Hydrothermally Synthesized Nanostructured $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0-0.3$) Cathode Materials With Enhanced Properties for Lithium-Ion Batteries

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Research Article

Keywords: Hydrothermal route, Olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$, Cathode materials, Li-ion batteries

Posted Date: February 19th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-209800/v1>

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**Hydrothermally synthesized nanostructured $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0-0.3$)
cathode materials with enhanced properties for lithium-ion batteries**

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Abstract

Nanostructured cathode materials based on Mn-doped olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0, 0.1, 0.2$, and 0.3) were successfully synthesized via a hydrothermal route. X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (SEM), and Raman spectroscopy indicated that the synthesized samples possessed a sphere-like nanostructure and a relatively homogeneous size distribution in the range of 100 - 200 nm. Electrochemical experiments and analysis showed that the Mn doping increased the redox potential and boosted the capacity. While the undoped olivine (LiFePO_4) had a capacity of 169 mAh g^{-1} with a slight reduction (10%) in the initial capacity after 50 cycles (150 mAh g^{-1}), the Mn-doped olivine samples ($\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$) demonstrated reliable cycling tests with negligible capacity loss, reaching 151, 147, and 157 mAh g^{-1} for $x = 0.1, 0.2$, and 0.3 , respectively. The results from electrochemical impedance spectroscopy (EIS) accompanied by the galvanostatic intermittent titration technique (GITT) confirmed that the Mn substitution for Fe promoted the charge transfer process and hence the rapid Li transport. These findings indicate that the $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ nanostructures are promising cathode materials for lithium ion battery applications.

Keywords: *Hydrothermal route; Olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$; Cathode materials, Li-ion batteries*

49 **1. Introduction**

50 The production and storage of new and clean energy are two major challenges that face humanity to
51 stop the depletion of natural resources. In modern life, a wide range of systems such as portable
52 electronic devices, computers, phones, cameras, and electric vehicles require stable and safe electrical
53 energy. Such diversity in the electronics market compels the development of different electrochemical
54 systems such as non-flammable batteries, superconductors, and other types of batteries [1-5]. Since
55 1970, the phosphorus-olivine structure has been tapped as a potential material for Li-ion batteries [6-
56 10]. In particular, lithium iron phosphate (LiFePO_4) and lithium manganese phosphate (LiMnPO_4) are
57 some of the most studied among transition metal oxide cathode materials due to their high theoretical
58 capacity ($\approx 170 \text{ mAh g}^{-1}$), inherent chemical stability, increased safety due to their lower explosion
59 risk from overcharging, better thermal stability, and lower material cost [11-14]. However, the
60 conductivity (σ) and Li-ion diffusion coefficient of LiFePO_4 and LiMnPO_4 are on the low end of the
61 spectrum; for example, $\sigma_{\text{LiFePO}_4} = 10^{-8} - 10^{-9} \text{ S cm}^{-1}$ and $\sigma_{\text{LiMnPO}_4} = 10^{-10} \text{ S cm}^{-1}$ [12, 14-16]. Due to the
62 disadvantage of these materials' conductivity on electronics and ion transport, there exists a major
63 constraint to commercial applications of these materials [17, 18]. To mitigate these issues, three
64 approaches are typically considered: (i) coating carbon on the surface of olivine to improve the electron
65 transfer process; (ii) substituting Fe with a 3d-metallic element, and (iii) reducing the particle size to
66 the nanoscale with different particle shapes like nanoparticles, nanorod plates, and nanorectangular
67 sheets [1, 13, 19-23]. Some studies have shown that cation mixing in $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ orthophosphates
68 is a great trade-off between the valuable capacity of LiFePO_4 and the high potential of LiMnPO_4
69 (voltage of oxidation pair compared with Li^+/Li) [20, 24, 25]. Other studies have also shown that doping
70 metal cations into LiFePO_4 or LiMnPO_4 causes a narrowing of the energy gap, which may improve
71 the electrical conductivity of this material [3, 25]. On the other hand, to achieve high electrochemical
72 efficiency in olivine phosphate cathode materials, several methods of nanomaterial synthesis have been
73 employed, such as solid-state reactions [1, 26], sol-gel methods [13, 27], and reactions from

hydrothermal routes [11, 21, 23, 28, 29]. Among these methods, the hydrothermal synthesis is a facile water-based precipitation technique that enables the control of the nucleation and development of the crystal.

In this work, we prepared the nano-olivine structure $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) by a facile hydrothermal route, and the as-prepared olivines were coated with carbon through pyrolysis. Electrochemical studies showed that the olivines were capable of delivering a reversible capacity around 160 mAh g^{-1} at a current density of $C/10$ in the voltage range of $2.5 - 4.3 \text{ V}$ (vs. Li^+/Li). The kinetics of Li transport in these olivines were also discussed.

2. Experimental

The chemicals $\text{Mn}(\text{NO}_3)_2$ ($\square 99 \text{ wt.}\%$), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ($\square 99 \text{ wt.}\%$), LiOH ($\square 98 \text{ wt.}\%$), NH_3 solution ($30 \text{ wt.}\%$), H_3PO_4 ($\square 85\%$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, $\square 99.5 \text{ \%wt.}$), polyvinylidene fluoride (PVDF), ethylene carbonate (EC, $98 \text{ wt.}\%$), and dimethyl carbonate (DMC, $\square 99 \text{ wt.}\%$) were purchased from Sigma-Aldrich. All the other chemicals were of analytical grade and used without further purification. All the aqueous solutions were prepared with deionized water (DI water, $18.2 \text{ M}\Omega\cdot\text{cm}$) for all the experiments.

Synthesis of olivine samples

A mixture of H_3PO_4 , $\text{Mn}(\text{NO}_3)_2$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were dissolved into 50 mL DI water under N_2 atmosphere at 1:9, 2:8, and 3:7 molar ratios of Mn:Fe. Then, 20 mL of 0.5 M LiOH was dropped into the mixture at a 3:1 ratio of $\text{Li}^+:\text{PO}_4^{3-}$. The NH_3 solution was dropped into the final mixture to adjust the pH to 6 - 6.5. The final mixture was stirred for 30 min at $60 - 80 \text{ }^\circ\text{C}$ to form the sol. The sol was transferred to the autoclave at $180 \text{ }^\circ\text{C}$ for 12 h. The precipitation was collected by filtering, washing, and drying at $95 \text{ }^\circ\text{C}$ for 24 h.

98 *Characterizations and Methods*

99 The X-ray diffraction spectra were recorded on a D5005-SIEMENS diffractometer with Cu-K α
100 radiation ($\lambda = 1.54056 \text{ \AA}$). The synthesized olivines were observed using a Hitachi FE-SEM S-4800
101 field-emission scanning electron microscope coupled with an Oxford 300 EDX analysis system. The
102 micro-Raman spectra were recorded on a LABRAM-1B spectrophotometer (Jobin Yvon, France). The
103 electrochemical properties of the synthesized olivines were evaluated by cyclic voltammetry (CV) at
104 a scan rate of 1 mV s^{-1} , galvanostatic charge/discharge tests, and electrochemical impedance
105 spectroscopy by using a VMP3 apparatus (BioLogic, France) in the frequency range 5 mHz to 105 Hz
106 and 10 mV peak-to-peak excitation signal.

107

108 *Devices preparation*

109 The synthesized olivine powders were mixed with carbon black as a conductive agent, polyvinylidene
110 fluoride (PVDF) as binder in the ratio of 90:5:5, respectively, in a porcelain mortar and pestle. The
111 prepared mixtures were coated onto a 0.1 mm aluminium sheet, dried at 120°C in an oven for 12 h,
112 and pressed on a press machine to create a thickness of $20 \text{ }\mu\text{m}$. The electrodes were then formed to
113 circular plates with a diameter of 1.6 cm on a stamping machine. Coin-cells CR-2032 were assembled
114 in an argon-filled glove box with an anode of lithium metal. The electrolyte solutions were 1 M LiPF₆
115 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a volumetric ratio of 2:1.

116 **3. Results and discussion**

117 *Structural and morphological characterizations*

118 The XRD spectra of the synthesized olivine samples (**Fig. 1A**) show a pure and very well crystallized
119 single olivine phase without impurity (e.g., MnO₂, Li₂O, and Fe₂O₃). All the diffraction peaks were
120 identified in an orthorhombic structure with a space group of P_{nma} (JCPDS 81-1173) [14, 20]. In the
121 olivine phase, the atoms are located at 4a for lithium, 4c for iron, 4c for phosphorous, and 4c and 8a

for oxygen. The Mn substitute of Fe is at the 4c site. The lattice parameters are calculated by the Celref program and detailed in **Table 1**. The lattice expansion of the Mn-doped olivine samples depended on the degree of Mn substitution as well as the larger ionic radius of Mn^{2+} ($r_{\text{Mn}^{2+}} = 0.08 \text{ nm} > r_{\text{Fe}^{2+}} = 0.074 \text{ nm}$) [14, 20]

The broadening of the diffraction peaks was attributed to the nanocrystallinity of the samples. The average crystalline size is calculated from the full width at half maximum (FWHM) through the Debye-Scherrer equation [23]:

$$d_{hkl} = \frac{k\lambda}{\beta \cdot \cos\theta} \quad (\text{Eq.1})$$

where d_{hkl} is the average particle size, k is the constant depending on the crystallite shape (0.9), λ is the wavelength of the copper $\text{K}\alpha$ X-ray radiation, β is the FWHM of the most intense peak (in rad), and θ is the diffraction angle. The average estimation of the crystallite size is around 20 nm for all samples. This sub-micron size could indicate fast kinetics of lithium insertion due to a shortening of the lithium pathway for diffusion.

The Raman spectra of the olivine $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ at high frequency 750 - 2000 cm^{-1} (**Fig. 1B**) confirms the typical fingerprints of an olivine-type structure as well as the successful carbon coating on surface olivines from the pyrolysis process. Three A_g bands (ν_1 , ν_2 , and ν_3 at 943 cm^{-1} , 993 cm^{-1} and 1065 cm^{-1} , respectively) represented the vibrational modes of the $[\text{PO}_4]$ tetrahedron. The mode ν_2 (993 cm^{-1}) was assigned to symmetric O–P–O bond bending, while the two modes ν_1 and ν_3 were characterized as symmetric and anti-symmetric P–O stretching, respectively [30, 31].

The SEM image in **Fig. 2** shows that the synthesized olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ samples crystallized with uniform size. The SEM of the original olivine LiFePO_4 sample (**Fig. 2a**) shows LiFePO_4 as consisting of spherical-like particles with a narrow particle size distribution in range from 200 nm to 400 nm. When Mn is doped into $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$, the particle size strongly reduces and the samples became more porous see **Fig. 2b**, **Fig. 2c**, and **Fig. 2d**. It can be seen that particle size decreased with increasing Mn. In particular, the particle size of $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$ is around 50 nm (**Fig. 2d**). The EDX spectra of

the three Mn-doped samples (**Fig. 3**) showed the indicators of Mn, Fe, P, and O and confirmed the stoichiometric relationship between Mn:Fe (**Table 2**) was similar to the desired composition.

Electrochemical measurements

The CVs of the $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) samples at a scan rate of 1 mV s^{-1} are shown in **Fig. 4A**. The original olivine LiFePO_4 was measured over a voltage range of 3 - 4 V while the Mn-doped olivines were scanned at a wider range of 2.5 - 4.5 V. As can be seen from the CVs, the traditional reversible peak of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at 3.45 - 3.55 V appeared in the obtained voltammograms. With a greater degree of Mn substitution, the redox peak in the high voltage region (~4 V) becomes more observable. On the other hand, Mn doping into the original olivine can also lead to a slight shift in the Fe-redox potential, which will be discussed further in cycling test section. The Nyquist plots of the EIS for the $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) samples (**Fig. 4B**) exhibited three regions: (i) a “quasi” semi-circle in the high-medium frequency corresponding to the charge-transfer; (ii) a straight line 45 degrees from the real axis in low frequency region (in frequency range from 1 Hz – 0.1 Hz) demonstrating the Warburg impedance, and (iii) at very low frequencies ($f < 10^{-3}$ Hz) the phase angle is increases due to the finite diffusion process [5, 32]. It is observed that Mn doping is helpful for decreasing charge transfer in olivine, which suggests fast electron transfer as well as stability in cycling performance.

The galvanostatic cycling tests at a constant current of 0.1C in the potential range of 2.5 - 4.3 V are shown in **Fig. 5A**. It is well known that the LiFePO_4 profile drops rapidly to plateau at a voltage of 3.39 V when discharging and leaps to 3.45 V when charging. This profile can be considered as a two-phase mechanism between the LiFePO_4 phase and FePO_4 phase (**Fig. 5A**, curve a). However, the Mn substitution in olivine leads a significant change in the cycling profile (**Fig. 5A**, curve b to curve d). The discharge curve of the lowest Mn-doped sample falls slowly with a light bend over 3.7 V and reaches the main plateau at 3.41 V, while the reverse plateau appears at 3.47 V. It was reasonable that

the Mn-redox signal of $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ was hardly seen in the obtained voltammogram. In the other Mn-doped samples, the cycling profiles are demonstrated by a well-defined plateau at over 3.45 V and a short one at around 3.90 V. It was recognized that increasing the degree of Mn doping prolongs the capacity in the high voltage region and shortens it in the lower region. Indeed, the capacity was boosted from 20 mAh g^{-1} for $\text{LiMn}_{0.2}\text{Fe}_{0.8}\text{PO}_4$ to nearly 40 mAh g^{-1} for $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$ [20, 21].

On the other hand, it was observed that Mn doping also lead to shifts in the redox potential as well as an expansion of the polarization. Notably, at mid-capacity ($\sim 75 \text{ mAh g}^{-1}$), the discharge potential shifted towards 50 mV for the Fe-redox potential (from 3.40 to 3.45 V) with an increase in the degree of Mn doping and the polarization considerably increased from 50 mV (for LiFePO_4) to 63 mV (for $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$). This finding is consistent with the obtained cyclic voltammograms and can be interpreted as (i) the Mn is more electropositive than Fe and (ii) the Mn substitution of Fe can be expected to strengthen the Fe–O covalence, which raises the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox energy and shifts the redox voltage of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple higher [33].

The cycling performance of the olivines are presented in **Fig. 5B**. The initial capacity of LiFePO_4 reached 169 mAh g^{-1} , which was close to the theoretical capacity, however 10% of the initial capacity was lost after 50 cycles with a final capacity of 152 mAh g^{-1} . For the Mn-doped olivines, $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0.1, 0.2, \text{ and } 0.3$), there was negligible capacity loss and their final capacity reached 151, 147, and 157 mAh g^{-1} , respectively. The capacity loss can be interpreted by the release of Mn during the charge-discharge process. The Coulombic retentions were over 95% during the cycling test, which indicated a reversible Li-intercalation into the olivine hosts.

The apparent chemical coefficient of diffusion of lithium (D_{Li}) is a key parameter that evaluates the lithium transport into the intercalation hosts, which can be determined by the galvanostatic intermittent titration technique (GITT). This method imposes a constant current through the cell for a certain time interval [34, 35]. The open circuit voltage (OCV) curve was measured with a constant discharge rate of C/50 for 30 min followed by an OCV relaxation period of 5 h to the equilibrium voltage. The

diffusion process within the host was assumed to obey Fick's second law of diffusion, and under galvanostatic conditions, it obeys the following Eq. 2:

$$D = \frac{4}{\pi} \left(\frac{V_M}{S \cdot F \cdot z_A} \right)^2 \left[I_0 \cdot \left(\frac{dE}{dx} \right) / \left(\frac{dE}{d\sqrt{t}} \right) \right]^2 \quad (\text{Eq. 2})$$

where V_M is the molar volume of the host, S is the active surface of the electrode, F is Faraday's constant ($F = 96500 \text{ C mol}^{-1}$), z_A is the charge of the mobile species ($z_{\text{Li}} = 1$), I_0 is the magnitude of the current pulse, dE/dx is the slope of the OCV curve, and $dE/dt^{1/2}$ was directly obtained from the measurement of the voltage as a function of time during the constant current flux. The olivine intercalates the Li ions in a domino-cascade mechanism that is a transition between the two phases LiFePO_4 and FePO_4 [36, 37]. Thus, the galvanostatic curve can be divided in three segments: (i) a quickly dropping voltage as a solid solution segment for Li content below 0.1, (ii) a phase transition segment with Li content ranging from 0.1 to 0.9, and (iii) other solid solution segments for Li content below 1. The D_{Li} in the solid solution segment is usually more rapid than those in the phase transition region due to the slope dE/dx . Indeed, the phase transition is characterized by a flat voltage that leads to a small dE/dx . **Figure 6** demonstrates the evolution of D_{Li} as a function of lithium content in the olivines. It is observed that the synthesized olivines have a D_{Li} in the range of $10^{-17} - 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at the phase transition with Li content ranging from 0.2 to 0.8 for LiFePO_4 and $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$ and from 0.35 to 0.8 for the two other olivines. Moreover, the evolution of D_{Li} in $\text{LiMn}_{0.2}\text{Fe}_{0.8}\text{PO}_4$ and $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$ shows a peak at $x_{\text{Li}} = 0.1$ due to a short plateau of the redox couple $\text{Mn}^{2+}/\text{Mn}^{3+}$, which is consistent with the galvanostatic curve. Except at the phase transition, the D_{Li} of the Mn-doped olivines were significantly higher than the original olivine, which can be explained by enlarged lattice due to Mn substitution as well as a 1D channel in the (010) plane that is favourable for Li transport. Briefly, the D_{Li} values in our results are comparable to previous reports which were determined by other electrochemical methods (EIS, GITT) [22, 24, 38, 39].

221 **Conclusion**

222 The olivine $\text{LiMn}_x\text{Fe}_{1-x}\text{PO}_4$ ($x = 0, 0.1, 0.2, \text{ and } 0.3$) were successfully synthesized via the
223 hydrothermal route and presented an orthorhombic structure with lattice parameters that agreed with
224 prior reports. The electrochemical results showed that the original LiFePO_4 lost 10% of its initial
225 capacity after 50 cycles with a remaining capacity of 152 mAh g^{-1} . For the Mn-doped olivine samples,
226 there was negligible capacity loss and they reached 151, 147, and 157 mAh g^{-1} capacity, respectively.
227 The EIS revealed a rapid charge-transfer with Mn doping and the D_{Li} value from GITT showed a
228 minimum in the two-phase transition segment range of $10^{-17} - 10^{-15} \text{ cm}^2 \text{ s}^{-1}$. The olivine $\text{LiMn}_x\text{Fe}_{1-x}$
229 PO_4 , therefore, can lead to the development of high-performance lithium-ion batteries.

230 **Author contribution statement**

231 Dung V. Trinh: Investigation.

232 Mai T. T. Nguyen : : Investigation.

233 Hue T. M. Dang : : Investigation, Dung T. Dang : Data curation.

234 Hang T. T. Le : Formal analysis.

235 Huynh T. N. Le : Formal analysis.

236 Hoang V. Tran : Writing - review & editing.

237 Chinh D. Huynh : Supervision, Writing - review & editing.

238 **Declaration of Conflict of Interest**

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

241 **Acknowledgments**

242 We acknowledge the Energy Storage Materials Lab in Dankook University (Chungnam, Republic of
243 Korea) for the help with electrochemical measurements. This research was funded by Vietnam

244 National Foundation for Science and Technology Development (NAFOSTED) under grant number
245 104.03-2017.349.

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Figure 2.

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420 **Figure 3.**

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436 **Figure 5.**

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Figure 6.

Table 1. Lattice parameters of Mn-doped olivine samples

Samples	a (Å)	b (Å)	c (Å)	V (Å ³)	Average crystalline size (nm)
LiFePO ₄	10.342	6.021	4.699	292.60	19.5
LiMn _{0.1} Fe _{0.9} PO ₄	10.330	6.012	4.702	292.01	22.5
LiMn _{0.2} Fe _{0.8} PO ₄	10.374	6.038	4.711	295.09	21.4
LiMn _{0.3} Fe _{0.7} PO ₄	10.390	6.048	4.718	296.47	21.0

482 **Table 2.** Elemental composition of Mn-doped olivine samples determined by SEM-EDX

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		LiMn _{0.1} Fe _{0.9} PO ₄		LiMn _{0.2} Fe _{0.8} PO ₄		LiMn _{0.3} Fe _{0.7} PO ₄	
Elements	keV	Atom%	Mn/Fe	Atom%	Mn/Fe	Atom%	Mn/Fe
Oxygen	0.525	63.58		62.34		64.79	
Phosphorus	2.013	16.11	0.12:0.88	17.20	0.19:0.8	14.03	0.26:0.72
Manganese	5.894	2.46		3.84		5.55	
Ferrous	6.398	17.85		16.61		15.63	

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Figure 1

(A) X-ray diffraction patterns of olivine samples: (a) LiFePO₄; (b) LiMn_{0.1}Fe_{0.9}PO₄; (c) LiMn_{0.2}Fe_{0.9}PO₄ and (d) LiMn_{0.3}Fe_{0.7}PO₄; (B) Raman spectra of LiMn_{0.1}Fe_{0.9}PO₄ sample.

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SEM images of synthesized olivine samples: (a) LiFePO_4 ; (b) $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$; (c) $\text{LiMn}_{0.2}\text{Fe}_{0.8}\text{PO}_4$ and (d) $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$.

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Evolution of D_{Li} as a function of lithium content in olivine samples: (a) LiFePO_4 ; (b) $\text{LiMn}_{0.1}\text{Fe}_{0.9}\text{PO}_4$; (c) $\text{LiMn}_{0.2}\text{Fe}_{0.8}\text{PO}_4$ and (d) $\text{LiMn}_{0.3}\text{Fe}_{0.7}\text{PO}_4$.