

Characterization of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ as a cathode material for solid-state lithium batteries: A study on its structural and electrical attributes

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Abstract

This study presents the synthesis of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ (LM9F) and its carbon-coated counterpart, $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ with 10% carbon (LM9F-10%C), through a straightforward solid-state method. The synthesis utilized lithium carbonate, manganese (II) acetate tetrahydrate, iron phosphate, ammonium dihydrogen phosphate, and glucose powder as the carbon source. To achieve a fine powder, a high-energy ball milling was performed at 270 rpm for 8 h, followed by calcination at 700 °C for 3 h and sintering at the same temperature for an additional 2 h, under a nitrogen atmosphere to prevent iron oxidation. Thermoanalytical techniques (TGA–DTA–DSC) were applied between 30 °C and 1000 °C to study the thermal decomposition behaviors of the precursors and pinpoint the phase formation temperature, which was identified at 416 °C. X-ray diffraction analysis verified the formation of a pure olivine orthorhombic structure, corroborated by Rietveld refinement. The morphology of the calcined powders, characterized by field emission scanning electron microscopy, showed agglomerated semi-spherical particles with an average size of 34 nm. Fourier transform infrared spectroscopy confirmed the presence of the phosphate groups integral to the olivine framework. Electrical properties measured via an LCR meter across 20 Hz to 100 kHz demonstrated that the inclusion of carbon significantly reduced impedance and improved the electrical performance of the materials.

Keywords

$\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$, solid state batteries, electrical properties, high energy ball milling

1. Introduction

Since their introduction by Padhi and colleagues in 1997 [1], lithium transition metal phosphates (LiMPO_4 , where $M = \text{Fe, Mn, Co, Ni}$) featuring an olivine structure have been recognized as some of the most promising cathode materials for lithium-ion batteries (LIBs) [2, 3]. These phospho-olivine compounds have garnered

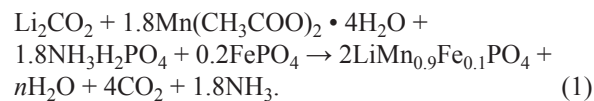
significant attention from both academic and industrial sectors for their potential to offer enhanced electrochemical properties. Olivine-structured cathodes are highly valued in the LIB community for their remarkable stability during the lithium insertion and extraction processes, excellent thermal properties, and superior discharge capacities. They stand out for their high theoretical capacity, affordability, abundance in nature, and minimal tox-

icity, especially when compared to conventional layered rock salt oxides like LiCoO_2 and LiNiO_2 [4–10]. Among these, lithium iron phosphate (LiFePO_4) has emerged as a standout cathode material, having been successfully commercialized due to its theoretical capacity of around 170 mA/h and an operational voltage of 3.45 V versus Li/Li^+ . However, LiFePO_4 is hindered by its low electronic conductivity (below 10^{-9} S/cm) and poor Li^+ ion diffusion, which limit its performance in high-power applications, such as in electric vehicles [11–13]. To address these challenges, strategies such as carbon coating [14, 15] particle size reduction [16–18] and elemental doping have been explored [19–22]. Lithium manganese phosphate (LiMnPO_4) is another promising olivine family member, noted for its higher operational voltage of 4.1 V compared to LiFePO_4 , positioning it well within the electrochemical stability window of conventional electrolytes for high-energy applications [9, 23, 24]. The use of manganese not only enhances the environmental friendliness and cost-effectiveness of the material but also presents challenges in cyclic stability and rate capability due to its slow kinetics and lower ionic and electronic conductivity [5, 23–26]. The instability caused by Mn^{3+} ions, susceptible to the Jahn–Teller distortion, further complicates its application [27, 28]. Addressing the conductivity issues of LiMnPO_4 has led to investigations into particle size reduction, carbon coating, and cation substitution with elements like Fe, Zn, and Mg [29–33]. The synthesis method is crucial, influencing the material's morphology, crystal size and orientation, porosity, carbon coating presence, and degree of agglomeration, all of which significantly impact electrochemical performance [34–37]. In this study, we successfully synthesized a solid solution of $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ through a conventional high-energy ball milling (HEBM) technique, aimed at producing fine particles efficiently and cost-effectively. Additionally, a $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ with 10% carbon (denoted as LM9F-10%C) was prepared to assess the influence of carbon on the electrical properties of this cathode material. We conducted a comprehensive analysis of the thermal properties of the precursors, along with detailed investigations into the structural, molecular, and morphological characteristics of the samples, herein referred to as LM9F for $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ and LM9F-10%C for the carbon-coated variant.

2. Materials and methods

The lithium olivine structure LM9F was produced using a single-step solid-state reaction, employing the high-energy ball milling technique. Monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) was employed as the source of PO_4 , while lithium carbonate (Li_2CO_3) served as the source of Li. Manganese (II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and iron phosphate (FePO_4) were utilized as the sources of Mn and Fe, respectively. Additionally, glucose powder served as the carbon source, while ethanol facilitated

the creation of a uniform mixture. The precise amounts of each component were measured under pre-established formulas as shown in Eq. (1).



Following the initial mixing, the blend was combined with ethanol and then subjected to pulverization through the application of three quartz balls within a vessel, using the HEBM technique. This was conducted at a rotational speed of 270 rpm over a period of 8 h. After milling, the mixture achieved a uniform powdery consistency and was then air-dried in an oven to remove any residual moisture. The semi-dry, finely textured powder was then placed in a zirconia boat and calcined in a tube furnace at 700 °C for three hours under a nitrogen gas atmosphere to prevent the oxidation of iron. After calcination, the powder was pressed into a disk, measuring 11.7 mm in diameter and 1.3 mm in thickness, under a force of 100 kN. This disk was then sintered in a tube furnace at 700 °C for 2 h, also under a nitrogen gas flow. For the preparation of the LM9F solid solution with carbon coating, stoichiometric proportions of the dried milled powder precursors were blended with 10% weight of glucose and milled at 270 rpm for 2 h, following the same subsequent preparation steps. To analyze the thermal decomposition of the LM9F sample's starting materials during calcination and to pinpoint the precise temperature for phase formation, a Q-600 Thermo-gravimetric analyzer was utilized. This analysis was carried out under a 60 ml/min argon gas flow and a heating rate of 20 °C/min, ranging from 30 °C to 1000 °C.

The analysis of crystalline structures in the calcined LM9F powder was performed through X-ray diffraction (XRD) analysis, utilizing a diffractometer with a copper source emitting rays of 0.15406 nm wavelength, set to function at 45 kV and 30 mA. The range of Bragg angles explored spanned from 20° to 80°, employing a step time of 1 s. Additionally, to delve into the molecular architecture of the particles, Fourier transform infrared spectroscopy (FTIR) assessments were carried out. These utilized a Shimadzu FTIR spectrometer, canvassing a wavenumber spectrum from 400 to 4000 cm^{-1} . The electrical properties of the sintered specimens were scrutinized using an LCR meter (Model WK4310), which measured across frequencies ranging from 20 Hz to 100 kHz and temperatures escalating from ambient (roughly 23 °C) to 168 °C. To facilitate these evaluations, samples were mounted between two electrodes and covered with silver paste to enhance electrical contact.

3. Results and discussion

The investigation into the thermal behavior of the solid solution LM9F precursors throughout the calcination

process offers pivotal insights into their stability and decomposition patterns, which are crucial for optimizing their synthesis for use as cathode materials in lithium-ion batteries. Figures 1a and 1b serve to visually represent these thermal characteristics, showcasing the thermos-gravimetric analysis (TGA) and the derivative thermos-gravimetry (DTG) curves, respectively. The TGA curve provides a foundational understanding of the weight changes that the LM9F precursors undergo as a function of temperature. Building upon this, the DTG curve, derived from the TGA data, offers a more nuanced view by pinpointing the specific temperatures at which these weight changes occur. This dual analysis approach not only enhances the accuracy of the thermal characterization but also simplifies the interpretation of the calcination behavior of LM9F precursors. The inclusion of the DTG curve is particularly advantageous as it elucidates the precise moments of significant thermal events, such as decomposition or phase transitions, by highlighting peaks corresponding to rates of weight loss. This analytical method facilitates a more detailed investigation into the thermal stability and decomposition pathways of the precursors, which are essential for understanding the formation mechanisms of the LM9F phase. Furthermore, by correlating these thermal events with specific temperatures, researchers can optimize the calcination process to ensure the complete conversion of precursors into the desired cathode material while minimizing unwanted by-products. The analysis of the thermal behavior of LM9F precursors is not just a procedural step in the material synthesis but a window into the complex interplay of chemical reactions occurring during heat treatment. As we delve deeper into the results and discussion sections, we will explore how these thermal characteristics influence the final material properties of LM9F, such as crystal structure, purity, and electrical performance. Additionally, understanding the thermal decomposition and stability of these materials underpins the development of more efficient and robust synthesis methods, potentially leading to cathode materials with improved performance

in lithium-ion batteries. This comprehensive approach to analyzing and discussing the thermal behavior of LM9F precursors sets the stage for a detailed exploration of the implications of these findings on the material's suitability for energy storage applications [18, 38–40].

The addition of glucose powder serves as a carbon source that, upon thermal decomposition, forms a carbon coating on the LM9F particles. This carbon coating is significant because it enhances the electronic conductivity of the cathode material, which is otherwise a poor conductor. This improvement in conductivity facilitates better charge transfer kinetics during electrochemical reactions. Furthermore, the carbon coating helps to mitigate particle agglomeration and provides a protective barrier against electrolyte decomposition, thereby enhancing the overall stability and performance of the LM9F solid solution.

In the TGA depicted in Fig. 1a, the data delineate four distinct intervals of mass reduction throughout the heating protocol. The initial phase, occurring between 51 °C and 110 °C and accounting for a 5.21% loss in mass, is primarily attributed to the evaporation of water molecules adsorbed on the surface and those incorporated within manganese acetate, resulting in the creation of its anhydrous form. This phase likely includes the dissipation of any lingering ethanol within the sample. Proceeding to the second interval, noted between 134 °C and 164 °C, there is an 8.01% decrease in mass. The third interval, identified between 182 °C and 215 °C, sees a reduction in mass by 4.88%. The final and most pronounced interval spans from 289 °C to 376 °C, where a significant 21.92% mass loss is observed, indicative of the breakdown of carbonates, decomposition of manganese acetate, degradation of organic phosphonates, and the loss of crystalline water, respectively [41]. As the thermos-gravimetric curve for the LM9F starting materials plateaus, indicating a shift to a stable mass range between 416 °C and 700 °C, it suggests the cessation of phase transitions and possibly marks the onset of the LM9F crystallization process around 416.21 °C. The crystallization of LM9F at this temperature is crucial as it indicates the formation

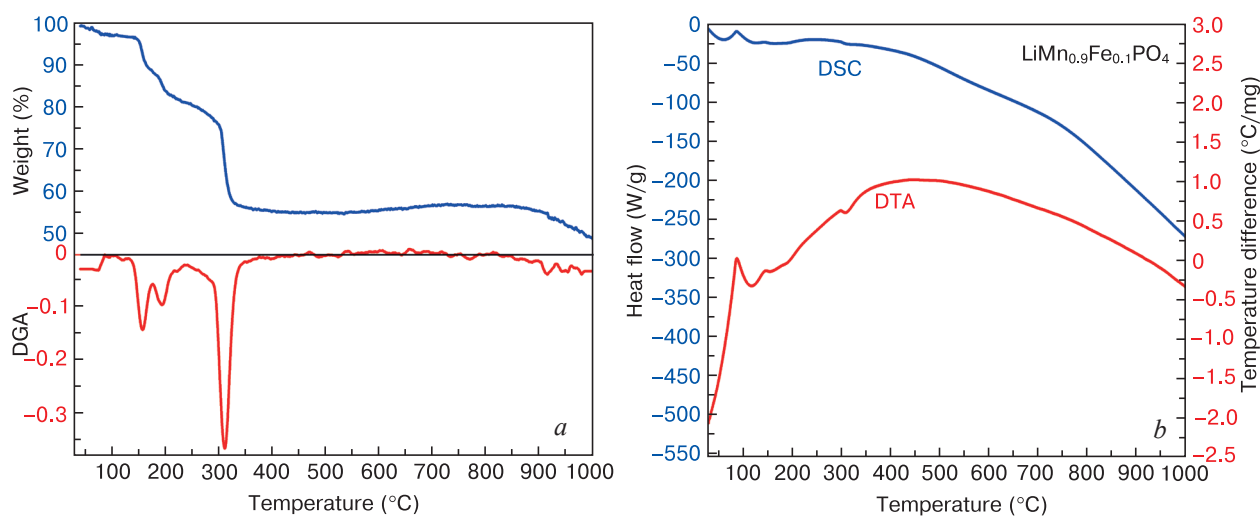


Figure 1. (a) TGA/DTGA and (b) DSC/DTA curves of precursors at 20 °C/min in Ar atmosphere

of a well-defined crystalline structure, which is essential for achieving optimal electrochemical performance. A well-crystallized LM9F structure ensures better lithium-ion diffusion pathways and structural stability during charge-discharge cycles, which directly enhances the electrochemical properties such as capacity, cycling stability, and rate capability. Complementary to the TGA findings, Fig. 1b showcases the differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves for the LM9F initial materials. An early exothermic peak at 44.5 °C on the DTA curve is linked to desorption processes. Additionally, a trio of exothermic peaks

ranging from 145.3 °C to 302.78 °C on the DTA curve, mirrored closely by the DSC curve within the same temperature band, signifies the stages of decomposition as outlined by the TGA. An endothermic peak on both the DTA and DSC curves signals a reduction reaction. Moreover, an endothermic peak at 416.21 °C observed on the DTA curve is associated with the crystallization phase of the sample, aligning with the thermogravimetric analysis's suggestion of the crystallization initiation at a similar temperature.

Figure 2a presents the XRD analysis of the calcined LM9F powder, showcasing a pattern that confirms the

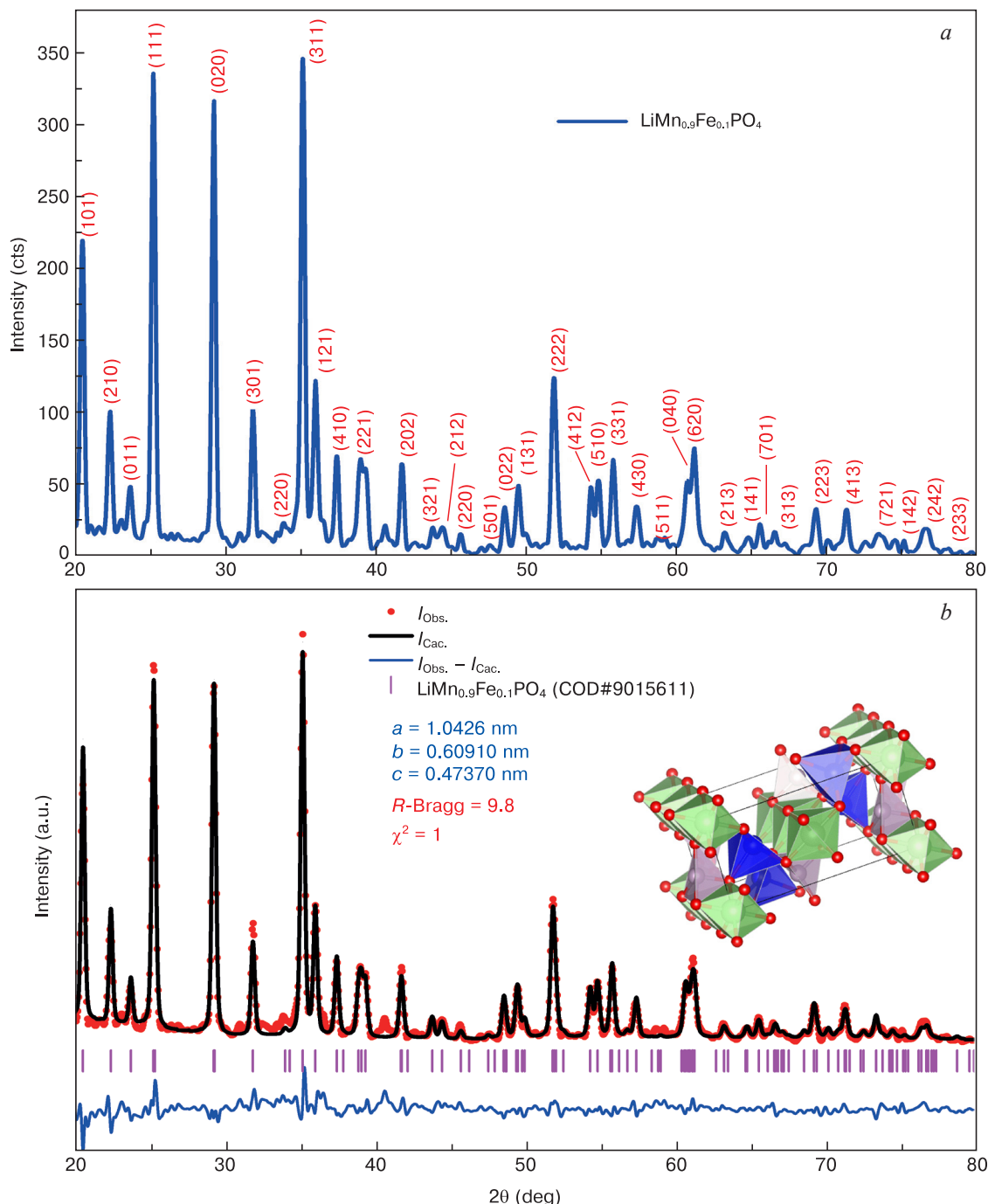


Figure 2. (a) XRD profile of LM9F post-calcination at 700 °C in a nitrogen atmosphere, (b) Rietveld analysis of LM9F powder post-calcination at 700 °C under nitrogen environment

Table 1. Crystallite size for $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ depending on Scherrer formula

2 θ (deg)	d (nm)	I/I_0	FWHM total	FWHM instr.	FWHM sample	Crystallite size (nm)
20.584	0.43115	561.7	0.3	0.09	0.21	40.19
22.384	0.39687	222.5	0.3	0.09	0.21	40.31
23.734	0.37459	83.7	0.3	0.09	0.21	40.41
25.284	0.35197	905	0.3	0.09	0.21	40.53
29.334	0.30423	845.4	0.3	0.09	0.21	40.88
31.934	0.28003	259.1	0.3	0.1227	0.1773	48.71
32.534	0.27500	21.9	1.4	0.1345	1.2655	6.84
33.984	0.26359	43.6	0.4	0.1381	0.2619	33.16
35.234	0.25452	1000	0.4	0.1158	0.2842	30.65
36.084	0.24871	292	0.4	0.1014	0.2986	29.25
37.484	0.23974	173.3	0.3	0.0802	0.2198	39.89
39.084	0.23029	176.6	0.5	0.0861	0.4139	21.29
40.684	0.22159	42.6	0.4	0.0915	0.3085	28.71
41.834	0.21576	164.4	0.4	0.0951	0.3049	29.16
44.534	0.20329	47.4	0.5	0.0979	0.4021	22.32
45.734	0.19823	32.2	0.3	0.0956	0.2044	44.09
48.684	0.18688	83.6	0.4	0.0904	0.3096	29.44
49.584	0.18370	121.3	0.4	0.09	0.31	29.51
51.934	0.17593	345.7	0.4	0.09	0.31	29.8
54.884	0.16715	133.7	0.4	0.09	0.31	30.18
55.884	0.16439	165.7	0.4	0.09	0.31	30.32
57.434	0.16032	84.9	0.4	0.09	0.31	30.54
58.834	0.15683	21.1	0.5	0.09	0.41	23.25
61.284	0.15114	194.5	0.4	0.09	0.31	31.14
63.334	0.14673	32.3	0.3	0.09	0.21	46.46
64.884	0.14359	24.0	0.5	0.09	0.41	24.00
65.634	0.14213	44.7	0.3	0.09	0.21	47.05
66.634	0.14024	32.5	0.4	0.09	0.31	32.06
69.384	0.13534	79.4	0.4	0.0945	0.3055	33.06
71.384	0.13203	77.5	0.4	0.0992	0.3008	33.99
73.534	0.12869	33.5	0.6	0.1	0.5	20.73
74.634	0.12706	21.1	0.4	0.1	0.3	34.81
76.684	0.12417	46.0	0.5	0.1	0.4	26.47
Average = 33.1 nm						

formation of a pure phase with no detectable secondary crystalline structures. The peaks observed in the XRD pattern correspond precisely with the standard data for the olivine orthorhombic structure, characterized by the space group $Pnma$ (COD #9015611) [42, 43]. The pronounced sharpness of these peaks suggests a high degree of crystallinity within the sample. Following phase identification, the XRD pattern for the calcined LM9F powder underwent Rietveld refinement, the details of which are illustrated in Fig. 2b. This refinement process, executed using the full-prof program, demonstrated an excellent concordance between the theoretical pattern derived from

the refinement and the actual experimental observations. The lattice parameters of the LM9F powder, refined to $a = 1.0462$ nm, $b = 0.60910$ nm, and $c = 0.47370$ nm, closely matched those listed in the COD database (COD #9015611) [42–44] which are recorded as $a = 1.04310$ nm, $b = 0.60947$ nm, and $c = 0.47366$ nm. The refinement concluded successfully with a goodness-of-fit value (χ^2) of 1, and an R -Bragg factor of 9.8, confirming the reliability of the analysis. Furthermore, the average crystallite size for the LM9F powder was calculated to be 33.1 nm, employing the Scherrer formula, with detailed values provided in Table 1. This analysis underscores the

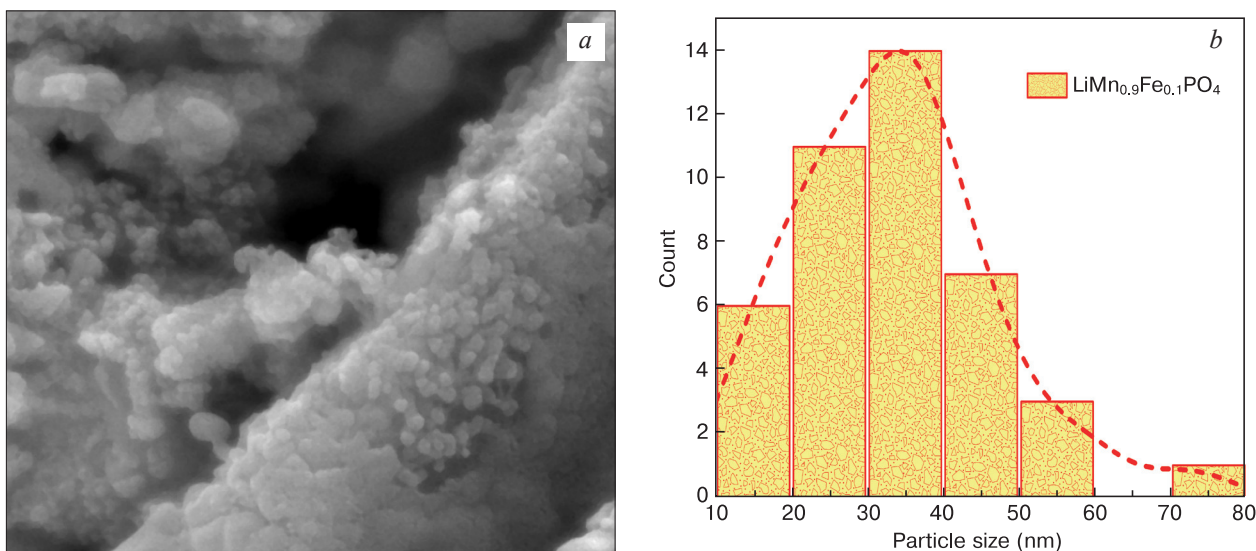


Figure 3. (a) FE-SEM image and (b) particle distribution of LM9F sample

precision in matching the observed data with the known crystalline structure and the high purity of the synthesized powder.

Figure 3a shows an field emission scanning electron microscopy (FE-SEM) image of calcined LM9F powder. The FE-SEM image reveals of agglomerating semi-sphere particle shape. The diagram reveals that the particles, which are semi-spherical in shape, have formed agglomerates, resembling clusters. Within these clusters, various imperfections such as voids and dislocations are evident. In Fig. 3b, the distribution of particle sizes for the calcined LM9F powder is depicted through a histogram. This graphical representation highlights that the mean particle size for the sample is 34 nm.

Figure 4 presents the FTIR spectral analysis of the LM9F powder post-calcination. The spectrum delineates distinct vibrational modes within two principal regions: from 400 to 560 cm^{-1} and 1000 to 1200 cm^{-1} . Notably, vibrations between 459.058 and 636.509 cm^{-1} correspond to the bending motions (both asymmetric and symmetric) of O–P–O linkages within the phosphate $[\text{PO}_4]^{3-}$ groups. Peaks observed in the range of 979.838 to 1138.001 cm^{-1} are indicative of the phosphate groups P–O bond stretching vibrations, both symmetric and asymmetric. Additional features of the spectrum include the presence of bands from 1523.764 to 1720.503 cm^{-1} , which are linked to the bending vibrations of water molecules. Moreover, the spectrum displays weaker peaks

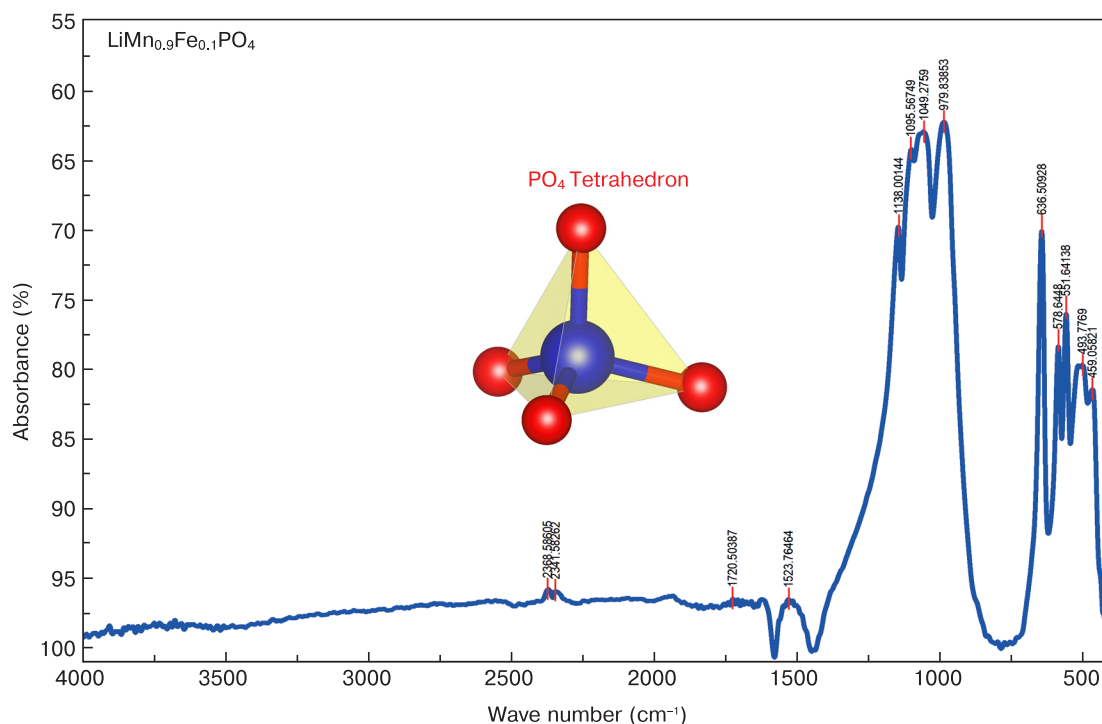


Figure 4. FTIR spectrum of solid solution LM9F sample

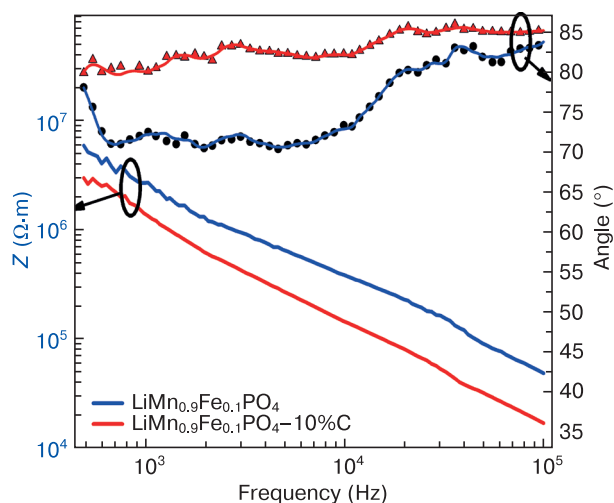
Table 2. FTIR vibrational modes for $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$

No.	Vibration	Peak (cm^{-1})
1	ASymm. Bend PO_4^{3-} (V_2)	459.05821
2		493.7769
3		551.64138
4		578.6448
5	Symm. Bend PO_4^{3-} (V_2)	636.50928
6	Symm. Stretch PO_4^{3-} (V_1)	979.83853
7	Asymm. Stretch PO_4^{3-} (V_3) B_{3g}	1049.2759
8	Asymm. Stretch PO_4^{3-} (V_3) B_{2g}	1095.56749
9	Symm. Stretch PO_4^{3-} (V_3)	1138.00144
10	Symm. Bend H_2O	1523.76464
11		1720.50387
12	Doublet CO_2 (C–O asymmetric stretching)	2341.58262
13		2368.58605

between 2341.582 and 2368.586 cm^{-1} , ascribed to the asymmetric stretch of C–O bonds in CO_2 . These FTIR findings are comprehensively tabulated in Table 2.

The Bode plots depicted in Fig. 5 present the impedance measurements for the samples LM9F and LM9F-10%C, illustrating the correlation between the impedance modulus and phase angle across a range of frequencies. These plots reveal a notable decrease in electrical impedance as the frequency increases, moving into higher frequency domains. This trend suggests that the samples exhibit capacitive behavior, where capacitance is inversely related to impedance. Notably, the inclusion of carbon, as seen in the LM9F-10%C sample, contributes to a reduction in electrical impedance, thereby enhancing the sample's capacitive properties. This phenomenon underscores the influence of carbon addition on the electrical characteristics of the material, improving its performance in applications requiring high capacitance.

The Nyquist plot presented in Fig. 6 displays the relationship between the real component of impedance

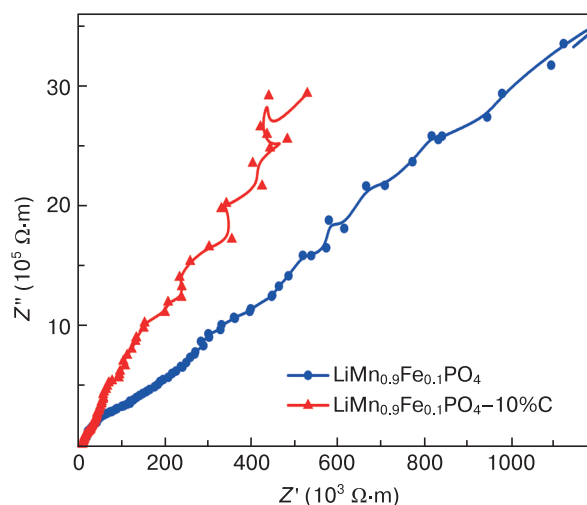
**Figure 5.** Bode plot for LM9F and LM9F-10%C sintering at 700 °C in N_2 atmosphere

(x-axis) and the imaginary component (y-axis). This plot demonstrates that the curves for both samples approximate semi-circular trajectories, suggesting the samples function akin to parallel RC circuits. Notably, the incorporation of carbon into LM9F (indicated by the red curve) manifests in a decreased resistance characteristic compared to the sample devoid of carbon, highlighting the conductive advantage provided by carbon addition.

The carbon coating substantially improves the electrochemical behavior of LM9F by enhancing its electronic conductivity and providing structural integrity during cycling. The improved conductivity ensures that electrons can move more freely within the electrode, reducing internal resistance and leading to higher specific capacities and better rate performance. Additionally, the carbon coating helps in maintaining the structural integrity of the cathode material, reducing degradation and capacity fading over repeated cycles. This results in improved cycling stability and longevity of the battery.

Figure 7a examines how different temperatures impact the electrical impedance of the solid solutions LM9F and LM9F-10%C. The observed trend in the impedance curves for both samples demonstrates a near stability at lower temperatures, with a minor decline as temperatures reach higher levels. Meanwhile, Fig. 7b explores how the phase angle varies with temperature, revealing that LM9F-10%C maintains a phase angle close to 90°, suggesting consistent capacitive behavior across temperature changes. In contrast, the phase angle for LM9F shows a decrease as temperature increases, indicating that the capacitive performance of LM9F-10%C is more stable with temperature variations.

Figures 8a and 8b represents the dielectric properties of solid solution LM9F and LM9F-10%C. The results show the presence of carbon led to slight increase in the value of dielectric constant and decrease the loss tangent, which means that the material has good stability with temperature and the effect of carbon coating lead to increase the value of dielectric constant and decrease the loss factor.

**Figure 6.** Nyquist plot for LM9F and LM9F-10%C sintering at 700 °C in N_2 atmosphere

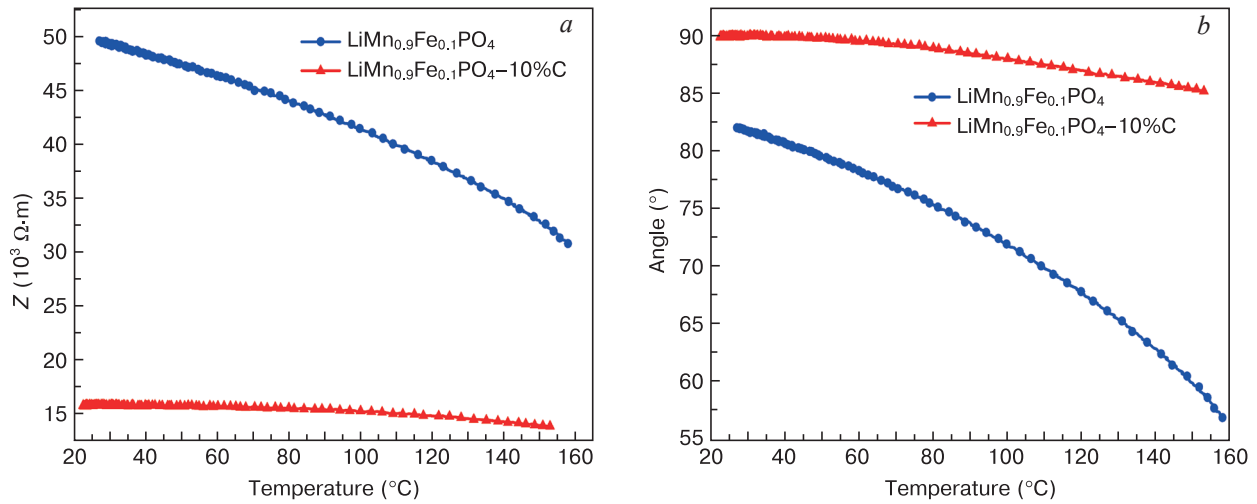


Figure 7. (a) Electrical impedance and (b) phase angle varied with temperature for LM9F and LM9F-10%C

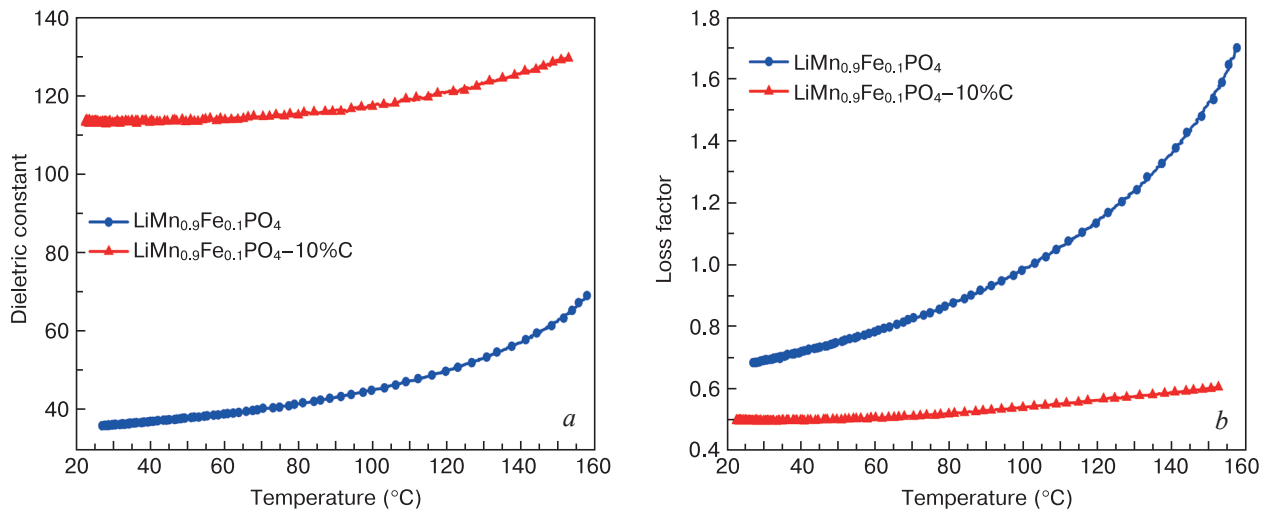


Figure 8. (a) Dielectric constant and (b) loss tangent varied with temperature for LM9F and LM9F-10%C

4. Conclusion

$\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ and $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ -10%C cathode materials were successfully synthesized using a single-step solid-state method, incorporating a high-energy ball-milling process at 270 rpm for 8 h to produce fine particles. Following milling, the powders underwent calcination and sintering at 700 $^\circ\text{C}$ under N_2 to prevent iron oxidation. Thermal analysis indicated the crystallization onset at 416 $^\circ\text{C}$. X-ray diffraction confirmed the formation of a pure olivine orthorhombic phase, closely matching reference data. FE-SEM images showed semi-spherical agglomerates with an average size of 34 nm. FTIR analysis verified the presence of $[\text{PO}_4]^{3-}$ vibrations, indicative of the phosphate structure. Electrical measurements highlighted that carbon addition notably enhances conductivity and capacitance, demonstrating its effectiveness in improving material performance.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors contribution statement

Natheer B. Mahmood: Conceptualization, Validation, Data curation, Co-Author, Formal analysis, Software;

Thamir Abdul-Jabbar Jumah: Project administration, Supervision, Methodology, Review & Editing; **Zahraa M. Jaafar:** Writing – Original draft, Visualization, Funding acquisition, Resources, Writing

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