrolyte, which reduces the resistance of the SEI layer, and increases the rate capability. The coating layer also stabilizes the layered network, with two beneficial effects: (i) it increases the cycle ability, which improves the cycle ability and (ii) it increases the diffusivity of Li$^+$, which contributes to enhancing the rate capability of the coated particles. In addition, the mesopores increase the effective surface area in contact with the electrolyte, which explains the high capacities reported in this work.

Improvement of calendar and cycling life together with safety issues of lithium-ion batteries require sophisticated technology to prevent degradation mechanisms. The surface modification of the electrode materials is part of the solution [91]. Among the unwanted degradation mechanisms occurring in LLNMOs, the creation of the solid electrolyte interphase (SEI), growth of a layered-to-spinel surface layer, unreacted residual lithium ingredients on the particle surface, formation of corrosion pits, and occurrence of inter-granular cracks inside primary particles have been widely documented [92–98].

To date, few works report the use of AlF$_3$ as a deposit on the surface of Li-rich Mn-rich particles [48,71,98–100]. Sun et al. [71] consider the AlF$_3$ coating layer as a “buffer” through which the activity of extracted oxygen is reduced; thus, the electrolyte decomposition is avoided at voltages above
4.5 V. AlF$_3$ is preferable to Al$_2$O$_3$, which is unstable in Li cells and can be peeled off from the cathode surface by conversion into AlF$_3$ in the presence of traces of HF in the electrolyte. AlF$_3$ is also preferable to Li$_3$PO$_4$. Kang and Thackeray reported a surface coating of Li-Ni-PO$_4$, leading to reversible capacity of 200 mAh g$^{-1}$ at 1C. They speculated that one of the components Li$_3$PO$_4$ acts as an excellent lithium ion conductor as well as an efficient protective layer stabilizing the electrode surface, though it is not clear how Li$_3$PO$_4$ stabilizes the electrode surface [101]. Then, Liu et al. used this coating to stabilize the interface and reduce the side reaction between the material and electrolyte and thus improve the cyclic stability of a Li-rich, Mn-containing layered material [101]. Lee et al. [102] synthesized a Li$_3$PO$_4$-coated Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$, which delivered 240 mAh g$^{-1}$ at 0.1C (25 mA g$^{-1}$), and 205 mAh g$^{-1}$ after 50 cycles at room temperature, which corresponds to 85% capacity retention over 50 cycles, compared to ~91% capacity retention after 100 cycles at 2C in our AlF$_3$-coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ electrode. More recently, Li-rich@Li$_3$PO$_4$ was synthesized via a template of polydopamine [103]. The nanoparticles were 100–200 nm thick, comparable to the particles in the present work (secondary particles 200 nm, primary particles 95 nm). The beneficial protection effects against side-reactions with the electrolyte were confirmed. Actually, almost all coatings that are chemically and electrochemically stable with the carbonate electrolytes (including Li$_3$PO$_4$ and AlF$_3$) have this function (see [104] for a review). However, the results were not competitive with the results obtained with other coatings such as AlF$_3$. For instance, at 0.2C (1C = 200 mA g$^{-1}$) in a potential window from 2.0 to 4.8 V (the same conditions as in the present work), Li-rich@Li$_3$PO$_4$ delivered a capacity of 230 mAh g$^{-1}$, which decreased to 130 mAh g$^{-1}$ after 100 cycles. Therefore, the Li$_3$PO$_4$ coat fails to reduce the kinetics of the phase transition to the spinel phase after Mn dissolution in the surface layer of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$, while it was found efficient in the case of NMC (Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$ and Li(Ni$_{0.5}$Mn$_{0.5}$Co$_{0.5}$)O$_2$), where it prevents NiO-like and Co-like phase formations on the surface [105,106]. Zheng et al. [98] analyzed the fundamental functions of the AlF$_3$ coating and concluded that the coating mitigates the acidic attack by the electrolyte of spinel-like networks formed on the particle surface. Figure 15 illustrates the transformation mechanism of an active particle of Li-rich layered oxide. Upon repeated cycling, the morphology of the uncoated particle is modified with the formation a spinel phase and corrosion pits, whereas a thin layer of coating protects the particles against corrosion and postpones the spinel growth. The efficiency of the AlF$_3$ coating is also evidenced by the fact that our results were obtained with only 5-wt.% AlF$_3$, while effective protection of cathode elements often need much thicker coats; for instance, 12 wt.% in the case of LiAlO$_2$/Al$_2$O$_3$-coated nano-LiCoO$_2$ [107].

**Figure 15.** Scheme of transformation of active particle of Li-rich layered oxide upon repeated cycling. Reproduced with permission from [97]. Copyright 2014, American Chemical Society.
4.2. Voltage Decay

Capacity fading and voltage decay are the important drawbacks of Li-rich cathode materials; they are the main challenges for the commercialization of LLNMOs. The voltage decay originates from a gradual phase transformation of the layered phase to a 3 V spinel-like phase. [13,76,108–113]. From GCD curves and dQ/dV plots, Lee and Manthiram showed that the length of the plateau region during first charge is the primary governing factor in the voltage decay process [111]. From first principles calculations, Xu et al. [112] have suggested that both the formation of Li\textsubscript{tet}−V(TM)Li−Li\textsubscript{tet} dumbbell structures (Li\textsubscript{tet} refers to the lithium ion in a tetrahedral site and V(TM)Li refers to the lithium-ion vacancy in the TM layer) and TM ion migration into the lithium layer can facilitate the formation of a 3 V spinel-like phase during charging in the high voltage region. The formation of such Li\textsubscript{tet}−V(TM)Li−Li\textsubscript{tet} dumbbell structures can be expected to increase with the length of the plateau region during the first charge process since lithium ions from the TM layer will be extracted once all of the lithium ions are extracted from the lithium layer.

From IC plots (Figure 10) the voltage decay is found to be 2.80 and 1.40 mV per cycle for pristine and AlF\textsubscript{3}-coated electrode, respectively, after 50 cycles. Table 5 lists the voltage decay rate for Li\textsubscript{1.2}Ni\textsubscript{0.2}Mn\textsubscript{0.6}O\textsubscript{2} cathode materials synthesized by different methods. Li et al. [76] inhibited the undesired layered-spinel intergrowth by doping with K\textsuperscript{+} ions, which weakened the creation of tri-vacancies in the Li layer and Mn migration. Chong et al. [112] fabricated a spherical core-shell structure, Li\textsubscript{1.2}Ni\textsubscript{0.2}Mn\textsubscript{0.6}O\textsubscript{2}@Li\textsubscript{1.2}Ni\textsubscript{0.4}Mn\textsubscript{0.4}O\textsubscript{2} by in situ hydrothermal technique, which exhibited a high voltage retention value of 3.335 V after 100 cycles. The most impressive low voltage decay rate of 1.09 mV per cycle was recently reported by Ding et al. [113] for Li\textsubscript{1.2}Mn\textsubscript{0.6}Ni\textsubscript{0.2}O\textsubscript{2} microspheres. The sophisticated modification made by a three-in-one surface treatment consisted of synchronous design of oxygen vacancies, spinel-phase integration, and N-doped carbon monolayers.

Table 5. Voltage decay rate for different Li-rich Li\textsubscript{1.2}Ni\textsubscript{0.2}Mn\textsubscript{0.6}O\textsubscript{2} cathode materials.

| Material                  | ∆V per Cycle (mV) | Measurement Conditions          | Ref.     |
|---------------------------|-------------------|---------------------------------|----------|
| Al\textsuperscript{3+} doping | 3.50              | 2.0–4.8 V, 100 cycles @ 25 mA g\textsuperscript{-1} | [26]     |
| Nb\textsuperscript{5+} doping | 2.61              | 2.0–4.8 V, 100 cycles @ 0.1C    | [114]    |
| pristine (sol-gel)        | 1.07              | 2.0–4.75 V, 200 cycles @ 0.2C   | [11]     |
| pristine (co-precipitation) | 1.25             | 2.0–4.75 V, 200 cycles @ 0.2C   | [11]     |
| pristine (hydrothermal) | 0.75              | 2.0–4.75 V, 200 cycles @ 0.2C   | [11]     |
| Li\textsubscript{2}ZrO\textsubscript{3} coating | 1.25             | 2.5–4.5 V, 100 cycles @ 1C      | [13]     |
| Li\textsubscript{1.4}Al\textsubscript{0.2}Ti\textsubscript{1.7}(PO\textsubscript{4})\textsubscript{3} coating | 4.68             | 2.0–4.75 V, 80 cycles @ 0.2C    | [29]     |
| pristine (co-precipitation) | 6.42             | 2.0–4.8 V, 100 cycles @ 0.2C    | [14]     |
| LiAlO\textsubscript{2} coating | 3.31             | 2.0–4.8 V, 100 cycles @ 0.2C    | [14]     |
| pristine (co-precipitation) | 7.16             | 2.0–4.75 V, 50 cycles @ 0.2C    | [43]     |
| ZnAl\textsubscript{2}O\textsubscript{4} coating | 5.26             | 2.0–4.75 V, 50 cycles @ 0.2C    | [43]     |
| N-doped carbon coating     | 1.09              | 500 cycles @ 5C                  | [115]    |
| pristine (hydrothermal) | 2.80              | 2.0–4.8 V, 50 cycles @ 0.1C     | this work|
| AlF\textsubscript{3} coating | 1.40              | 2.0–4.8 V, 50 cycles @ 0.1C     | this work|

The remarkable results by Zheng et al. deserve to be cited [11]. The voltage fade was mitigated by improving the atomic level uniformity of elemental distribution at the Li\textsubscript{1.2}Ni\textsubscript{0.2}Mn\textsubscript{0.6}O\textsubscript{2} surface. Studies of the influence of the synthesis methods (i.e., sol-gel (SG), co-precipitation (CP), and hydrothermal (HT)) on the voltage-decay rate were carried out using secondary ion mass spectroscopy (SIMS), and it was suggested that one of the main reasons for the high voltage-decay rate in HT samples is the non-uniform distribution of Ni ions with a Ni-rich particle surface leading to an easy reduction of the Mn\textsuperscript{4+} ions. Ni-segregated materials also exhibit poor cycling stability.
5. Conclusions

In summary, this work has shown that significant improvements of the electrochemical performance of Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 electrode materials synthesized by hydrothermal technique have been obtained by an optimized AlF_3 coating layer (5 wt.%) deposited on the surface of the 200-nm thick particles. This coating improved all aspects of the electrochemical properties: discharge capacity, capacity retention (~91% over 100 cycles for the coated electrode in contrast with ~59% for the pristine one), and rate capability. The mesoporous morphology of hydrothermally synthesized Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 electrode materials contributed to enhancing the capacity. Another advantage of the AlF_3 coating is the smaller loss of the operating voltage, half that of the pristine sample. Finally, despite certain claims in the literature, these studies have demonstrated the effectiveness of this coating in terms of structural stability, migration of Mn^{3+} cations, attenuation of cross growth in the spinel phase, and protection against side reactions with the electrolyte. Note the results have been obtained by coating pristine Li_{1.2}Ni_{0.2}Mn_{0.6}O_2. The next step should then be to coat doped-Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 using the doping processes mentioned in the introduction, which improved the rate capability by increasing the diffusion coefficient of Li^+ ions in the structure and mitigated the oxidation of O^{2-} ions, in order to benefit from the synergetic effects.

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References

1. Zaghib, K.; Mauger, A.; Groult, H.; Goodenough, J.B.; Julien, C.M. Advanced electrodes for high power Li-ion batteries. Materials 2013, 6, 1028. [CrossRef] [PubMed]
2. Li, X.; Qiao, Y.; Guo, S.; Xu, Z.; Zhu, H.; Zhang, X.; Yuan, Y.; He, P.; Ishida, M.; Zhou, H. Direct visualization of the reversible O^{2−}/O^{−} redox process in Li-rich cathode materials. Adv. Mater. 2018, 30, 1705197. [CrossRef]
3. Lu, Z.H.; MacNeil, D.D.; Dahn, J.R. Layered cathode materials Li[Ni_{1/3}(1-x)Mn_{2/3}O_{2}] for lithium-ion batteries. Electrochem. Solid State Lett. 2001, 4, A191–A194. [CrossRef]
4. Lu, Z.; Beaulieu, L.Y.; Donaberger, R.A.; Thomas, C.L.; Dahn, J.R. Synthesis and electrochemical behavior of Li[Ni_{1/3}(1-x)Mn_{2/3}O_{2}] compounds. J. Electrochem. Soc. 2002, 149, A778–A791. [CrossRef]
5. Kang, S.H.; Sun, Y.K.; Amine, K. Electrochemical and ex situ X-ray study of Li[(Li_{0.2}Ni_{0.2}Mn_{0.6})O_{2}] cathode material for Li secondary batteries. Electrochem. Solid State Lett. 2003, 6, A183–A186. [CrossRef]
6. Wang, J.; He, X.; Paillard, E.; Laszczynski, N.; Li, J.; Passerini, S. Lithium- and manganese-rich oxide cathode materials for high-energy lithium ion batteries. Adv. Energy Mater. 2016, 6, 1600906. [CrossRef]
7. Gu, M.; Genc, A.; Belharouak, I.; Wang, D.; Amine, K.; Thevuthasan, S.; Baer, D.R.; Zhang, J.G.; Browning, N.D.; Liu, J.; et al. Nanoscale phase separation, cation ordering, and surface chemistry in pristine Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 for Li-ion batteries. Chem. Mater. 2013, 25, 2319–2326. [CrossRef]
8. Hong, J.; Seo, D.H.; Kim, S.W.; Gwon, H.; Oh, S.T.; Kang, K. Structural evolution of layered Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 upon electrochemical cycling in a Li rechargeable battery. J. Mater. Chem. 2010, 20, 10179–10186. [CrossRef]
9. Yan, P.; Nie, A.; Zheng, J.; Zhou, Y.; Lu, D.; Zhang, X.; Xu, R.; Belharouak, I.; Xu, Z.; Xiao, J.; et al. Evolution of lattice structure and chemical composition of the surface reconstruction layer in Li_{1.2}Ni_{0.2}Mn_{0.6}O_2 cathode material for lithium ion batteries. Nano Lett. 2015, 15, 514–522. [CrossRef]
10. Hua, W.; Wang, S.; Knapp, M.; Leake, S.J.; Senyshyn, A.; Richter, C.; Yavuz, M.; Binder, J.R.; Grey, C.P.; Ehrenberg, H.; et al. Structural insights into the formation and voltage degradation of lithium- and manganese-rich layered oxides. Nat. Commun. 2019, 10, 5365. [CrossRef]
11. Zheng, J.; Gu, M.; Genc, A.; Xiao, J.; Xu, P.; Chen, X.; Zhu, Z.; Zhao, W.; Pullan, L.; Wang, C.; et al. Mitigating voltage fade in cathode materials by improving the atomic level uniformity of elemental distribution. Nano Lett. 2014, 14, 2628–2635. [CrossRef] [PubMed]
12. Qian, D.; Xu, B.; Chi, M.; Meng, Y.S. Uncovering the roles of oxygen vacancies in cation migration in lithium excess layered oxides. Phys. Chem. Chem. Phys. 2014, 16, 14665–14668. [CrossRef] [PubMed]
13. Zhang, J.; Zhang, H.; Gao, R.; Li, Z.; Hu, Z.; Liu, X. New insights into the modification mechanism of Li-rich Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ coated by Li$_4$ZrO$_3$. *Phys. Chem. Chem. Phys.* **2016**, *18*, 13322–13331. [CrossRef]

14. Liu, Y.; Fan, X.; Zhang, Z.; Wu, H.-H.; Liu, D.; Dou, A.; Su, M.; Zhang, Q.; Chu, D.D. Enhanced electrochemical performance of Li-rich layered cathode materials by combined Cr doping and LiAlO$_2$ coating. *ACS Sustain. Chem. Eng.* **2019**, *7*, 2225–2235. [CrossRef]

15. Abdel-Ghany, A.; El-Tawil, R.S.; Hashem, A.M.; Mauger, A.; Julien, C.M. Improved electrochemical performance of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ by Li-enrichment and AlF$_3$ coating. *Materials* **2019**, *5*, 100207. [CrossRef]

16. Lee, H.J.; Par, Y.J. Synthesis of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ nanoparticles and their surface modification using a polypodamine layer. *J. Power Sources* **2013**, *244*, 222–233. [CrossRef]

17. Liu, Y.J.; Lv, J.; Liu, S.B.; Chen, L.; Chen, X.H. Improved electrochemical performance of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode materials by ball milling and carbon coating. *Powder Technol.* **2013**, *239*, 461–466. [CrossRef]

18. Liu, Y.J.; Gao, Y.Y.; Lv, J.; Chen, L. A Facile method to synthesize carbon coated Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ with improved performance. *Mater. Res. Bull.* **2013**, *48*, 4930–4934. [CrossRef]

19. Singh, G.; Thomas, R.; Kumar, A.; Katiyar, R.S.; Manivannan, A. Electrochemical and structural investigations on ZnO treated 0.5Li$_2$MnO$_3$-0.5LiNi$_{0.5}$Mn$_{0.5}$O$_2$ layered composite cathode material for lithium ion battery. *J. Electrochem. Soc.* **2012**, *159*, A470–A478. [CrossRef]

20. Shi, J.L.; Zhang, J.N.; He, M.; Zhang, X.D.; Yin, Y.X.; Li, H.; Guo, Y.G.; Gu, L.; Wan, L.J. Mitigating voltage decay of Li-rich cathode material via increasing Ni content for lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2016**, *8*, 20138–20146. [CrossRef]

21. Uzun, D. Boron-doped Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ as a cathode active material for lithium ion battery. *Solid State Ion.* **2015**, *281*, 73–81. [CrossRef]

22. Yamamoto, S.; Noguchi, H.; Zhao, W. Improvement of cycling performance in Ti substituted 0.5Li$_2$MnO$_3$-0.5LiNi$_{0.5}$Mn$_{0.5}$O$_2$ through suppressing metal dissolution. *J. Power Sources* **2015**, *278*, 76–86. [CrossRef]

23. Wang, C.C.; Manthiram, A. Influence of cationic substitutions on the first charge and reversible capacities of lithium-rich layered oxide cathodes. *J. Mater. Chem. A* **2013**, *1*, 10209–10217. [CrossRef]

24. Li, J.; Nie, A.; Zhan, C.; Lu, J.; Yuan, Y.; Shabbarizan-Yassar, R.; Qiu, X.; Amine, K. Improve first-cycle efficiency and rate performance of layered-layered Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$ using oxygen stabilizing dopant. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16040–16045. [CrossRef] [PubMed]

25. Zhuang, Y.; Du, F.; Zhu, L.; Cao, H.; Dai, H.; Adkins, J.; Zhou, Q.; Zheng, J. Trimethylsilyl (trimethylsiloxy) acetate as a novel electrolyte additive for improvement of electrochemical performance of lithium-rich Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode in lithium-ion batteries. *Electrochim. Acta* **2018**, *290*, 220–227. [CrossRef]

26. Wang, C.C.; Lin, Y.C.; Chou, P.H. Mitigation of layer to spinel conversion of a lithium rich layered oxide cathode by substitution of Al in a lithium ion battery. *RSC Adv.* **2015**, *5*, 68919–68928. [CrossRef]

27. Wang, D.; Huang, Y.; Hua, Z.; Chen, L. Synthesize and electrochemical characterization of Mg-doped Li-rich layered Li[Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ cathode material. *Electrochim. Acta* **2013**, *107*, 461–466. [CrossRef]

28. Huang, J.-X.; Li, B.; Liu, B.; Liu, B.-J.; Zhao, J.-B.; Ren, B. Structural evolution of NM (Ni and Mn) lithium-rich layered material revealed by in-situ electrochemical Raman spectroscopic study. *J. Power Sources* **2016**, *310*, 85–90. [CrossRef]

29. Liu, Y.; Fan, X.; Huang, X.; Liu, D.; Dou, A.; Su, M.; Chu, D. Electrochemical performance of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ coated with a facilely synthesized Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$. *J. Power Sources* **2018**, *403*, 27–37. [CrossRef]

30. Zhong, Z.; Ye, N.; Wang, H.; Ma, Z. Low temperature combustion synthesis and performance of spherical 0.5Li$_2$MnO$_3$-LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cathode material for Li-ion batteries. *Chem. Eng. J.* **2011**, *175*, 579–584. [CrossRef]

31. Zhang, Q.; Mei, J.; Xie, X.; Wang, X.; Zhang, J. Solution combustion synthesis and enhanced electrochemical performance Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ nanoparticles by controlling NO$_3^-$/CH$_3$COO$^-$ ratio of the precursors. *Mater. Res. Bull.* **2015**, *70*, 397–402. [CrossRef]

32. Yang, P.; Li, H.; Wei, X.; Zhang, S.; Xing, Y. Structure tuned Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$ with low cation mixing and Ni segregation as high performance cathode materials for Li-ion batteries. *Electrochim. Acta* **2018**, *271*, 276–283. [CrossRef]

33. Liu, Y.; Liu, D.; Wu, H.-H.; Fan, X.; Dou, A.; Zhang, Q.; Su, M. Improved cycling stability of Na-doped cathode materials Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ via a facile synthesis. *ACS Sustain. Chem. Eng.* **2018**, *6*, 13045–13055. [CrossRef]
34. He, X.; Wang, J.; Wang, L.; Li, J. Nano-crystalline Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$ prepared via amorphous complex precursor and its electrochemical performances as cathode material for Lithium-ion batteries. *Materials* 2016, 9, 661. [CrossRef] [PubMed]

35. Liu, J.; Chen, H.; Xie, J.; Sun, Z.; Wu, N.; Wu, B. Electrochemical performance studies of Li-rich cathode materials with different primary particle sizes. *J. Power Sources* 2014, 251, 208–214. [CrossRef]

36. Zhang, L.; Wu, B.; Li, N.; Mu, D.; Zhang, C.; Wu, F. Rod-like hierarchical nano/micro Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ as high performance cathode materials for lithium-ion batteries. *J. Power Sources* 2013, 240, 644–652. [CrossRef]

37. Zhao, T.; Gao, X.; Wei, Z.; Guo, K.; Wu, F.; Li, L.; Chen, R. Three-dimensional Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode materials synthesized by a novel hydrothermal method for lithium-ion batteries. *J. Alloy. Compd.* 2018, 757, 16–23. [CrossRef]

38. Li, L.; Wang, L.; Zhang, X.; Xue, Q.; Wei, L.; Wu, F.; Chen, R. 3D reticular Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode material for lithium-ion batteries. *ACS Appl. Mater. Interfaces* 2017, 9, 1516–1523. [CrossRef]

39. Yang, P.; Wang, W.; Zhang, X.; Li, H.; Zhang, S.; Xing, Y. Self-standing Li$_{1.2}$Mn$_{0.6}$Ni$_{0.2}$O$_2$/graphene membrane as a binder-free cathode for Li-ion batteries. *RSC Adv.* 2018, 8, 39769–39776.

40. Hao, R.; Liang, J.; Yang, Z.; Liang, C.; Cuan, X.; Gao, A.; Chen, H. Synthesis and Investigation of the nanocrystalline Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathodes for Li-ion batteries by using ultrasonic/microwave-assisted co-precipitation method with different ultrasonic time. *J. South China Norm. Univ.* 2017, 49, 6–10.

41. Wang, H.; Li, X.; Zhou, Q.; Ming, H.; Adkins, J.; Jin, L.; Jia, Z.; Fu, Y.; Zheng, J. Diversified Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ nanoparticles from birnessite towards application specificity and enhancement in lithium-ion batteries. *J. Alloy. Compd.* 2014, 604, 217–225. [CrossRef]

42. Sun, L.; Yi, X.; Shi, C.; Ren, X.; Gao, Y.; Li, Y.; Zhang, P. A Li-rich Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ cathode material in situ coated with polyaniline. *Int. J. Electrochem. Sci.* 2017, 12, 4756–4767. [CrossRef]

43. Liu, Y.; Zhang, Z.; Fu, Y.; Wang, Q.; Pan, J.; Su, M.; Battaglia, V.S. Investigation the electrochemical performance of Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ cathode material with ZnAl$_2$O$_4$ coating for lithium ion batteries. *J. Alloy. Compd.* 2016, 685, 523–532. [CrossRef]

44. Lin, J.; Mu, D.; Jin, Y.; Wu, B.; Wu, F. Li-rich layered composite Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ synthesized by a novel approach as cathode material for lithium ion battery. *J. Power Sources* 2013, 230, 76–80. [CrossRef]

45. Lee, D.K.; Park, S.H.; Amine, K.; Bang, H.J.; Parakash, J.; Sun, Y.-K. High capacity Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ cathode materials via a carbonate co-precipitation method. *J. Power Sources* 2006, 162, 1346–1350. [CrossRef]

46. Barrett, E.P.; Joyner, L.G.; Halenda, P.P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* 1951, 73, 373–380. [CrossRef]

47. Wang, G.; Xie, J.; Cao, G.; Zhu, T.; Zhao, X.; Zhang, S. Electrochemical performance of 0.5Li$_2$MnO$_2$-0.5LiNiO$_2$-0.5Mn$_2$O$_3$ nanotubes prepared by a self-templating route. *ECS Electrochem. Lett.* 2013, 2, A98–A101. [CrossRef]
56. Reimers, J.N.; Rossen, E.; Jones, C.D.; Dahn, J.R. Structure and electrochemistry of Li$_x$Fe$_{2-y}$Ni$_{1+y}$O$_2$. Solid State Ion. 1993, 61, 335–344. [CrossRef]

57. Hashem, A.M.; Abdel-Ghany, A.E.; Scheuermann, M.; Indris, S.; Ehrenberg, H.; Mauger, A.; Julien, C.M. Doped nanoscale NMC333 cathode materials for Li-ion batteries. Materials 2019, 12, 2899. [CrossRef]

58. A. A.; Zhang, M.; Hy, S.; Cela, D.; Fang, C.; Wynn, T.A.; Qiu, B.; Xia, Y.; Liu, Z.; Ulvestad, A.; et al. Nucleation of dislocations and their dynamics in layered oxide cathode materials during battery charging. Nat. Energy 2018, 3, 641–647. [CrossRef]

59. Li, Y.; Wu, C.; Bai, Y.; Liu, L.; Wang, H.; Wu, F.; Zhang, N.; Zou, Y. Hierarchical mesoporous lithium-rich Li$_{0.2}$Ni$_{0.45}$Mn$_{0.35}$O$_2$ cathode material synthesized via ice templating for lithium-ion battery. ACS Appl. Mater. Interfaces 2016, 8, 18832–18840. [CrossRef]

60. Poyraz, A.S.; Kuo, C.-H.; Biswas, S.; King’ondo, C.K.; Suib, S.L. A general approach to crystalline and monomodal pore size mesoporous materials. Nat. Commun. 2013, 4, 2952. [CrossRef]

61. Chang, C.; Dong, J.; Guan, L.; Zhang, D. Enhanced electrochemical performance of Li$_{1.27}$Cr$_{0.2}$Mn$_{0.53}$O$_2$ layered cathode materials via a nanomilling-assisted solid-state process. Materials 2019, 12, 468. [CrossRef]

62. Lu, Z.; Dahn, J.R. Understanding the anomalous capacity of Li$_{1.2}$Mn$_{0.53}$O$_2$ cathode materials studied by GITT and EIS. J. Phys. Chem. C 2010, 114, 22751–22757. [CrossRef]

63. Thiele, G.; Poston, M.; Brown, R. A Case Study in Sizing Nanoparticles. Micromeritics Instrument Corporation. Available online: http://www.particletesting.com/library (accessed on 1 January 2019).

64. Thackeray, M.M.; Kang, S.-H.; Johnson, C.S.; Vaughey, J.T.; Hackney, S.A. Comments on the structural complexity of lithium-rich Li$_{1+y}$M$_{1-x}$O$_2$ electrodes (M = Mn, Ni, Co) for lithium batteries. Electrochem. Commun. 2006, 8, 1531–1538. [CrossRef]

65. Thackeray, M.M.; Kang, S.-H.; Johnson, C.S.; Vaughey, J.T.; Hackney, S.A. Comments on the structural complexity of lithium-rich Li$_{1+y}$M$_{1-x}$O$_2$ electrodes (M = Mn, Ni, Co) for lithium batteries. Electrochem. Commun. 2006, 8, 1531–1538. [CrossRef]

66. Lu, Z.; Dahn, J.R. Understanding the anomalous capacity of Li/Li[Li$_{1/3}$Mn$_{2/3}$O$_2$] cathode materials using in situ X-ray diffraction and electrochemical studies. J. Electrochem. Soc. 2002, 149, A815–A822. [CrossRef]

67. Hwang, B.-J.; Wang, C.-J.; Chen, C.-H.; Tsai, Y.-W.; Venkateswarlu, M. Electrochemical properties of Li$_x$Ni$\text{Li}_{1-x}$Mn$_{2/3}$O$_2$ positive electrode material for Li-ion battery. In Portable Emergency Energy Sources from Materials to Systems; Stoynov, Z., Vladikova, D., Eds.; Prof. Martin Drinov Academic Publishing House of BAS: Sofia, Bulgaria, 2006; pp. 1–36.

68. Julien, C.; Massot, M. Lattice vibrations of materials for lithium rechargeable batteries. III. Lithium manganese oxides. Mater. Sci. Eng. B 2003, 100, 69–78. [CrossRef]

69. Sun, Y.K.; Lee, M.J.; Yoon, C.S.; Hassoun, J.; Amine, K.; Scrosati, B. The role of ALF$_3$ coatings in improving electrochemical cycling of Li-enriched nickel-manganese oxide electrodes for Li-ion batteries. Adv. Mater. 2012, 24, 1192–1196. [CrossRef] [PubMed]

70. Hwang, B.-J.; Wang, C.-J.; Chen, C.-H.; Tsai, Y.-W.; Venkateswarlu, M. Electrochemical properties of Li$_x$Ni$\text{Li}_{1-x}$Mn$_{2/3}$O$_2$ positive electrode material for Li-ion battery. In Portable Emergency Energy Sources from Materials to Systems; Stoynov, Z., Vladikova, D., Eds.; Prof. Martin Drinov Academic Publishing House of BAS: Sofia, Bulgaria, 2006; pp. 1–36.

71. Julien, C.M.; Massot, M. Lattice vibrations of materials for lithium rechargeable batteries. III. Lithium manganese oxides. Mater. Sci. Eng. B 2003, 100, 69–78. [CrossRef]

72. Sun, Y.K.; Lee, M.J.; Yoon, C.S.; Hassoun, J.; Amine, K.; Scrosati, B. The role of ALF$_3$ coatings in improving electrochemical cycling of Li-enriched nickel-manganese oxide electrodes for Li-ion batteries. Adv. Mater. 2012, 24, 1192–1196. [CrossRef] [PubMed]

73. Mohanty, D.; Sefat, A.S.; Kalnaua, S.; Li, J.; Meisner, R.A.; Payzant, E.A.; Abraham, D.P.; Wood, D.L.; Daniel, C. Investigating phase transformation in the Li$_{1.1}$Co$_{0.1}$Mn$_{0.5}$O$_{2}$ lithium-ion battery cathode during high-voltage hold (4.5 V) via magnetic, X-ray diffraction and electron microscopy studies. J. Mater. Chem. A 2013, 1, 6249–6261. [CrossRef]

74. Song, B.; Lai, M.O.; Lu, L. Influence of Ru substitution on Li-rich 0.55Li$_2$MnO$_3$·0.45LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode for Li-ion batteries. Electrochim. Acta 2012, 80, 187–195. [CrossRef]
76. Li, X.; Xin, H.; Liu, Y.; Li, D.; Yuan, X.; Qin, X. Effect of niobium doping on the microstructure and electrochemical properties of lithium-rich layered Li[Li0.2Ni0.2Mn0.6]O2 as cathode materials for lithium ion batteries. RSC Adv. 2015, 5, 45351–45358. [CrossRef]

77. Zheng, J.M.; Zhang, Z.R.; Wu, X.B.; Dong, Z.X.; Zhu, Z.; Yang, Y. The effects of AlF3 coating on the performance of Li[Li0.2Mn0.54Ni0.15Co0.15]O2 positive electrode material for lithium-ion battery. J. Electrochem. Soc. 2008, 155, A775–A782. [CrossRef]

78. Xiang, X.; Li, W. Self-directed chemical synthesis of lithium-rich layered oxide Li[Li0.2Ni0.2Mn0.6]O2 with tightly interconnected particles as cathode of lithium ion batteries with improved rate capability. Electrochim. Acta 2014, 127, 259–265. [CrossRef]

79. Armstrong, A.R.; Holzapfel, M.; Novak, P.; Johnson, C.S.; Kang, S.; Thackeray, M.M.; Bruce, P.G. Demonstrating oxygen loss and associated structural reorganization in the lithium battery cathode Li[Li0.2Ni0.2Mn0.6]O2. J. Am. Chem. Soc. 2006, 128, 8694–8698. [CrossRef]

80. Hy, S.; Su, W.N.; Chen, J.M.; Hwang, B.J. Soft X-ray absorption spectroscopy and Raman study on Li1.2Ni0.2Mn0.6O2 for lithium-ion batteries. J. Phys. Chem. C 2012, 116, 25242–25247. [CrossRef]

81. Guan, X.T.; Ding, B.; Liu, X.F.; Zhu, J.J.; Mi, C.H.; Zhang, X.G. Enhancing the electrochemical performance of Li1.2Ni0.2Mn0.6O2 by surface modification with nickel-manganese composite oxide. J. Solid State Electrochem. 2013, 17, 2087–2093. [CrossRef]

82. Chen, L.; Su, Y.F.; Chen, S.; Li, N.; Bao, L.Y.; Li, W.K.; Wang, Z.; Wang, M.; Wu, F. Hierarchical Li1.2Ni0.2Mn0.6O2 nanoplates with exposed {010} planes as high-performance cathode material for lithium-ion batteries. Adv. Mater. 2014, 26, 6756–6760. [CrossRef]

83. Nayak, P.K.; Grinblat, J.; Levi, M.; Aurbach, D. Electrochemical and structural characterization of carbon coated Li1.2Mn0.56Ni0.18Co0.06O2 and Li1.2Mn0.6Ni0.4O2 as cathode materials for Li-ion batteries. Electrochim. Acta 2014, 137, 546–556. [CrossRef]

84. Ho, C.; Raistrick, I.D.; Huggins, R.A. Application of a-c techniques to the study of lithium diffusion in tungsten trioxide thin films. J. Electrochem. Soc. 1980, 127, 343–350. [CrossRef]

85. Bard, A.J.; Faulkner, L.R. Electrochemical Methods: Fundamentals and Applications; John Wiley & Sons Inc.: New York, NY, USA, 2001; pp. 226–260.

86. Sasakawa, T.; Harada, Y.; Takami, N.; Kitamura, N.; Idemoto, Y. Influence of initial charge condition on structural stability and electrochemical properties of Li1.2Ni0.2Mn0.6O2 cathode materials. Electrochim. Acta 2015, 174, 406–410. [CrossRef]

87. Xiao, P.; Lv, T.; Chen, X.; Chang, C. LiNio0.8Co0.15Al0.05O2 enhanced electrochemical performance from reduced cationic disordering in Li slab. Sci. Rep. 2017, 7, 1408. [CrossRef] [PubMed]

88. Ku, K.; Kim, B.; Jung, S.-K.; Gong, Y.; Eum, D.; Yoon, G.; Park, K.; Hong, J.; Cho, S.-P.; Kim, D.-H.; et al. A new lithium diffusion model in layered oxides based on asymmetric but reversible transition metal migration. Energy Environ. Sci. 2020, 13, 1269–1278. [CrossRef]

89. Julien, C.M.; Mauger, A. In situ Raman analyses of electrode materials for Li-ion batteries. AIMS Mater. Sci. 2018, 5, 650–698. [CrossRef]

90. Lin, M.-H.; Cheng, J.-H.; Huang, H.-F.; Chen, U.-F.; Huang, C.-M.; Hsieh, H.-W.; Lee, J.-M.; Chen, J.-M.; Su, W.-N.; Hwang, B.J. Revealing the mitigation of intrinsic structure transformation and oxygen evolution in a layered Li1.2Ni0.2Mn0.6O2 cathode using restricted charging protocols. J. Power Sources 2017, 359, 539–548. [CrossRef]

91. Julien, C.M.; Mauger, A. Functional behavior of AlF3 coatings for high-performance cathode materials for lithium-ion batteries. AIMS Mater. Sci. 2019, 6, 406–440. [CrossRef]

92. Vetter, J.; Nováč, P.; Wagner, M.R.; Veit, C.; Möller, K.-C.; Besenhard, J.O.; Winter, M.; Wohlfarth-Mehrens, M.; Vogler, C.; Hammouche, A. Ageing mechanisms in lithium-ion batteries. J. Power Sources 2005, 147, 269–281. [CrossRef]

93. Töltész, U.; Kanoun, O.; Tränker, H.R. Characterizing aging effects of lithium ion batteries by impedance spectroscopy. Electrochim. Acta 2006, 51, 1664–1672. [CrossRef]

94. Kizilias-Yavuz, N.; Herklots, M.; Hashem, A.M.; Abuzeid, H.M.; Schwarz, B.; Ehrenberg, H.; Mauger, A.; Julien, C.M. Synthesis, structural, magnetic and electrochemical properties of LiNi1/3Mn1/3Co1/3O2 prepared by a sol-gel method using table sugar as chelating agent. Electrochim. Acta 2013, 113, 313–321. [CrossRef]

95. Birk, C.R.; Roberts, M.R.; McTurk, E.; Bruce, P.G.; Howey, D.A. Degradation diagnostics for lithium ion cells. J. Power Sources 2017, 341, 373–386. [CrossRef]
96. Cabana, J.; Kwon, B.J.; Hu, L. Mechanisms of degradation and strategies for the stabilization of cathode–electrolyte interfaces in Li-ion batteries. Acc. Chem. Res. 2018, 51, 299–308. [CrossRef] [PubMed]
97. Xu, Z.; Rahman, M.M.; Mu, L.; Liu, L.; Lin, F. Chemomechanical behaviors of layered cathode materials in alkali metal ion batteries. J. Mater. Chem. A 2018, 6, 21859–21884. [CrossRef]
98. Zheng, J.M.; Gu, M.; Xiao, J.; Polzin, B.J.; Yan, P.; Chen, X.; Wang, C.; Zhang, J.-G. Functioning mechanism of AlF3 coating on the Li- and Mn-rich cathode materials. Chem. Mater. 2014, 26, 6320–6327. [CrossRef]
99. Deng, H.; Belharouak, I.; Yoon, C.S.; Sun, Y.-K.; Amine, K. High temperature performance of surface-treated Li1.1(Ni0.11Co0.17Mn0.52)O1.94 layered oxide. J. Electrochem. Soc. 2010, 157, A1035–A1039. [CrossRef]
100. Lee, E.-S.; Manthiram, A. Smart design of lithium-rich layered oxide cathode compositions with suppressed LiF coating on the Li- and Mn-rich cathode materials. Electrochim. Acta 2019, 301, 8–22. [CrossRef]
101. Chen, D.; Zheng, F.; Li, L.; Chen, M.; Zhong, X.; Li, W.; Lu, L. Effect of LiF coating of layered lithium-rich oxide on electrochemical performance. J. Power Sources 2017, 34, 1147–1155. [CrossRef]
102. Shaw, L.; Ashuri, M. Coating—a potent method to enhance electrochemical performance of Li(Ni0.8Mn0.2)O2 cathodes for Li-ion batteries. Adv. Mater. Lett. 2019, 10, 369–380.
103. Sahni, K.; Ashuri, M.; He, Q.; Sahore, R.; Bloom, I.D.; Liu, Y.; Kaduk, J.A.; Shaw, L.L. H3PO4 treatment to enhance the electrochemical properties of Li[Ni0.5Mn0.2Co0.3]O2 and Li[Ni0.5Mn0.5Co0.2]O2 cathodes. Electrochim. Acta 2019, 301, 8–22. [CrossRef]
104. Lee, E.-S.; Huq, A.; Chang, H.-Y.; Manthiram, A. High-voltage, high-energy layered-spinel composite cathodes with superior cycle life for lithium-ion batteries. Chem. Mater. 2012, 24, 600–612. [CrossRef]
105. Lee, E.-S.; Huq, A.; Manthiram, A. Understanding the effect of synthesis temperature on the structural and electrochemical characteristics of layered-spinel composite cathodes for lithium-ion batteries. J. Power Sources 2013, 240, 193–203. [CrossRef]
106. Zhang, X.; Meng, X.; Elam, J.W.; Belharouak, I. Electrochemical characterization of voltage fade of Li1.2Ni0.2Mn0.6O2 cathode. Solid State Ion. 2014, 268, 231–235. [CrossRef]
107. Lee, E.-S.; Manthiram, A. Smart design of lithium-rich layered oxide cathode compositions with suppressed voltage decay. J. Mater. Chem. A 2014, 2, 3932–3939. [CrossRef]
108. Xu, B.; Fell, C.R.; Chi, M.; Meng, Y.S. Identifying surface structural changes in layered Li-excess nickel manganese oxides in high voltage lithium ion batteries: A joint experimental and theoretical study. Energy Environ. Sci. 2011, 4, 2223–2233. [CrossRef]
109. Li, Q.; Li, G.; Fu, C.; Luo, D.; Fan, J.; Li, L. K⁺-Doped Li1.2Mn0.54Co0.13Ni0.13O2: A novel cathode material with an enhanced cycling stability for lithium-ion batteries. ACS Appl. Mater. Interfaces 2014, 6, 10330–10341. [CrossRef]
110. Chong, S.; Wu, Y.; Chen, Y.; Shu, C.; Liu, Y. A strategy of constructing spherical core-shell structure of Li1.2Ni0.2Mn0.6O2@Li1.2Ni0.4Mn0.4O2 cathode material for high-performance lithium-ion batteries. J. Power Sources 2017, 356, 153–162. [CrossRef]
111. Ding, X.; Luo, D.; Cui, J.; Xie, H.; Ren, Q.; Lin, Z. An ultra-long-life lithium-rich Li1.2Mn0.6Ni0.2O2 cathode by three-in-one surface modification for lithium-ion batteries. Angew. Chem. Int. Ed. 2020. [CrossRef]