

Panawan Vanaphuti and Arumugam Manthiram*

The concerns on the cost of lithium-ion batteries have created enormous interest on LiFePO, (LFP) and LiMn, Fe, PO, (LMFP) cathodes However, the inclusion of Mn into the olivine structure causes a non-uniform atomic distribution of Fe and Mn, resulting in a lowering of reversible capacity and hindering their practical application. Herein, a co-doping of LMFP with Nb and Mg is presented through a co-precipitation reaction, followed by a spray-drying process and calcination. It is found that LiNbO₃ formed with the aliovalent Nb doping resides mainly on the surface, while the isovalent Mg²⁺ doping occurs into the bulk of the particle. Full cells assembled with the co-doped LMFP cathode and graphite anode demonstrate superior cycling stability and specific capacity, while maintaining good tap density, compared to the undoped or mono-doped (only with Nb or Mg). The co-doped sample exhibits a capacity retention of 99% over 300 cycles at a C/2 rate. The superior performance stems from the enhanced ionic/electronic transport facilitated by Nb coating and the enhanced $Mn^{2+/3+}$ redox kinetics resulting from bulk Mg doping. Altogether, this work reveals the importance of the synergistic effect of different dopants in enhancing the capacity and cycle stability of LMFP.

1. Introduction

The scarcity, cost, and environmental impact of battery materials urge the need to reconsider cathode compositions to improve sustainability. LiFePO₄ (LFP) and LiMn_{1-x}Fe_xPO₄ (LMFP) are potential candidates compared to other types of cathodes due to their inexpensive raw materials, excellent cycle stability, and high thermal safety.^[1–3] The outstanding thermal stability and safety of LFP and LMFP cathodes are particularly appealing compared to other cathode materials, as it can eliminate the need for additional modification processes in the battery system.^[4–6] Without the need for Ni and Co as in other commercial cathodes in lithium-ion batteries, cost and environmental concerns can be alleviated. Replacing Fe²⁺ with Mn²⁺ in LFP also improves the overall energy density, benefiting from the higher operating voltage

P. Vanaphuti, A. Manthiram

Materials Science and Engineering Program and Texas Materials Institute The University of Texas at Austin Austin, TX 78712, USA

E-mail: manth@austin.utexas.edu

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of Mn (\approx 4.0 V).^[7,8] Regardless of these advantages, LMFP cathodes cannot fulfill the new requirements of electric vehicles due to several challenges, including poor electronic and ionic conductivity, and sluggish kinetics from the Jahn-Teller distortion of Mn³⁺.^[9–12]

Various strategies have been explored to address these challenges, including coating, doping, and morphological engineering.^[13-16] In particular, porous carbon coatings greatly benefit LMFP cathodes, enhancing their electronic conductivity.^[17–20] Additionally, amorphous surface coatings can improve the ionic conductivity of LMFP cathodes by promoting a 3D diffusion channel for Li ions. Studies indicate that high-valent ions, such as Nb, V, Ti, Zr, and Si, are capable of forming amorphous layers based on their oxide composition and can be prepared with several methods, including sol-gel, dry mixing, wet chemical process, and atomic layer deposition (ALD).^[7,21-23] For

instance, a LiNbO₃/Li₃NbO₄ coating has found to improve the lithium-ion diffusion kinetics and the cycling stability of different cathode materials, including high-nickel layered oxides and spinel cathodes.^[24–26] Furthermore, the LiNbO₃/Li₃NbO₄ coating also mitigates surface reactivity between the cathode and electrolyte, thereby reducing active material loss over extended cycling periods. Additionally, LiNbO₃ is more favorable due to its ability to form at lower temperatures while exhibiting performance comparable to Li₃NbO₄.^[24,27–29]

In addition to surface coating, bulk doping plays a crucial role in mitigating the Jahn-Teller distortion of Mn^{3+} , which results from $\geq 40\%$ Mn content in LMFP. Unlike $Fe^{2+/3+}$, $Mn^{2+/3+}$ undergoes both a two-phase transition through a metastable phase and a single-phase solid solution, with Li-ion diffusion occurring solely along a thin phase boundary. This phenomenon imposes kinetic limitations on LMFP cathodes.^[30,31] Electrochemically inactive divalent ions, such as Mg, Co, Ni, and Zn, can minimize the effect of the Jahn-Teller distortion and improve the structural stability by substituting into the Fe^{2+}/Mn^{2+} sites.^[32–34] Among these divalent ions, Mg is a promising candidate due to its costeffectiveness and environmental benefits, as well as its ability to promote solid-solution behavior as seen in LiFePO₄.^[11,32,33,35] Although several studies have demonstrated improved LMFP

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Figure 1. Morphological and structural analyses of the as-prepared LMFP cathodes: a) Schematic diagram of the synthesis process from precursor to LMFP cathode, SEM images of b) undoped, c) 1Nb, d) 3Mg and e) 1Nb3Mg samples, and f) XRD patterns in comparison to the reference pattern for LiMn_{0.5}Fe_{0.5}PO₄ (COD# 2300354).

performance through different carbon coating techniques and morphology design, the synergistic effect of coating and doping remains underexamined.

We present here the impact of LiNbO₃ coating on the surface and Mg doping into the bulk on the performance of LMFP cathode. LMFP cathodes are prepared with a facile co-precipitation reaction, followed by a spray-drying process and calcination. Structural, morphological, and surface analyses are conducted with, respectively, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). The electrochemical performances of the undoped and doped LMFP samples are evaluated through rate capability and cyclability tests, as well as through galvanostatic electrochemical impedance spectroscopy (GEIS). Full cells are assembled with graphite anode and the synthesized cathodes. LiNbO₃ coating on the surface improves the surface ionic conductivity, resulting in a higher specific capacity due to a synergistic effect compared to the undoped and Mg-only-doped or Nb-only-doped samples.

Table 1. Rietveld refinement parameters for the LMFP cathodes from the FullProf Suite software with a $LiMn_{0.5}Fe_{0.5}PO_4$ pattern (COD#2 300 354) as the reference.

Sample	a axis [Å]	b axis [Å]	c axis [Å]	cell volume [Å ³]	χ^2	R _{wp} [%]
Undoped	10.39176	6.05575	4.72070	297.073	1.05	12.6
1Nb	10.39200	6.05489	4.72010	297.000	0.99	12.1
3Mg	10.38736	6.05294	4.72009	296.771	1.14	11.3
1Nb3Mg	10.38498	6.05171	4.71903	296.576	1.14	11.0

2. Results and Discussion

2.1. Morphological and Structural Analysis of the As-Prepared LMFP Cathodes

The morphologies of the as-prepared LMFP samples were examined with SEM after the spray-drying process and calcining (Figure 1a–d). The average particle size is found to be $\approx 6 - 8 \,\mu m$, with a tap density of ≈ 1.0 g cm⁻³, where the primary particle size ranges from 100 to 200 nm. The LMFP precursor was initially synthesized through a facile co-precipitation reaction targeting the (Mn, Fe)₅(PO₄)₂(HPO₄)₂·4H₂O phase (Figure S1, Supporting Information). Subsequently, the LMFP precursor was ball-milled before the spray-drying process, resulting in a decrease in particle size from micrometer to nanometer range. Energy-dispersive X-ray spectroscopy (EDS) mapping confirmed the presence of expected elements with a homogeneous distribution within the secondary particles, as shown in Figures S2-S5 (Supporting Information). To further verify the elemental ratio in all samples, Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was conducted, comparing the results to a commercial FePO₄ powder as a reference. The elemental ratios presented in Table S1 (Supporting Information) indicate that the values closely match the target values, except for P and Nb. This can be attributed to the insensitivity of ICP-OES toward nonmetal elements and the relatively small amount of Nb.

The XRD patterns (Figure 1e of the LMFP samples reveal that they can be well-indexed to the structure of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{PO}_4$ (COD# 2300354) without any impurity peaks. Rietveld refinement was conducted to examine the influence of Nb or Mg on the LMFP structure, and the refinement profile is shown in Figure S6 (Supporting Information). Table 1 implies that the lattice parameters of the 1Nb sample resemble closely those of the undoped sample, suggesting that the Nb coating does not significantly alter the bulk structure. In contrast, the addition of 3 mol% Mg leads to a slight decrease in the lattice parameters due to the smaller ionic radius of Mg²⁺ (0.072 nm) compared to Mn²⁺ (0.083 nm) or Fe²⁺ (0.078 nm).^[32] These results confirm that the as-prepared LMFP materials are both phases pure and possess a reliable composition, validating their suitability for further study.

2.2. Surface Analysis of the As-Prepared LMFP Cathodes

To examine the carbon and Nb coating on the surface of LMFP particles, surface analyses were conducted. To ensure uniform carbon coating across all samples and to exclude it as a factor in performance differences, the carbon coating amount was cal-

culated based on thermogravimetric analysis (TGA) data, involving heating to 700 °C under an air atmosphere. The formation of Fe₂O₃, MnO₂, and Li₃PO₄ from LMFP decomposition resulted in a 2.5% weight gain, with detailed calculation methods explained in the experimental section. According to the mass change in the TGA data (Figure S7, Supporting Information), the carbon content in the undoped, 1Nb, 3Mg, and 1Nb3Mg samples are found to be, respectively, 3.34, 2.96, 2.55, and 2.87 wt.%, which are similar, allowing for a fair comparison of the roles of Mg and Nb. Furthermore, the Fourier-transform infrared spectroscopy (FTIR) spectra in Figure 2a compare the changes in the PO_4^{3-} environment from the impact of carbon coating. The intramolecular vibration (stretching mode) of PO₄³⁻, which happens ≈ 850 – 1200 cm⁻¹, is similar among all samples where the multiplet spectra are correlated to different PO₄³⁻ coupling with Mn/Fe-O in the structure.^[36,37] As the phosphate environmental bonding remains unchanged, it is expected that the carbon coating should be consistent across all samples.

XPS analysis was employed to investigate the presence of Nb coating on the surfaces of the uncoated, 1Nb, and 1Nb3Mg samples. Without sputtering, small peaks in the Nb 3d spectra are observed in the 1Nb and 1Nb3Mg samples, as expected. However, the peaks in the Nb 3d spectra decrease after sputtering for 7 mins (\approx 210 nm), verifying that Nb is present largely on the particle surface rather than in the bulk, although at the calcining temperature of 650 °C, there is a possibility that Nb could slightly diffuse into the inner surface. In contrast to Nb, the Mg 2p spectra show no differences, even in the 1Nb3Mg sample, indicating that Mg is located throughout the bulk. Another indication of particle etching is observed in the C 1s spectra, where the intensity decreases after sputtering, suggesting that the carbon coating is burned off. The long scans of C 1s, Mn 2p, and Fe 2p spectra are shown in Figure 2e-h and S8. Overall, there are no significant differences among the three samples regarding the Mn 2p and Fe 2p spectra. This suggests that the quantities of Mg and Nb added are relatively small, and thus, insufficient to exhibit a noticeable impact on the surface oxidation state. Fe₂P species at \approx 710 eV are found on the particle surface due to the reduction by carbon coating at high calcination temperatures.^[22] However, this species completely disappears after sputtering, indicating that it is only present on the particle surface. Compared to the uncoated sample, the presence of both Mg and Nb promotes the formation of Fe₂P, as indicated by the increased peak area in the Fe₂P spectra. As Fe₂P exhibits good electronic conductivity, it can also benefit the electronic transport in the LMFP cathode.[32]

Studies have shown that Nb coating can form both LiNbO₃ and Li₃NbO₄ phases in layered oxide cathodes depending on the synthesis conditions and the amount of Nb and/or Li availability.^[24,29] To determine the phase formed on the LMFP surface, 10 mol% Nb with 30 mol% excess Li (denoted as 10Nb) was prepared, aiming for the formation of Li₃NbO₄ phase. The high amount of Nb was used to make sure that the phase can be observed on the XRD pattern. As depicted in Figure S9a (Supporting Information), LiNbO₃ is formed instead of the targeted Li₃NbO₄, suggesting that the reducing calcination conditions at 650 °C for LMFP favor the formation of LiNbO₃ phase over Li₃NbO₄. This aligns with other studies, which have reported that LiNbO₃ can be formed at temperatures lower than

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Figure 2. Surface analysis of the as-prepared LMFP cathodes: a) FTIR spectra of the PO_4^{3-} vibrational modes and the XPS b) C 1s, c) Nb 3d3/2, and d) Mg 2p data of the undoped, 1Nb, and 1Nb3Mg samples. The etched samples are those that have undergone sputtering with Ar⁺ for 7 min and the dotted lines indicate the region of interest. Long-scan XPS C 1s, Mn 2p, and Fe 2p data for the e) 1Nb, f) 1Nb etched, g) 1Nb3Mg, and h) 1Nb3Mg etched samples.





Figure 3. Electrochemical testing of the LMFP cathodes: a) EIS data of LMFP || LMFP symmetric cells, showing the contact resistance, b) rate capability tests of half cells from a C/10 to 5C rate, c) first charge-discharge profiles of half cells at a C/10 rate, d) cycling performances of half cells at a C/3 rate, and e) the corresponding Coulombic efficiencies. The nominal capacity for 1C is set to 155 mAh g⁻¹.

that required for Li₃NbO₄ synthesis. According to the binary $Li_2O-Nb_2O_5$ phase diagram, the pure Li_3NbO_4 phase, without the presence of LiNbO3, exists at temperatures above 1150 °C or when the amount of Nb₂O₅ is \geq 25 mol%.^[28,29] The kinetics of the Li₃NbO₄ phase formation may be slower than that of the LiNbO3 phase, as the reaction initially forms as a lithiumfree Nb_xO_y coating, suggesting that the LiNbO₃ phase should have a shorter reaction pathway. Additionally, other impurities, such as Nb₂O₅ and Li₃PO₄, are presented on the XRD pattern. Li₃PO₄ arises from the excess Li used for aiming Li₃NbO₄ formation, while Nb2O5 results from an excessive amount of unreacted Nb source. SEM images in Figure S9b (Supporting Information) show spherical secondary particles with particle sizes of $\approx 6 - 8 \,\mu\text{m}$, consistent with the other as-prepared LMFP samples in this study. The EDS mapping reveals a homogeneous distribution of all the elements, with the computed atomic weight percent for Nb at \approx 9.57%, which is very close to the targeted value (Figure S9c, Supporting Information). These findings further support the reliability of our obtained results.

2.3. Electrochemical Performance of LMFP Cathodes in Half Cells

Prior to electrochemical testing with a Li-metal anode, LMFP || LMFP symmetric cells were employed to assess the effectiveness of carbon coating. The use of tetraethylammonium tetrafluoroborate (Et4NBF4) in acetonitrile as the electrolyte enables a direct measurement of electronic conductivity by impeding Li-ion diffusion through the system. In **Figure 3**a, the EIS data indicate that all the samples exhibit relatively low contact resistance, as evidenced by the small semicircle at the high-frequency range. It is important to note that the slight variations observed in each sample may be attributed to slight reproducibility issues in the spray-drying process. Therefore, the carbon coating is unlikely to significantly influence performance differences. The rate performances from C/10 to 5C rate are shown in Figure 3b. While all the samples exhibit comparable rate capabilities, the 1Nb3Mg sample demonstrates the highest specific capacity, outperforming the other samples. The redox reactions of Fe^{2+/3+} and Mn^{2+/3+} are more clearly observed from the dQ/dV plots in Figure S10 (Supporting Information). At C rates of above 1C, the Nb-doped samples show a better utilization of both redox reactions, as evidenced by their higher peak intensities compared to undoped and Mg-doped samples.^[38,39]

The charge-discharge profiles in Figure 3c consist of two distinct plateaus, with approximately equal ratios of Fe^{2+/3+} at \approx 3.5 V and $Mn^{2+/3+}$ at \approx 4.1 V. Upon closer look at the first chargedischarge profile, it is evident that the Nb coating contributes to improved Li-ion diffusion kinetics, as indicated by the higher specific capacities of the samples containing 1 mol% Nb (1Nb and 1Nb3Mg) compared to the undoped and 3Mg samples. The constant voltage hold further supports this improvement in kinetics at the end of the charging process. This is evident as the time required to reach the current at a C/20 rate or complete the $Mn^{2+/3+}$ redox reaction is significantly shorter for the 1Nb and 1Nb3Mg samples compared to the undoped and 3Mg samples. In addition, the galvanostatic intermittent titration technique (GITT) profiles in Figure 4 support the enhanced kinetics. They indicate that the 1Nb and 1Nb3Mg samples display a smaller voltage drop (ΔV) during the relaxation period of the $Mn^{2+/3+}$ redox reaction, as evidenced by the close-up view of the \approx 4.10 V region on the GITT

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Figure 4. GITT profiles and close-up view regions around the 4.1 V region of the (a,b) undoped, (c,d) 1Nb, (e,f) 3Mg, and (g,h) 1Nb3Mg samples with a Li-metal anode at a C/10 rate where the half cells were cycled between 2.0 and 4.4 V with a current pulse duration of 10 min, followed by a rest period of 3 h.

profiles. It is worth noting that the Li-ion diffusion coefficient was not calculated due to the two-phase reaction of LMFP, unlike layered oxides that have a solid-solution behavior.^[30,40–42] This characteristic makes it challenging to derive quantitative results from the GITT data.

Except for the higher specific capacity of the 1Nb3Mg sample, all samples exhibit excellent cycling stability after 200 cycles at a C/3 rate (Figure 3d,e) with a capacity retention of \geq 98%. To be specific, the capacity retention of undoped, 1Nb, 3Mg, and 1Nb3Mg samples, respectively, are 98%, 99%, 100%, and 99%. The lower specific capacity of the as-prepared LMFP samples is due to their larger particle size and higher tap density compared to those in other reported studies, which typically consist of smaller particle size, higher surface area, and lower tap density.^[8,22,43-45] A higher tap density of our LMFP cathodes can enhance the volumetric energy density of the batteries. Given the abundance of Li from the Li-metal anode in half cells, the next section examines full cells with a graphite anode to observe the performance differences in more practical manner.

2.4. Electrochemical Performance of LMFP Cathodes in Full Cells

The cycling performance and the Coulombic efficiencies of full cells with graphite anode are shown in Figure 5a,b. Benefiting from the synergistic effect of Nb coating and Mg doping, the 1Nb3Mg sample outperforms the other samples with the highest specific capacity and cycle stability with a capacity retention of 99% after 300 cycles at a C/2 rate. It is worth noting that the fluctuating capacity is attributed to changes in room temperature during battery testing. In comparison to the half-cell data, full cells show a more pronounced capacity decay for all samples. Evidently, Mg doping more effectively maintains the structural stability of LMFP cathode compared to the Nb coating, as indicated by the better capacity retention (99%) after 300 cycles compared to undoped (95%) and 1Nb (97%) samples. Figure 5c-f present the charge-discharge profiles of each sample at a C/2 rate for every 100 cycles, suggesting an \approx 50: 50 ratio of Fe and Mn redox reaction. As expected, the 3Mg and 1Nb3Mg samples have smaller capacity drops than the undoped and 1Nb samples. To evaluate the capacity loss without the contribution from cell

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Figure 5. Electrochemical testing of the LMFP cathodes in full cells: a) cycling performances at a C/2 rate, b) the corresponding Coulombic efficiencies, charge–discharge profiles at every 100 cycles for the c) undoped, d) 1Nb, e) 3Mg, and f) 1Nb3Mg samples, and g) the specific capacity at a C/10 rate for every 50 cycles to show the capacity fade. The voltage window is between 2.5 and 4.3 V with an N/P ratio of \approx 1.15.

polarization, the specific capacity at a C/10 rate was collected every 50 cycles as shown in Figure 5g where the charge-discharge profile is presented in Figure S11 (Supporting Information). The 1Nb3Mg sample has the least capacity loss, which further confirms its superior performance in both half cells and full cells.

2.5. Role of Nb and Mg on the Performance of LMFP Cathodes

Based on the electrochemical data presented above, both Nb coating and Mg doping contribute to enhancing the overall performance of LMFP cathodes. While Nb coating increases the specific capacity, Mg doping contributes to structural stability. To gain a deeper understanding of their impacts on kinetic aspects, crucial for LMFP compared to LFP, *operando* GEIS analysis was conducted.^[46] This is because the introduction of Mn can lead to uneven atomic distributions of Fe and Mn. Moreover, the Jahn-Teller distortion of Mn³⁺ ions can induce kinetic limitations for Li-ion diffusion.^[11,31,40] The operando GEIS data of all the samples, shown in Figures 6a-c and S12 (Supporting Information), were collected by controlling the current at a C/20 rate for ≈ 15 h to observe the changes in resistance during the charging process. It is worth noting that LTO was chosen as the anode because its spectra remained unchanged during the region of interest, ensuring that any observed changes would originate solely from the cathode side (Figure S13, Supporting Information). These data include the Fe^{2+/3+} redox region, the transition to Mn redox, and the $Mn^{2+/3+}$ redox region, each separated by the red dotted line on the plot. While the spectra exhibit a similar trend, the 1Nb sample shows slightly higher contact resistance compared to the other samples. This aligns with our previous study on LiNiO₂ cathode, which suggests that Nb coating can impede Li diffusion in the initial cycles and may require an activation process.^[26]



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Figure 6. Operando GEIS analysis of the LMFP samples with LTO anode at a C/20 rate and 25 °C for the a) undoped, b) 1Nb, and c) 3Mg samples where the dotted red lines separate the $Fe^{2+/3+}$ redox region, the transition to Mn redox, and the $Mn^{2+/3+}$ redox region. The N/P ratio was kept at 1.20. The data were collected for 15 h, a duration time determined by the charging time to reach a specific capacity of 25 to 100 mA h g⁻¹. d) Plot of the fitted R_{ct} values during the charging process at the $Mn^{2+/3+}$ redox region, showing the changes in resistance.

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Upon a closer examination of each region, the $Fe^{2+/3+}$ redox suggests a smooth transition, with the spectra showing relatively consistent small contact resistance and no charge-transfer resistance (R_{ct}) at a low-frequency range. It is worth noting that the R_{ct} is the charge-transfer resistance at the interfaces of the electrode and electrolyte. In contrast, the $Mn^{2+/3+}$ redox is more complex, behaving as a two-phase reaction when Mn content \geq 40%.^[47-49] The EIS data during Mn redox comprises contact resistance at high frequency and R_{ct} at low frequency, followed by a diagonal line known as the Warburg impedance element. R_{et} can be calculated by fitting the spectra, and the resulting R_{ct} values during Mn^{2+/3+} redox are plotted versus the specific capacity in Figure 6d. The doped samples show a lower R_{ct} compared to the undoped sample, especially the samples with Mg dopant, where the $R_{\mbox{\tiny ct}}$ remains unchanged across the Mn redox region. This suggests that Mg improves the electronic conductivity at the electrode surface as well, allowing better Li-ion diffusion. Meanwhile, the Nb coating also reduces the R_{ct} to a certain degree but still shows fluctuations similar to the undoped sample. This further emphasizes the importance of the co-doping strategy.

3. Conclusion

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In this work, LiNbO₃ coating and Mg doping were introduced to LMFP cathodes via a spray-drying process, followed by calcination. The precursor for LMFP synthesis was obtained with an ammonia-free co-precipitation reaction. Based on the surface analyses and Rietveld refinement, the Nb coating is mainly located on the particle surface, while Mg acts as a bulk dopant. Electrochemical testing reveals that this co-doping strategy significantly enhances the specific capacity and cycle stability, while maintaining good tap density, compared to Nb coating alone or Mg doping alone. In particular, the full-cell of the 1Nb3Mg sample provides the best performance with a capacity retention of 99% after 300 cycles at a C/2 rate. The cycle degradation with a graphite anode primarily results from the loss of Li inventory. From the GITT and operando GEIS results, it is found that Nb coating improves electronic and ionic conductivities, resulting in a higher reversible capacity compared to undoped and 3Mg samples. Meanwhile, Mg doping supports structural stability by minimizing the Jahn-Teller effect of Mn³⁺ during cycling, facilitating the Mn^{2+/3+} redox region, and enhancing electronic conductivity. Overall, this work offers an inexpensive, yet effective approach, to enhance the performance of LMFP cathodes and promotes its potential for practical cells.

4. Experimental Section

Materials Preparation: The (Mn, Fe)₅ (PO₄)₂ (HPO₄)₂·4H₂O (MFP) precursor was synthesized with a conventional co-precipitation method. The transition metal solution, containing stoichiometric ratios of MnSO₄·H₂O (0.125 mol), FeSO₄·7H₂O (0.125 mol), and H₃PO₄ (0.20 mol) in a 250 mL aqueous solution, was added dropwise to a reaction solution consisting of H₃PO₄ (0.02 mol) and NaOH (0.02 mol) in a 350 mL aqueous solution te constant feed rate of 5 rpm. A small amount of ascorbic acid (0.001 mol) was included in the transition-metal solution to prevent the oxidation of Fe²⁺ to Fe³⁺. A basic solution, consisting of 0.5 mol NaOH in 100 mL aqueous solution, was used to control the pH and added dropwise at a constant feed rate of 1.5 rpm. The reaction was

conducted at a temperature of 75 °C, a pH of \approx 5, and a stirring speed of 450 rpm. The resulting precipitate was filtered, washed thoroughly with deionized water, and dried in an oven at 100 °C overnight.

The precursor was mixed uniformly with the carbon sources (lactose (ChemCenter) and maltodextrin (Sigma-Aldrich) in a 0.7: 0.3 weight ratio), with a total carbon content of 4.0 mol%. Additionally, a Li source (Li₂CO₃) with a 5 mol% excess, and stoichiometric amounts of P and Li sources (Li_3PO_4) were added to obtain $LiMn_{0.5}Fe_{0.5}PO_4$. In the case of doped samples, a 1 mol% Nb and/or 3 mol% of Mg was incorporated into the mixture with NH₄[NbO(C₂O₄)₂(H₂O)₂]·H₂O (CBMM) and $MgC_2O_4 \cdot 2H_2O$ (Alfa Aesar) as the respective precursor sources with the assumption that Mg and/or Nb would substitute the Mn and Fe equally. A 1.5 wt.% carboxymethyl cellulose (CMC) solution in water served as a dispersant. Specifically, a mixture of 0.93 g of lactose, 0.40 g of maltodextrin, 0.33 g of 1.5 wt.% CMC, 0.66 g of Li_2CO_3 , 2.07 g of Li_3PO_4 , \approx 8.50 g of MFP precursor, 0.22 g of $NH_4[NbO(C_2O_4)_2(H_2O)_2] \cdot H_2O$, and 0.27 g of MgC₂O₄·2H₂O was prepared in 33 g of deionized water. The slurry was milled at 450 rpm for 3 h in a planetary ball mill (FRITSCH Pulverisette 6) with a solid loading of 27 wt.%. To mitigate water evaporation caused by the intensive milling process, a 30-min rest period was implemented after every 10 min of milling. After ball-milling, the slurry was spray-dried (LABFREEZ SD-501) at a pumping rate of 2 rpm where the inlet temperature, outlet temperature, air flow rate, nozzle pressure, and nozzle size were controlled to be, respectively, 130 °C, 102 °C, 17 cfm, 0.16 MPa, and 0.7 mm. The obtained powder was calcined in a two-step process; 350 °C for 1 h and 650 °C for 2 h under an argon atmosphere with a ramping rate of 10 °C min⁻¹. Subsequently, the LMFP powder was passivated for 30 min in 10% air at room temperature to create a thin, uniform oxidation product on the outermost carbon layer. A total of four samples were synthesized including $LiMn_{0.5}Fe_{0.5}PO_4$ (undoped), $LiMn_{0.495}Fe_{0.495}Nb_{0.01}PO_4$ (referred to as 1Nb), LiMn_{0.485}Fe_{0.485}Mg_{0.03}PO₄ (referred to as 3Mg), and $LiMn_{0.48}Fe_{0.48}Mg_{0.03}Nb_{0.01}PO_4 \text{ (referred to as 1Nb3Mg)}.$

Materials Characterization: XRD analysis was performed with a Rigaku Miniflex 600 instrument with a Cu K_a target ($\lambda = 1.54$ Å), whileSEM with EDS was conducted with a Tescan Vega3 system coupled with a Bruker XFlash Detector 630 M. These analyses were carried out to investigate the structural and morphological characteristics of the as-prepared LMFP cathodes. The XRD patterns were collected over a 2 θ range of 10°–80° with a step size of 0.02° and a scan rate of 1.5° min⁻¹. Structural information on the LMFP cathodes was obtained with the FullProf Suite software, which compared the obtained patterns to the reference pattern COD# 2300354. ICP-OES (Agilent 5800) analysis was conducted to confirm the ratio of each element. The samples were dissolved in a mixture of nitric acid and hydrochloric acid in a 1: 1 ratio and diluted into an appropriate concentration (parts per million). The tap density was measured with Quantachrome Autotap Tap Density Analyzer.

The carbon content in the LMFP samples was determined via TGA with a Netzsch STA 449 F3 instrument under an air atmosphere. The analysis was conducted over a temperature range of 30 to 700 °C, with a ramping rate of 5 °C min⁻¹ in an alumina crucible. The theoretical weight gained by LMFP is \approx 2.5 wt.% without any carbon, as it decomposes in air atmosphere, yielding Fe_2O_3 , $Mn_3(PO_4)_2$, and Li_2O byproducts. Therefore, the carbon content for each sample was calculated based on the TGA data (2.5 wt.% minus the mass change from TGA (%)). The impact of carbon coating on the phosphate neighboring environment was studied through FTIR in the attenuated total reflectance (ATR) mode with a Thermo Scientific Nicolet-iS5 instrument. Spectra were collected between 500 to 1600 cm⁻¹ under ambient condition, with each spectrum composed of 32 scans at a resolution of 4 cm^{-1} . To confirm the presence of Nb coating on the LMFP surface, XPS data were collected with a Kratos Axis Ultra DLD spectrometer with an Al K_{α} radiation excitation source ($h\nu = 1486.5 \text{ eV}$). LMFP particles were sputtered with Ar⁺ ions (500 V) for 7 mins to observe the inner surface. CasaXPS software was used to analyze the XPS data, with all peak positions calibrated with respect to the carbon peak at 248.8 eV.

Electrochemical Evaluation: The LMFP electrodes were prepared by mixing the active material, Super C65, along with 10 wt.% polyvinylidene fluoride (PVDF) dissolved in N-Methyl-2-pyrrolidone (NMP) in a weight ratio of 94: 3: 3 with a solid loading of 38 wt.%. The slurry was mixed with

a Thinky mixer and then coated onto a carbon-coated aluminum foil current collector. The coated electrodes were dried overnight at 120 °C under a vacuum to eliminate excess NMP and moisture. The LMFP electrodes were calendared to achieve a packing density of ≈ 1.8 g cm⁻³ before being punched into disks with a diameter of 12.7 mm in half cells and 14.3 mm in full cells. The active material loading is ≈ 1.7 mA h cm⁻².

Coin cells were assembled inside an argon-filled glove box, consisting of the LMFP cathode, Celgard 2325 separator, lithium-metal anode (450 μ m thick), and 60 μ L of electrolyte. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3:7 by volume) with a 2% vinylene carbonate (VC) additive (denoted as LP57 from Gotion). Full cells were assembled following the same procedure, except that the anode was switched from Li metal to graphite (Imerys) with a diameter of 15.9 mm. The N/P ratio was kept at 1.15 by accounting for the theoretical capacity of LMFP as 155 mÅ h g^{-1} and graphite as 350 mA h g^{-1} . The graphite electrode consisted of active material, super C65, and a water-based binder (0.5 wt.% of 5 wt.% dialdehyde sodium alginate (DSA) in water, 1.0 wt.% of 1.5 wt.% sodium carboxymethyl cellulose (CMC) in water, 2.5 wt.% of 25 wt.% styrene-butadiene rubber (SBR) in water, 0.05 wt.% of 1 wt.% oxalic acid in water) in a 95: 2.5: 2.5 ratio. The solid loading was kept at 53 wt.% and the active material loading was \approx 2.0 mA h cm⁻²

The cells were evaluated with a Land Battery Testing System (CT2001A) at room temperature (\approx 25 °C), following a 5-h rest period. For cycling performance evaluations, three formation cycles were conducted at a C/10 rate, followed by subsequent charge-discharge cycles at a C/3 rate, with a nominal capacity where 1C rate is equal to 155 mA h g^{-1} . The voltage range was maintained between 2.0 and 4.4 V, with a constant voltage held at 4.4 V during each charge cycle until the current dropped below the C/50 rate. The rate capability tests were conducted similarly, but the testing range extended from a C/10 to 5C rate. During the cycle test of full cells, the voltage range was held between 2.5 and 4.3 V, with a constant voltage hold of 4.3 V applied during each charge cycle until the current dropped below the C/50 rate. Following the three formation cycles at a C/10 rate, the cells underwent charge-discharge cycles at a C/2 rate. EIS data for the LMFP || LMFP symmetric cells were acquired with a Biologic VMP3 potentiostat over a frequency range of 100 mHz to 500 kHz with a 10 mV amplitude. The test was conducted at the open-circuit voltage (OCV) state, \approx 0.00 V. To assess the contact resistance between the active materials and the current collector of these symmetric cells, 1.0 M Et4NBF4 in acetonitrile was used as the blocking electrolyte to minimize ionic diffusion and measure only electronic conductivity.

To evaluate the ionic conductivity in half-cell configuration, GITT was performed following three formation cycles at a C/10 rate, cycling between 2.0 and 4.4 V with a current pulse duration of 10 min, followed by a rest period of 3 h. To monitor the resistance changes during the charging cycle, operando GEIS was conducted by applying a current at a C/20 rate, ranging from 10 mHz to 500 kHz, with a 10-mV amplitude. Before operando GEIS testing, the full cells underwent two formation cycles at the C/20 rate. The data were collected for \approx 15 h, a duration time determined by the charging time to reach a specific capacity of 25 to 100 mA h g^{-1} . The theoretical capacity for this calculation was based on the experimental capacity of each sample at the C/20 rate, with the PR, 1Nb, and 3Mg samples at \approx 130 mAh g⁻¹, and the 1Nb3Mg sample at \approx 140 mA h g⁻¹. To ensure no influence from the anode side on the resistance value, a $Li_4Ti_5O_{12}$ (LTO) anode was used instead of graphite or Li metal, as LTO resistance remains constant across the testing region. The LTO electrode preparation involved mixing the active material, Super C65, with PVDF (10 wt.% dissolved in NMP at a weight ratio of 90: 5: 5, achieving a solid loading of 38 wt.%. Subsequently, the mixture was punched into 14.3 mm discs, maintaining an N/P ratio of \approx 1.20. The theoretical capacity of LTO used for the calculations was 160 mA h g^{-1} .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrochemistry, lithium manganese iron phosphate, lithium-ion batteries, Mn redox kinetics, niobium doping

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